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Containment and Dewatering of Heavy Metal Contaminated Sediments using Reactive Soil Minerals and Cellulose Materials

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ABSTRACT

The aim of this study is to investigate effective and sustainable measures to contain heavy metal contaminated sediments inside a geotextile tube during dewatering process. The efficacy of cellulosic materials (Jute fibers, Peanut hull, and Kraft pulp) on adsorption of selected heavy metals (Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) and dewatering performance inside a geotextile tube was studied by a series of Batch Adsorption and Pressure Filtration tests (PFT). The cellulosic materials were chosen keeping in mind their cost, accessibility, ease of handling and use, and sustainability. The studied adsorbents are inexpensive, easily available, and sustainable. In order to understand the optimum amount of cellulosic materials to be added into the slurry as well as the optimum mixing time for maximum removal, an independent study was conducted with the heavy metal ions and the cellulose materials. In this study, batch adsorption tests were conducted on a 500 ppm metal solution by changing the amount of cellulose materials from 0.5 g to 2g equilibrated for 4 hours. Two filtrate samples were collected at tested for metal concentration using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at 0.5hr, 1 hr, 2 hr, and 4 hr to understand the time of mixing on removal efficiency of studied heavy metal ions. The adsorption data were fitted using Langmuir isotherm to quantify their maximum adsorption capacity to heavy metal ions. It was found out that among the studied metals, all adsorbents exhibited highest affinity towards Pb ions, the order being jute> peanut hull> kraft pulp. A removal efficiency of 47% and maximum adsorption capacity of 100 mg/g Pb ions was highest for all combinations of adsorbents and metal ions. A maximum removal efficiency of 28% of Cu was achieved by the kraft pulp and the decreasing affinity was kraft pulp>peanut hull>jute. The maximum adsorption

capacity of kraft pulp determined from Langmuir isotherm for Cu was 13 mg/g. Similarly, kraft pulp exhibited highest affinity for Cd and Zn followed by peanut hull and jute. The removal efficiency of Cd and Zn by kraft pulp was almost 28%, significantly higher than 13% removal of Cu or Pb. The maximum adsorption capacity of kraft pulp for Cd and Zn were 24 mg/g and 11 mg/g respectively.

It has been seen that the dredged sediments contain soil particles with varying sizes and properties. Hence, understanding the role of different sediments in adsorption and retention of heavy metal ions inside geotextile tube is very important to predict the fate of contaminants leaching out from the tubes. To address this issue, a separate study was conducted where two soil sediments, Tully coarse (55% coarse and 45% fine fractions), and Tully fines (100% fine fractions) were mixed with heavy metal solution (500 ppm-2500 ppm) to form a 15% solid concentration slurry. The slurries was mixed for 1 hour and the filtrate samples collected after mixing were tested for metal concentration using ICP-OES. Moreover, Kaolinite clay was also used in this study. It was seen from these tests that the presence of fine fractions, hydrous oxides of iron and aluminum, reactive clay minerals Illite and Chlorite, surface charge, and pH of a soil play dominant role in adsorption and retention of heavy metal ions specially Pb and Cu. Tully fine sediments exhibited excessively high affinity towards Pb as the more than 99% of Pb was adsorbed and retained. Tully coarse also had high affinity to Pb and Cu with removal efficiency ranging between 85-95%. Kaolinite (1:1 clay) being less reactive and having high molecular stability than most of the 2:1 clays (e.g. Illites, Smectites) exhibited less affinity towards Pb and Cu. However, Kaolinite had better affinity towards Cd ions (approximately 3 times) than both Tully fine and Tully coarse soils. In terms of adsorption of Zn, both Tully soils adsorbed more than Kaolinite. Generally, it was concluded that the presence of reactive clay minerals plays a significant role in adsorption of Pb and Cu.

After the understanding of the role of cellulose materials as well as soil sediments in studied heavy metal adsorption, PFT tests were conducted to see the role of cellulose materials in dewatering performance. A 15% solid concentration contaminated slurry was prepared by mixing soil, cellulose materials (2% weight of solids) and heavy metal solution (1000 ppm Pb+500 ppm Cu+500 ppm Cd+500 ppm Zn). It was observed from the PFT tests that in both sediment slurries, the addition of cellulose materials except kraft pulp significantly increased the dewatering rate irrespective of the contamination. However, profound effect of jute fibers and peanut hull on increasing dewatering rate was observed in case of contaminated slurries. A reduction in turbidity of more than 80% was observed with the addition of jute fibers. Peanut and kraft pulp were successful in reducing the turbidity of the filtrate by 78 and 69% respectively. Addition of peanut hulls and jute on contaminated Tully coarse increased the solid content by approximately 33% and 46% respectively. However, in case of contaminated Tully fines a minor increase of 12% was achieved with the addition of jute. The addition of kraft pulp had no significant effect in the solids content. The filtrates collected from dewatering of contaminated Tully fines showed that approximately 98-99% of Cu and Pb was retained, whereas, in Tully coarse slurries 89% Cu and 96% Pb were retained. Although not very high adsorption, both Tully soils were able to retain more than 75% Cd and Zn.

CONTAINMENT AND DEWATERING OF HEAVY METAL CONTAMINATED SLURRIES USING REACTIVE SOIL MINERALS AND CELLULOSE MATERIALS

by

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B.S., Pulchowk Engineering Campus, Lalitpur, Nepal, 2010

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CHAPTER 1

GEOTEXTILE DEWATERING AND ITS FUNDAMENTALS

1.1 Introduction

Geotextile tube technology has gained significant popularity because of its use in wide range of civil and environmental engineering applications. Geotextile tubes are manufactured by sewing layers of permeable and high strength geotextile to form tubes that serve to contain and dewater the pumped high-water-content sediments (Satyamurthy and Bhatia 2009).The main application areas are hydraulic, marine, and environmental remediation (Lawson 2008). In hydraulic and marine applications, geotextile tubes are hydraulically or mechanically filled with dredged sands and functions to control flood, prevent erosion, and protect shorelines. Water permeates through the pores of the geotextile during filling and the retained sediments form a stable mass inside the tube. In hydraulic and marine applications, the fill material is predominantly sand as it would not undergo consolidation thereby preventing a change in the geometry of a tube. In environmental applications, geotextile tubes are widely used to contain and dewater high water content contaminated slurries (Yee and Lawson 2012), mine tailings, fly ash (Kutay and Aydilek 2004), and industrial and municipal sludge (Worley et al. 2008). As most of these wastes are in slurry form, they pose a major problem in handling and disposal. Geotextile tubes not only reduce the volume of the slurry, it also changes the consistency of waste from liquid to semi solid or solid so that handling and disposal becomes easy. High water content slurries in the past were treated by allowing them to settle in sedimentation ponds. However, since most of these slurries contain fine particulates and would take long time to settle, treatment using sedimentation tanks would require large area for settling ponds and is not time effective. In order to expedite the settling of fine particulates, chemicals are added to flocculate and coagulate the suspension. Although this approach is time effective, it poses environmental issues as the chemical additives often spill to the water bodies. Some mechanical methods such as centrifuge and belt filter press have been effective in dewatering wastes; however the energy required to run these machines is significant (Newman et al. 2004). Geotextile tubes in addition to being relatively simple to utilize compared to other mechanical methods, they can be fabricated to sizes and numbers that fits the scale of the dewatering operation (Satyamurthy and Bhatia 2009).

The origin of geotextile tubes goes back to 1980s where it was used in Europe for erosion control and containment purpose (Moo-Young and Tucker 2002). The earliest application of geotextile tubes was as containment dikes in Brazil and France (Bogossian et al.1982) and to fill scour holes in the Netherlands (Jagt1988). In the United States, the enactment of some stringent legislations such as Clean Water Act has prevented the disposal of wastes in the natural water bodies. Specifically 40 CFR, Part 503, enforced and regulated by US Environmental Protection Agency (US EPA), requires wastewater managers to discontinue use of lagoons and find a suitable alternative for dewatering and disposal. United States Army Corps of Engineers estimates that more than 250 million cubic meters of dredged sediments needs to be removed to maintain harbors and ports (Moo-Young and Tucker 2002). With this in context, hundreds of geotextile tubes have been successfully employed all over United States to contain and dewater low solids content sediment slurries.

1.2 Stages in geotextile dewatering

The geotextile tube dewatering can be defined in three processes namely: containment, dewatering, and consolidation. The stages involved during dewatering has been shown in Figure 1.1 (after Lawson 2008). In the containment process the geotextile tube is filled with the slurry. The geotextile should have enough strength to withstand the tensile stresses generated during filling. The capacity of tube is governed by several factors such as its dimensions, tensile strength of the geotextile and seams (Lawson 2008). As the slurry is pumped inside the tube, the coarser particles in the slurry settle first followed by the fines. As the soils settle they form a filter cake and the rate of dewatering decreases due to the formation of a filter cake. Once all the free water has drained out from the tube, the filter cake begins to consolidate because of its own weight. The tubes are filled multiple times and the final consolidation may take up to 6 months depending upon the slurry and final solids concentration (Lawson 2008).

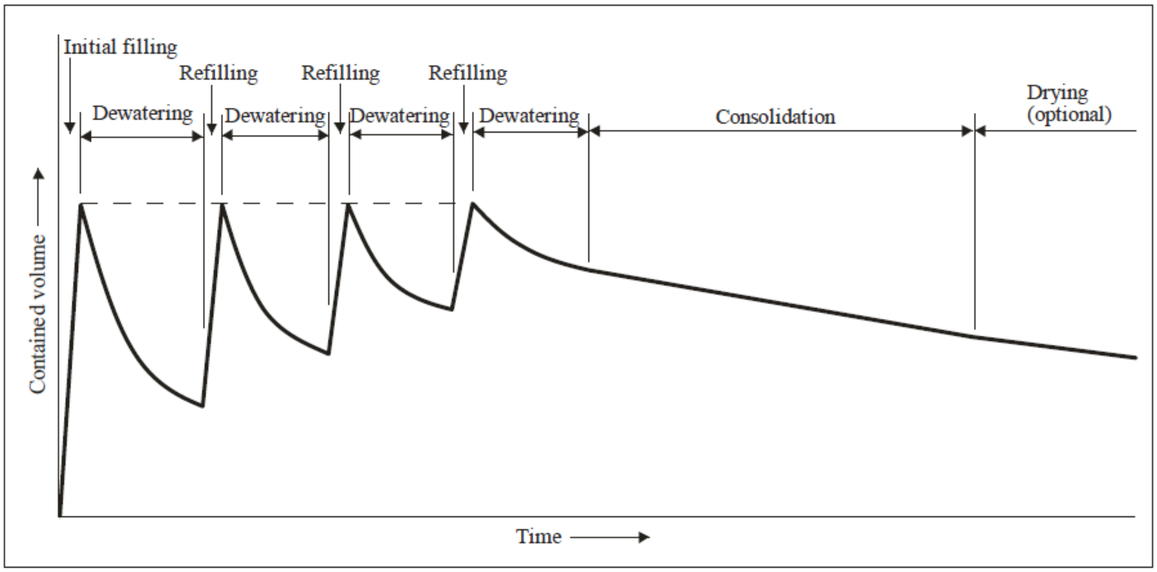

Figure 1.1 Stages in geotextile dewatering process (Lawson 2008)

1.3 Fundamentals of geotextile dewatering

The final solids concentration and contained volume of the filter cake is of particular interest in geotextile dewatering projects. In addition, the properties of the filter cake and the effluent quality also determines the success of the geotextile dewatering process. Lawson (2008) presented a simple relationship between the contained volume, and solids concentration with the dewatering time and given by Equation 1.1.

$$\frac{V_t}{V_o} = \left(\frac{1 - S_t}{S_t} \right) \Big/ \left[(1 - S_o) / S_o \right] \qquad \text{[Equation 1.1]}$$

where, V_t and S_t are the volume and solids concentration at time “t” and V_o and S_o are the volume and solids concentration at time 0 or the start of dewatering. It can be seen that initially the contained volume is high (V_o) and the solids concentration is low (S_o). As dewatering proceeds, the contained volume decreases and simultaneously the solids concentration increases because of the formation of filter cake.

If ΔV_t is the reduction in volume after time “t”, the solids concentration at same “t” can be expressed by using Equation 1.2 given by Lawson (2008).

$$S_t = \frac{\left(\frac{1}{1 - \Delta V_t} \right) * \left(\frac{S_o}{1 - S_o} \right)}{1 + \left(\frac{1}{1 - \Delta V_t} \right) * \left(\frac{S_o}{1 - S_o} \right)} \qquad \text{[Equation 1.2]}$$

The relationship between the contained volume, dewatering time, and solids concentration can be represented graphically as shown in Figures 1.2 (a) and (b).

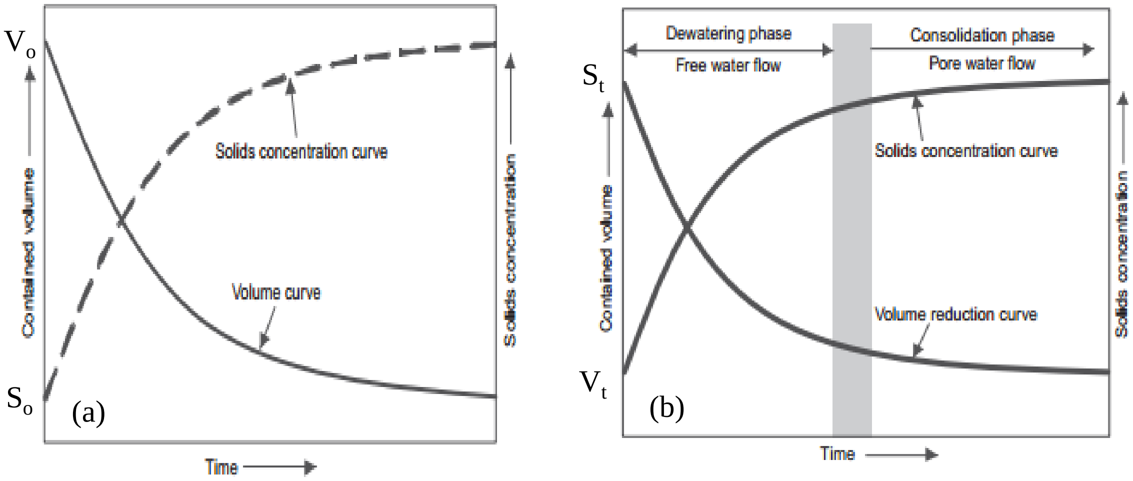

Figure 1.2 (a) Volume and solids concentration change with time during dewatering (b) Dewatering and consolidation phase (Lawson 2008)

The addition of flocculants and coagulants has been a standard practice in geotextile dewatering projects. Specifically, polyacrylamide-based polymer flocculants have been used to increase the retention of suspended solids and the rate of dewatering (Gaffney et al. 2011; Maurer et al. 2012).These chemical conditioners or accelerants bind the fine sediments to form flocs by bridging and/or charge neutralization. The formation of larger flocs of fine sediments increases the permeability of the filter cake and maximize retention of fines. Since it maximizes the retention of fines, the turbidity of the effluent is greatly reduced. Bhatia et al. (2013) investigated the role of polymers on dewatering efficiency and performance by conducting lab tests on slurries with and without chemical conditioning. It was found that the dewatering efficiency was 12-15% higher with the use of flocculants. Also, it was found that the solid concentration was 4-7% higher with the use of flocculants. However, the use of flocculants resulted in an increase in the water content of the filter cake. Similar results were found by Worley et al. (2007), Myers and Elton (2010), and Khachan et al. (2011).

1.4 Tests to assess geotextile dewatering performance

Various types of performance tests have been conducted to understand the dewatering performance of the slurry at full scale. The performance tests are small-scale laboratory scale tests performed on small representative sample of the slurry, or medium scale that may be performed in the lab or field (Grzelak 2011). These tests not only help to characterize the sample and provide information about dewatering efficiency, but also aids in finding the optimum type of chemical conditioner keeping in mind the project guidelines and specifications. The small scale tests that have been widely used are pressure filtration test (PFT) and the falling head test (FHT). Specially, PFT tests have been used by many researchers to assess the dewatering performance (Moo-Young et al. 2002; Kutay and Aydilek 2004; Liao and Bhatia 2005; Muthukumaran and Ilamparuhti 2006; Satyamurthy and Bhatia 2009). Some of the commonly used medium-scale tests are hanging bag test (HBT) and geotextile tube dewatering test (GDT). Grzelak et al. (2011) compared the lab scale tests (FHT and PFT) with medium scale tests (HBT and GDT) using a woven geotextile and silt slurry at 33% solids concentration. It was found out that the dewatering efficiency was similar for the PFT, HBT, and GDT, while filtration efficiency was similar for the HBT and GDT. However, FHT was determined to be a poor indicator to assess the dewatering performance compared to other test methods studied. It was concluded that because of the simplicity, ease of use, and cost, the PFT was determined to be a good indicator to assess the dewatering performance.

The schematic of typical geotextile dewatering is shown in Figure 1.3.

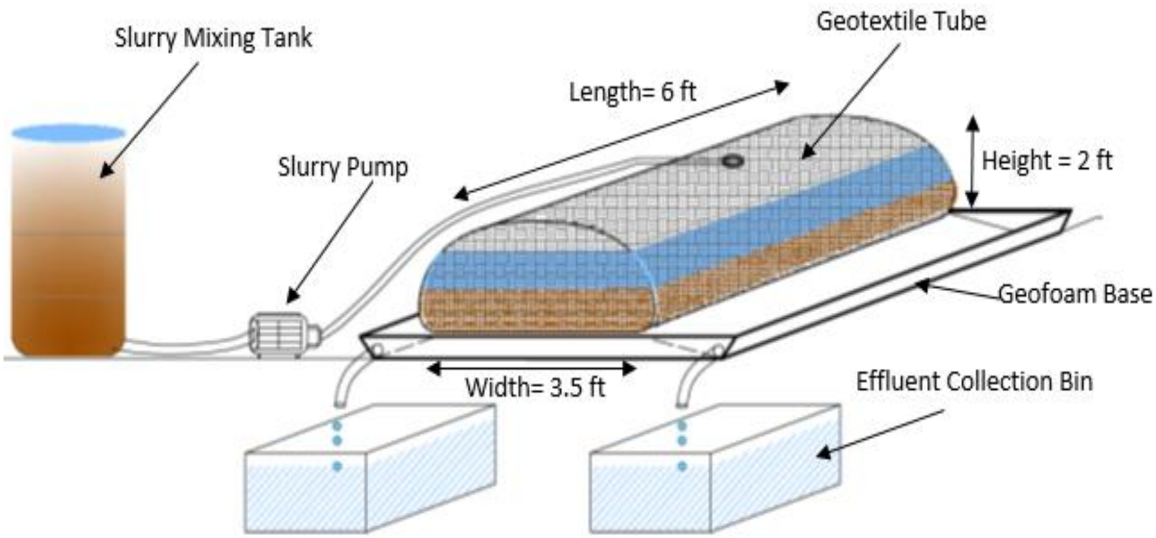

Figure 1.3 Geotextile dewatering process (schematic)

1.5 Scope of the study

Generally the geotextile dewatering technology is used in conjuction with wastewaer treatment technlogy to ensure the effluent meets the regulatory standards. The dewatered effluent is collected and discharged in the treatment facility. Various treatment methods such as activated carbon adsorption or sand filtration are generally used to treat the dewatered effluent. In recent years, researchers and practitinioers have realized the need to investigate sustainable measures to effectively contain contaminated slurries so that the cost incurred during post treatment can be reduced. Studies have been performed to investigate different additives inside the geotetile tube to improve the dewatering performance. Maurer et al (2012) investigated the use of flexible polyvinyl alcohol (PVA) resin bundled chopped fibers to dewater class F and C fly ash slurries. The effects of these fibers on dewatering performance and filter cake characteristics were studied by performing Pressure Filtration Tests (PFT). It was concluded that the strength of the filter cake improved significantly using randomly dispersed fibers. It was also found out that

polymer flocculants signficantly increased the dewatering rate and strength of the retained solids but heavy metal still leached out. Koerner and Huang (2005) investigated the use of reactive additives such as activated carbon and phosporic rock to retain organic pollutants and heavy metals inside the geotextile tube. It was found out that adding a small fraction (0.5 wt%) of charcoal can cause signifcant reduction (an order of magnitude) in concentrations of the organic and inorganic pollutants. Although many studies have investigated the measures to effectively contain contaminated slurries, very few studies have been performed to investigate the dewatering of heavy metal contaminated slurries using geotextile tubes. Moreover, studies focusing on sustainable measures to contain these heavy metal contaminated sediment slurries is scarce.
Hence, this study aims to investigate the effective and sustainable measures not only to contain heavy metal contaminated sediments but also to improve the dewatering performance. For this purpose, dewatering tests using PFT were conducted on heavy metal contaminated slurries in the lab using three cellulosic materials (Peanut hulls, jute fibers, and kraft pulp). The contaminated slurries were preapred with two soil sediments retrieved from local quarry at Tully, NY. In addition to measuring the concentration of metal ions in the effluent using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), various dewatering parameters such as solid content of the filter cake , filtrate quality were measured.

1.6 Organization of thesis

In order to investigate the effectiveness of the cellulosic materials and sediments in heavy metal adsorption as well as retention, it is imperative to quanitfy their adsorption capacity to the metal ions. For this purpose, this study has been divided into 5 chapters. Chapter 1 of this study describes about the basic fundamentals of the geotextile dewatering technology inluding different test methods to assess the dewatering performance, and the scope of the study. In chapter 2, the effectiveness of cellulosic materials to adsorb heavy metals have been studied using batch adsorption tests. Specifically, different amounts of cellulosic materials (0.5g, 1g, 1.5g, and 2g) have been used to investigate 500 ppm of heavy metal solution (Pb, Cu, Cd, and Zn). Chapter 3 describes the adsorption capacity of three soil sediments (Tully fines, Tully coarse, and Kaolinite) to adsorb the above mentioned heavy metals. Batch adsorption tests were employed to understand the role of studied sediments to adsorb metal ions on a 15% concenration slurry. In Chapter 4, results of the dewatering tests conducted on a slurry with cellulosic fibers using PFT in the lab are presented. Chapter 5 concludes the major findings of the study including future recommendations.

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CHAPTER 2

A STUDY ON ADSORPTION OF SELECTED HEAVY METALS BY CELLULOSIC MATERIALS

2.1 Introduction

The large industrial and municipal activities over the last forty years has contaminated many waterbodies around the world with many organic and inorganic pollutants. Specifically, many inland and coastal waters have been polluted with heavy metals as a result of discharge from industrial processes including mining operations, smelting, metal plating, tanning, battery manufacturing and rubber manufacturing (Bailey et al.1999; Shukla et al. 2002; Mackie et al. 2007). Since the heavy metal ions cannot be degraded or destroyed, they pose a stable and persistent environmental problems to aquatic life and human health (Demirbas 2008).

Heavy metals have been defined in different ways based on specific gravity, atomic number, and atomic weight. Heavy metals are elements that have atomic weight greater than sodium (Bennet 1986). Heavy metals are wide range of metals of high atomic weight, particularly those transition metals that are toxic and cannot be processed by living organisms, such as lead (Pb), mercury (Hg), cadmium (Cd) (Harrison and Waites1998). Based on atomic number, heavy metals are any metals with an atomic number beyond calcium (Venugopal and Luckey1975).Particularly, they are metals with an atomic number between 21 (scandium) and 92 (uranium) (Lyman1995). Heavy metals are elements having atomic weights between 63.5 and 200.6, and specific gravity greater than 5 (Srivastava and Majumder 2008). More than 20 heavy metals are classified as toxic with half of them emitted in the environment in concentrations that pose great risks to human health (Akpor and Muchie 2010). The common heavy metals found in polluted water are lead, cadmium, arsenic, copper, chromium, zinc, nickel, and mercury. The release of these metals without proper treatment expose living organisms to reduced growth, organ and nervous system damage, cancer, and even death.

As the contamination of water sources with heavy metal pose such severe problems, several guidelines and legislations have been enacted in recent years to reduce pollution sources and remediate polluted water resources. US EPA under the Clean Water Act implements, enforces and regulates the standards for level of pollutants discharged into navigable water bodies. Of the 75,243 water bodies listed as impaired by the United States Environmental Protection Agency (USEPA), 7,143 are impaired as a result of heavy metals other than mercury (US EPA 2014). These metals include lead, copper, arsenic, manganese, zinc, cadmium, aluminum, nickel silver and chromium, impacting both water and sediments. As per U.S. EPA estimates, every year in the U.S, 1.2 trillion gallons of sewage from household, industry and restaurants is dumped in to U.S. water annually of which most are contaminated with the heavy metals previously mentioned. National Primary Drinking Water Regulations (NPDWRs or primary standards), a legally enforceable standards that apply to public water systems, have been enacted by US EPA to limit the maximum contaminant level (MCL) for various metals and contaminants. The summary of MCL for several metals along with their potential health effects and sources of production is shown in Table 2.1.

Table 2.1 Maximum contaminant level (National Primary Drinking Water Regulations, Title 40 Part 141)

Contaminant	**Maximum contaminant level (ppm)**	**Potential health effects**	**Sources**
Lead (Pb) (Atomic wt.=207.2)	0	Delays in physical or mental development in children, kidney problems and high blood pressure in adults	Corrosion of household plumbing systems; erosion of natural deposits
Mercury (Hg) (Atomic wt.=200.59)	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Cadmium (Cd) (Atomic wt.=112.4)	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries
Arsenic (As) (Atomic wt.= 74.9)	0.010	Skin damage or problems with circulatory systems	Erosion of natural deposits; runoff from
Copper (Atomic wt.= 63.5)	1.300	Gastrointestinal distress, Kidney or liver damage	Corrosion of household plumbing systems; erosion of natural deposits
Zinc (Atomic wt.= 65.38)	NA	Metal fume fever, carcinogenic to animals, long term chronic health effects	Mining, coal and waste combustion, steel processing

The processes generally involved in the removal of heavy metals from aqueous solution are chemical precipitation, ion exchange, membrane filtration, adsorption, electrochemical processes, coagulation-flocculation etc. (Fu and Wang 2011). A brief summary of some of these processes is presented below.

2.1.1 Chemical precipitation

Chemical precipitation is an effective and the most widely used process in industry because of its relative simplicity and inexpensiveness in operation (Ku and Jung 2001). Heavy metal ions react with chemicals to form insoluble precipitates which are removed by sedimentation or filtration. The most common precipitation techniques are hydroxide and sulfide precipitation.

2.1.2 Ion exchange

Ion exchange is a widely used technology because of its high removal efficiency, great removal capacity, and fast kinetics (Kang et al. 2004). Although synthetic as well as natural resins are used, synthetic resins are most commonly used because of its higher ability to exchange cations with the heavy metals from the aqueous solution (Alyüz and Veli 2009).

2.1.3 Membrane filtration

Membrane filtration uses different types of membranes and have gained wide popularity in heavy metal removal due to its high efficiency, easy operation and space saving. The membrane processes are ultra-filtration, reverse osmosis, nanofiltration, and electrodialysis.

2.1.4 Coagulation and flocculation

Coagulation and flocculation in conjunction with sedimentation and filtration is also a popular method to remove heavy metals from polluted water. Coagulation destabilizes the colloids by neutralizing the force that keep them apart. Aluminum, ferric chloride, ferrous sulfate are some of the widely used coagulants used in the wastewater treatment.

Flocculation is binding of the particles into large clumps or flocs by forming bridges between the fine particulates. The flocs of suspended particles are removed by filtration or floatation. Commonly used flocculants are polyacrylamide (PAM), polyferric sulfate (PFS), and polyaluminum chloride (PAC).

2.1.5 Adsorption

Adsorption is realized as an economical and effective method of removing heavy metal ions from the aqueous solution. Adsorption, in general, is the accumulation of solute molecules at an interface, which can be liquid-liquid, gas-liquid, gas-solid or liquid-solid. Chemical adsorption results in the formation of a monomolecular layer of the adsorbate (material being adsorbed) on the surface. Physical adsorption results from molecular condensation in the capillaries of the solid. Adsorption is considered superior because of its high effectiveness to reduce metal ions to a very low concentration. Removing heavy metal ions using adsorbents (material that adsorbs) such as activated carbon, aerogel, zeolites is quite common. However, recently many studies have focused on use of low cost and effective adsorbents for the removal of heavy metals. Low cost, high efficiency, reduced contaminated sludge, regeneration of adsorbent are the major advantages of these materials over conventional adsorbents or treatment methods. Some of the popular low cost adsorbents are sawdust (Bryan et al.1992), lignin (Masri et al.1974; Srivastava et al.1994), rice hulls (Roy et al.1993), zeolites (Leppert 1990), fly ash (Grover and Narayanaswamy1982), peat moss (Chen et al.1990), peanut husk (Li et al. 2006a), unmodified, dye loaded, and oxidized jute (Shukla and Pai 2005).

The adsorption of heavy metals from aqueous solutions by low cost lignocellulosic materials has proven to be very promising in removing contaminants from aqueous effluents (Demirbas 2008). A brief summary of some of the previous studies conducted on the adsorbents to adsorb heavy metals used in this study is presented.

Peanut hulls, an abundant agricultural by-product in the south-eastern United States, are plentiful, inexpensive, and a renewable resource. Previously thought of as a waste product, peanut hulls are gaining status as a useful commodity. Recently developed applications include their use in agriculture as a carrier for soil conditioning chemicals and pesticides, and as filler in chicken feed. Periasamy and Namasivayamk (1995) investigated the removal of Cu by activated carbon prepared from peanut hull and compared it with commercial granular activated carbon. It was shown from the adsorption studies that the time required for maximum removal of 25 mg/L Cu by peanut hull carbon (120 min) was 2.5 times less than that required by the granular activated carbon (300 min). In addition, the maximum adsorption capacity of peanut hull carbon was 65.57 mg/g, which is significantly higher than 3.60 mg/g achieved by commercial granular activated carbon. Johns et al. (1998) investigated the adsorption of peanut shells and other adsorbents to Pb, Cu, Cd, Zn and Ni ions. They found that the peanut shell exhibited highest affinity towards Pb followed by Cu, Cd, Ni and Zn. Brown et al. (2000) evaluated the adsorption capacity of peanut hull pellets to Pb, Cu, Cd, and Zn ions and compared their performance to that of raw peanut hulls and ion exchange resin. Adsorption capacities of 30 mg/g of Pb, 8 mg/g of Cu, 9 mg/g of Zn, and 6 mg/g of Cd was reported to have been achieved by peanut hull pellets. The kinetic study showed that for all cases, over 85% of the total metal ion capture occurred within the first 10 minutes of mixing, over 90% within the first 20 minutes, and over 96% within 40 minutes. It was also shown that pelleting the raw peanut hulls had little effect on the adsorption capacity.

Ricordel et al. (2001) studied the adsorption of Pb, Zn, Ni, and Cd over a range of initial metal ion concentration (0.15mM) onto carbon prepared from peanut husks. Adsorption in excess of 98% Pb and, 87%, 83%, and 75% of Zn, Ni, and Cd, respectively were found. In general, the amount of metal ion adsorbed increased in the order of Cd<Ni<Zn<Pb, and was related to the ionic radii, hydration energy, ionic mobility, and diffusion coefficient. The maximum adsorption capacities for Pb, Cd, Ni, and Zn were 0.87 mg/g, 0.47 mg/g, 0.26 mg/g, and 0.19 mg/g, respectively. Zacaria et al. (2002) investigated the potential of peanut hulls to adsorb heavy metals. They found the adsorption capacities of 30.04 mg/g Pb, 8 mg/g of Cu, 8.96 mg/g of Zn, and 5.96 mg/g of Cd ions by the peanut hulls. Qin et al. (2007a) investigated the kinetics and adsorption of Pb, Cr, and Cu from aqueous solution by modified peanut husk and sawdust. Batch adsorption tests were conducted by mixing 0.2 g of the adsorbent with metal solutions with concentrations varying from 5 to 50 ppm. Although the equilibrium reached after 6 hours, the rate of uptake of heavy metals by modified peanut was faster than the sawdust. The maximum adsorption capacity for Pb of 29.14 mg/g was highest among the studied metals, followed by 10.15 mg/g Cu, and 7.67 mg/g Cr. Qin et al. (2007b) studied the adsorption of same metals by peanut husk under different pH, initial concentration of metal ions, time and temperature. They found that adsorption was very poor in acidic medium and increased in the alkaline medium. For a peanut hull amount of 2 g/L and initial metal ion concentration of 10 mg/L, the adsorption capacities were 3.34 m/g Pb, 3.34 mg/g Cr and 2.96 mg/g Cu. Zhu et al. (2009) studied the removal of Cu from aqueous solution by peanut hull. They found the adsorption of Cu to be highly pH dependent, reaching maximum at pH 5.5, and the sorption reaching equilibrium at 2

hours. The equilibrium adsorption capacity determined from Langmuir isotherm was 21.25 mg/g. Krowiak et al. (2011) investigated the biosorption of Cu and Cr ions from aqueous solution by peanut shell as a function of pH, initial concentration and temperature. A maximum adsorption capacity of 25.39 mg/g Cu and 27.86 mg/g Cd was found. The majority of studies have focused on modifying the properties of peanut in order to increase its adsorption capacity to heavy metals from aqueous solution. Also, many forms of peanut such as peanut hull carbon, peanut hull, peanut shell, peanut hull pellet, peanut husk have been found to be used in the literature. However, this study focuses not only to investigate the adsorption capacity of ground peanut husk (called as peanut hull) to adsorb heavy metals, but also to study its interaction in a slurry comprising soil sediments and heavy metal solution. No studies have yet been conducted to investigate the potential use of peanut hulls in geotextile dewatering technology.

Jute fibers are primarily composed of cellulose and lignin, hence are partially textile fiber and partially wood. Being one of the most abundant natural fiber, it is very cheap and easily found. Studies have shown them to be an excellent adsorbent for various heavy metal ions. Shukla and Pai (2005a) investigated the adsorption of Cu, Ni, and Zn from aqueous solutions by unmodified, dye loaded, and oxidized jute. The adsorption capacity of unmodified jute reported was 4.23 mg/g Cu, 3.37 mg/g Ni, and 3.55 mg/g Zn. They found higher adsorption capacity with the use of dye loaded or oxidized jute as compared to the unmodified jute. Shukla and Pai (2005b) investigated the removal of Pb ions using cellulose containing materials; jute (1 cm long), sawdust, and groundnut shells. It was observed that the adsorption attained equilibrium around 2 hours. The maximum adsorption capacity of unmodified and modified jute were 25.5 mg/g and 29.47 mg/g respectively. Phan et al. (2006) studied the efficacy of fibrous activated carbon prepared from natural jute (cellulose content: 58-63%, lignin content: 12-15%) and coir fibers on removal of Cu and organic contaminates. The adsorption capacity of raw jute fibers to Cu ions was found to be 22.7 mg/g. Furthermore, raw jute fibers were found to be more efficient than modified fibers for Cu ions removal because of the greater influence of carboxylic –COOH surface groups. The majority of studies have focused on investigating the adsorption capacity of jute fibers from aqueous solution. However, in this study jute fibers have been ground to increase its specific surface area for adsorption. In context of geotextile dewatering tests, long jute fibers might create blinding spots or might even clog the geotextile leading to reduced dewatering and performance. The ground jute fibers also help to form homogenous slurry with the soil and is believed to enhance dewatering rate.

Kraft pulp is made by mixing wood fibers with a solution of caustic soda and sodium sulfide, and cooking them inside a digester. The cooking process attacks and dissolves the phenolic material called lignin that glues the fibers to each other in the wood. After cooking, they are blown by reducing the pressure to the atmospheric pressure in the blowing process. The finished product is brown in color and fluffy in nature termed kraft pulp. Although significant number of studies have been done on the adsorption of metal ions by kraft lignin, studies involving kraft pulp are very limited. Sciban and Klasnja (2004) investigated the abilities of different types of wood sawdust and wood originate such as kraft pulp of 1mm length for removing Cu, Zn, Cd, and Ni. Among the investigated adsorbents, pulp had a fair adsorption efficiencies of 17.1% Cu, 6% Zn, 10% Cd, and 8.2% Ni.

It can be seen that most of the studies have been performed at lower concentration of metal ions and under controlled pH. Also, many studies have focused on modifying the adsorbents to increase its adsorption capacity. However in order to design effective amendment strategies to treat heavy metal solutions, the interaction of the adsorbent with heavy metal ions has to be studied under different conditions such as time of contact and amount of adsorbent. In this study, the adsorption capacity of all adsorbents to 500 ppm metal ion solutions have been assessed by sampling and Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) testing the effluents at regular time interval (30 min, 1 hr, 2hr, 4hr). Moreover, in order to optimize the amount of these adsorbents to be mixed, all the tests have been performed with 0.5g, 1g, 1.5g, and 2 g of adsorbents. Since wide range of pH is found at many heavy metal contaminated environments, setting the pH of the system to a predetermined constant value is not realistic and practical. Hence, all the adsorption tests in this study is not pH controlled.

2.2 Objectives

The primary objective of this study is to investigate the efficacy of three cellulosic materials (peanut hulls, jute fibers, kraft pulp) to adsorb most commonly encountered heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}) from aqueous solutions. The cellulosic materials were chosen keeping in mind their cost, accessibility, ease of handling and use, and sustainability. The studied adsorbents are inexpensive, easily available, and sustainable. Peanut shells are produced in large quantities in US, and are very cheap and accessible. Jute fibers is one of the most common and economical natural fiber grown in most tropical parts of the world. Kraft pulp is a waste produced during the paper pulping process and large quantities of such waste is produced worldwide. All the adsorbents were ground to ease its mixing with the metal solution and also to increase the specific surface area for adsorption. The studied metals are listed by USEPA as the most common and dangerous heavy metal ions found in water.

The overall objective of this study is to investigate the efficacy of these cellulosic adsorbents not only to prevent heavy metals leaching out in effluents during geotextile dewatering but also to improve dewatering performance. However, proper information about the amount and time of mixing the adsorbents with the particular metal ion species is very important for its effectiveness. If the amount of adsorbents to be added is not properly determined in geotextile dewatering application, it might lead to clogging of bag and reduced dewatering rate, higher turbidity of the filtrate and weaker filter cake. Hence, the results from this study will be used to quantify as well as optimize the amount and time of mixing for geotextile dewatering tests.   Also, the performance and the advantages of these adsorbents are compared.

2.3 Materials and Test Method

2.3.1 Materials

Peanut husks were obtained from Birdsong Peanuts, a peanut shelling company out of Suffolk, VA. The jute fibers 1 cm in length were obtained from Korea through Bast Fibers LLC, headquartered in Cresskill, NJ. Kraft pulp was obtained from kraft pulping process at State University of New York, College of Environmental Science and Forestry (SUNY-ESF).

All of the adsorbents were ground to particulate form to increase its specific surface area for adsorption. Adsorbents with greater surface area possess an increased number of available active sites for binding with metal ions (Bozic et al. 2009). To determine the impact of surface area on adsorption, Brown tested the uptake of copper onto peanut hulls sieved through 80,40 and 25 mesh seives (Brown et al. 2000). It was determined that particles passing sieve size 80 had the greatest adsorption capacity; thus showing that increased external suface area increases adsorption capacity.

The peanut husks (shown in Figure 2.1a) were ground using a blender for 10 minutes and sieved through US sieve no 60 to obtain fine particles ranging from 50 µm to 250 µm (see Figure 2.1b). Preparation of jute also involved grinding the fibers in a blender for 10 minutes. The fibrous nature of the jute prevented sieving. The ground 1 cm jute fibers (see Figure 2.2a) resulted in approximately 300 µm long fibers with diameter around 50 µm (see Figure 2.2b). Kraft pulp (see Figure 2.3a) after drying in oven for 24 hours at 100°C was ground for 45 minutes using a blender. During grinding, the small chunks of pulp expanded into large volume and resulted into fluffy fiber bundles approximately 350 µm and larger (see Figure 2.3b). The Scanning Electron Microscope (SEM) image of peanut hulls, jute fibers and kraft pulp are shown in 2.1c, 2.2c and 2.3c respectively.

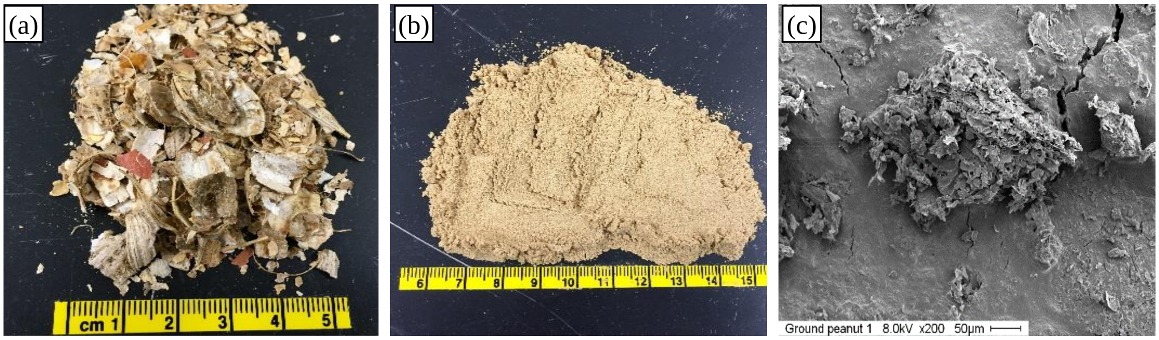

Figure 2.1 (a) Peanut husk, (b) Ground peanut husk, and (c) SEM image of ground peanut hull

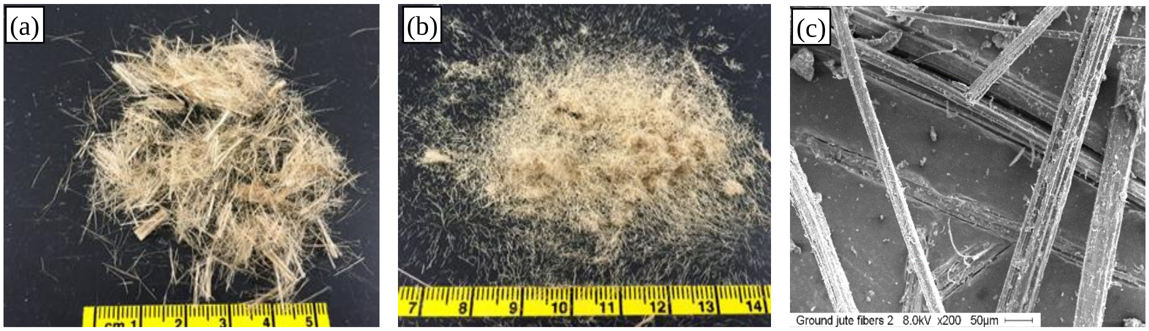

Figure 2.2 (a) Jute fibers, (b) Ground jute fibers, and (c) SEM image of ground jute fibers

Figure 2.3 (a) Kraft pulp, (b) Ground kraft pulp, and (c) SEM image of ground kraft pulp

2.3.1.1 Characterization of adsorbents

The adsorbents were characterized for their cellulose and lignin content. The TAPPI standard test (T203 cm-99) was carried out to measure the amount of cellulose and hemicellulose. The amount of lignin was calculated using the Kappa number. The lignin content was estimated by using TAPPI standard test (T222 om-06). The adsorbent was mixed with 100 mL of Sodium Hydroxide reagent and was stirred until it was fully dispersed in the reagent. Then 100 mL of water was added and mixing was continued for one hour at temperature of 25°C. This adsorbent suspension was then filtered and 25 mL of filtrate was taken and mixed with 10 mL of 0.5N potassium dichromate solution in a 250 mL conical flask. Then 50 mL of concentrated sulfuric acid was added carefully with swirling. The mixture was allowed to rest for 15 minutes and then 50 mL of water was added to bring it to the room temperature. Then, 2 to 4 drops of ferroin indicator was added and titrated with 0.1N ferrous ammonium sulfate till the color changed to purple. Finally, blank titration was carried out with just NaOH and water. The alpha cellulose was calculated using the following equation.

$$\text{Alpha-Cellulose \%} = 100 - ((6.85(V2-V1)*N*20)/ (A*W))$$

where, V1= titration of filtrate, mL

V2= Blank titration mL

N = normality of ferrous ammonium sulfate

A = volume of filtrate

W= dry weight of adsorbent

For the determination of gamma cellulose 50 mL of adsorbent filtrate was mixed with 50 mL of sulfuric acid. The mixture was heated using a 70-90°C hot water bath for few minutes to `pipette, 50 mL of clear solution was added to 10 mL of 0.5N potassium dichromate solution in a beaker and 90 mL of concentrated sulfuric acid was added carefully. The solution was kept in the hot water bath for 15 minutes and the titration followed the same procedure as the alpha cellulose.

$$\text{Gamma Cellulose \%} = [6.85(V4-V3)*N*20]/ [25*W]$$

$$\text{Beta Cellulose \%} = 100- (\text{alpha \%}+\text{gamma \%})$$

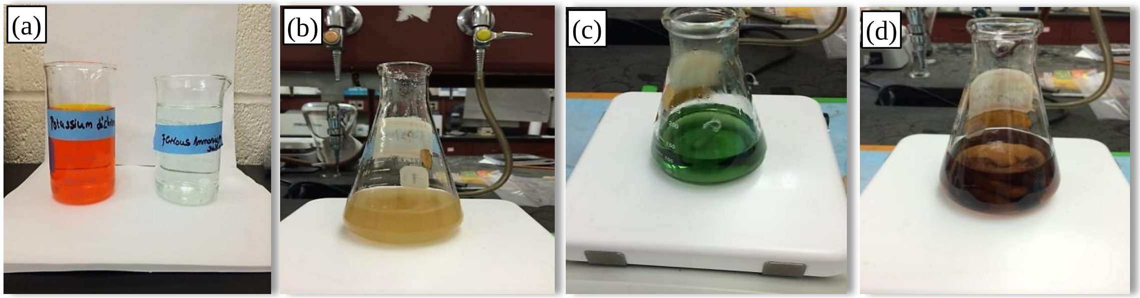

Figure 2.4 (a) & (b) Pulp Filtrate solution after extracting with NaOH, (c) Pulp filtrate with potassium dichromate and sulfuric acid, and (d) Color change after the addition of ferrous ammonium sulfate

Lignin content was determined by calculating the Kappa number. The lignin content in adsorbents was estimated by using TAPPI standard test T222 om-06. In this method, the carbohydrates in wood and pulp are hydrolyzed and solubilized by sulfuric acid. The acid insoluble lignin is filtered off, dried and weighed. 15 mL of 72% sulfuric acid for jute fibers and peanut hulls and 40 mL for pulp powder was added to the beaker containing the test specimen. During the addition of sulfuric acid the beaker containing the test specimen was kept stirring using magnetic stir bar. After the complete addition of sulfuric acid, the beaker was placed in a bath at 20˚C and kept macerating using a glass rod. After the specimen was completely dispersed in sulfuric acid, the beaker was covered with watch glass and kept in a bath at 20˙°C for 2 hours. The material was stirred frequently during this time to ensure proper mixing. The material in the beaker was diluted to 3% sulfuric acid, by the addition of water. This solution was then boiled for 4 hours, maintaining the constant volume, either by using reflux condenser or by the frequent addition of hot water. Then the beaker was kept in an inclined position overnight to allow the insoluble material (lignin) to settle. Without disturbing the precipitate, the solution was decanted through a filtering crucible, and then the precipitate (lignin) was washed with hot water, kept in the oven at 105 °C, cooled and weighed. Lignin content was then calculated using the formula:

$$\text{Lignin\%} = A*100/W$$

where, A = Weight of lignin, gm

W = Oven-dry weight of test specimen, gm

The percentages of cellulose and lignin for the selected adsorbents are given in Table 2.2.

Table 2.2 Cellulose and Lignin Content of the Adsorbents

Adsorbent	**% Cellulose**	**% Lignin**
Peanut hulls	55.1	27.6
Jute fibers	85-88	12-15
Kraft pulp	98	2.7

2.3.2 Reagents

All the compounds used to prepare reagent solutions were of analytic grade. The reagents were purchased from Sigma Aldrich. Stock solutions of the test reagents were made by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$ in de-ionized water. The initial concentration of the all heavy metal ions was 500 ppm.

2.3.3 Method

Batch adsorption tests were carried out by fixing the concentration of metal ion and varying the amount of adsorbent. 500 ppm single heavy metal solutions were prepared by adding a calculated amount of Lead Nitrate, Copper Nitrate, Cadmium Nitrate, or Zinc Nitrate into 1,000 mL of distilled water. To ensure proper mixing, each metal solution was stirred with a magnetic stirrer for 15 minutes prior to the start of each test.

For each adsorbent material, samples were prepared by adding 0.5, 1, 1.5, and 2 grams of adsorbent into 500 mL of the prepared 500 ppm single heavy metal solutions. The blanks were also collected and measured, and the initial concentration as measured from blanks were 500 ppm Pb, 456 ppm Cd, 516 ppm Cu, and 510 ppm Zn. The samples were mixed continuously using a magnetic stirrer for 4 hours. Sampling was conducted at 30 min, 1 hour, 2 hours and 4 hours. At each sampling point, two samples were taken by extracting using a 15 mL pipette and filtering with 41 Whatman filter paper. Hence, for each heavy metal, for three adsorbents, 48 samples were prepared. Following filtering, samples were centrifuged in Champion S-50 D centrifuge meter and decanted into new vials to reduce the potential for remaining adsorbent particles to clog the testing instrument. Each filtrate sample was tested for heavy metal ions using Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES).

Presence of some small chunks that remained ungrounded during the grinding of kraft pulp prevented to form a homogenous mix with the metal solution. However, a homogenous mix was achieved for peanut hulls and jute fibers (see Figure 2.5a and 2.5b).

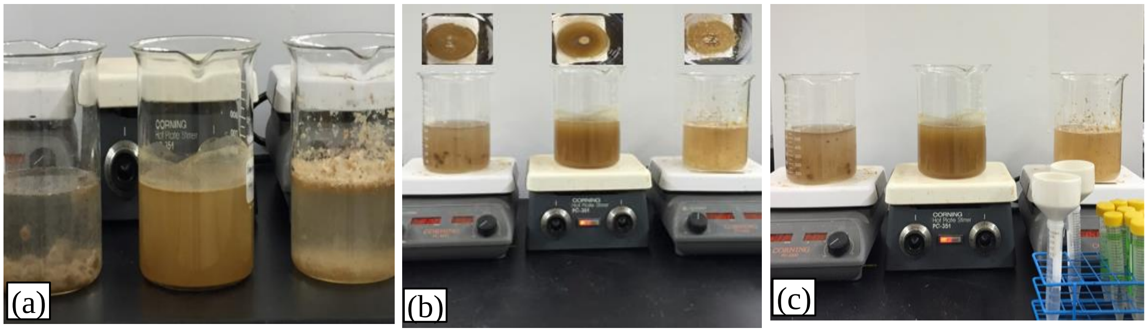

Figure 2.5 (a) 2 grams of adsorbents (From left to right: jute, peanut hull and kraft pulp) mixed with the metal solution, (b) Mixing, and (c) Sampling at 0.5, 1, and 4 hours

2.4 Results and Discussion

2.4.1 Kinetics and removal percentages

To understand the effect of time on adsorption of heavy metal ions, adsorption tests were carried out for 4 hours. The samples were collected at 0.5, 1, 2, and 4 hours, and at each sampling point, two samples were filtered into a 15 mL vial and centrifuged. The results presented are the average of readings conducted on two samples at each sampling point. The samples were tested for metal concentration using ICP-OES. Kinetic studies were performed with 0.5, 1, 1.5, and 2 grams of adsorbents. The removal percentage was calculated from the initial concentration (C_i) of the heavy metal solution and the final concentration (C_f) in the filtrate, and is given by:

$$\text{Removal Efficiency (\%)}=\frac{C_i-C_f}{C_i}*100\%$$

The adsorption of metal ions by different dosage of peanut hulls as a function of time is shown in Figure 2.6 and the summary of removal efficiencies is given in Table 2.3. It can be seen that although equilibrium was reached at different times, majority of the adsorption of all metal ions occurred during the first 30 minutes and the adsorption proceeded at a slow rate till equilibrium was attained. From Figure 2.6 (a), it can be seen that the removal of Pb ions increased with the increase in amount of peanut as evident by the decrease in filtrate concentration with time for all dosage of peanut hull. The maximum removal efficiency of 38% of Pb achieved by 2g of peanut hull was almost double compared to 21% achieved by dosage of 0.5g. However, for all dosage of peanut hull except 2g, the concentration of Pb in the filtrate did not decrease beyond 1 hr mixing referring to adsorption equilibrium. For 2g dosage of peanut hull, equilibrium for adsorption of Pb was achieved in 2 hrs. It was also observed that for all dosage of peanut hull after equilibrium time, concentration of Pb in the filtrate increased. This increase in concentration could be because of desorption of Pb ions in the solution from the adsorbed sites. From Figure 2.6 (b), it can be seen that the adsorption of Cd ions increased with the increase in dosage of the peanut hull from 0.5 g to 2g, and a maximum removal efficiency of 21 % was achieved with 2 g dosage. Except one anomaly shown by 1.5 g peanut hull, the adsorption of Cd ions by all dosage of peanut hull reached equilibrium at 4 hours. Compared to Pb ions, the adsorption of Cd into all dosage of peanut hull took longer to reach equilibrium, and the maximum removal efficiency was found to be 11-17% lower. The adsorption of Cu into all dosage of peanut hull is shown in Figure 2.6 (c). It can be seen that all dosage of peanut hull reached equilibrium at different times. The maximum removal efficiency of 20.78% was achieved by 1.5 gram dosage at 2 hrs. (Refer Table 2.3). The removal efficiency for Cu decreased slightly when the dosage of peanut hull was increased from 1.5 g to 2g. The adsorption of Zn by all dosage of peanut is shown in Figure 2.6 (d). It was observed that the adsorption of Zn ions into peanut hull did not depend upon the dosage as opposed to Pb, Cd, and Cu. A maximum removal efficiency of 15-17% was achieved by peanut hull irrespective of the dosage. The adsorption of Zn was also observed to be slow as the equilibrium was attained at 4 hrs.

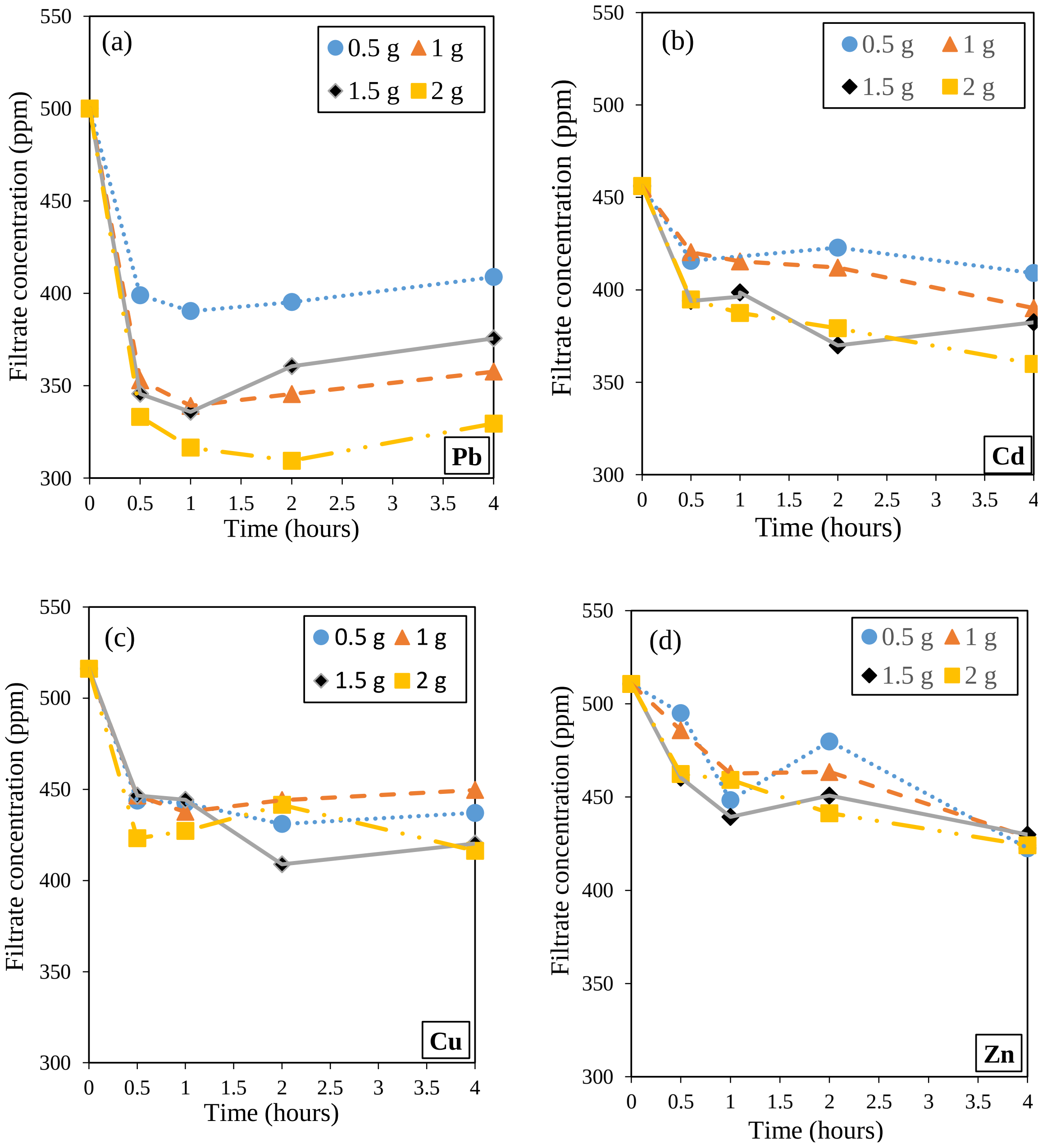

Figure 2.6 Kinetic study: peanut hull (a) Adsorption of Pb, (b) Adsorption of Cd, (c) Adsorption of Cu, and (d) Adsorption of Zn

Table 2.3 Summary of removal percentages for all dosage of peanut hulls

PEANUT HULL	Amount (g)	Initial Concentration (ppm)	Equilibrium time (hours)	Equilibrium concentration (ppm)	Removal %
Pb	0.5	500.00	1	390.42	21.92
	1	500.00	1	339.09	32.18
	1.5	500.00	1	335.93	32.81
	2	500.00	2	309.42	38.12
Cd	0.5	456.24	4	409.05	10.34
	1	456.24	4	390.09	14.50
	1.5	456.24	2	369.99	18.90
	2	456.24	4	359.93	21.11
Cu	0.5	516.09	2	430.98	16.49
	1	516.09	1	437.64	15.20
	1.5	516.09	2	408.85	20.78
	2	516.09	4	416.33	19.33
Zn	0.5	510.70	4	422.58	17.26
	1	510.70	4	428.62	16.07
	1.5	510.70	4	429.95	15.81
	2	510.70	4	424.12	16.95

The kinetics of adsorption of Pb, Cd, Cu, and Zn ions on jute fibers is shown in Figure 2.7 (a), (b), (c), and (d) respectively. The summary of removal percentages for all dosage is given in Table 2.4. It can be seen that for all dosage of jute fibers except 2 g, adsorption of Pb reached equilibrium in approximately 4 hours. The equilibrium of adsorption of Pb into 2 g dosage of jute fibers reached equilibrium much faster (2 hours) than other dosage of jute. Although different dosage of jute fibers reached equilibrium at different times, maximum removal efficiency of 47% Pb was achieved by all dosages. Interestingly, the removal efficiency of 0.5 g jute to Pb was highest compared to the higher dosages (Refer Table 2.4). In case of 2 g dosage of jute fibers, increase in concentration of metal at the filtrate was observed past the equilibrium state. The adsorption of Cd onto different dosage of jute fibers is shown in Figure 2.7 (b). It can be seen that all other dosage of jute fibers except 0.5 g took 4 hours to reach equilibrium for adsorption of Cd. The equilibrium in case of 0.5 g dosage was achieved much faster (2 hour). The adsorption capacity of jute fibers to Cd increased very slightly with the increase in its dosage. When the dose of jute fibers was increased from 0.5 g to 2g, only 2% increase in removal efficiency of Cd was observed (Refer Table 2.4). The maximum removal efficiency of Cd that could be achieved by jute fibers was 12%. Based on these results, it can also be seen that the removal efficiency of Cd by jute fibers is approximately 8% lower than that of peanut hull. The adsorption of all dosage of jute fibers to Cu is shown in Figure 2.7 (c). The adsorption of Cu by all dosage except 0.5 g reached equilibrium at 2 hours. However, adsorption of Cu by 0.5 g jute fibers attained equilibrium faster (1 hour). The removal efficiency of Cu by jute fibers could not be related to the dosage. Maximum removal efficiency of 15% Cu was achieved by 1.5 g jute fiber. However, the removal efficiency dropped to 11% when the dosage was increased from 1.5 g to 2 g of jute fiber. It can be seen that the adsorption capacity of jute fibers to Cu is approximately 6-7% lower than the peanut hulls. The adsorption of Zn onto jute fibers is shown in Figure 2.7 (d). The equilibrium of Zn adsorption for all dosage of jute except 0.5 g reached at 4 hours. The removal efficiency of Zn increased with the increase in the dosage of jute fibers. However, a minor increase of 3% in removal efficiency was observed when the dose of jute fibers was increased from 0.5 g to 2 g. Also, jute fibers had lesser affinity (3-4%) than peanut hull to Zn ions. In summary, it can be concluded that jute fibers exhibited highest affinity to Pb as the removal efficiency of Pb (47%) was approximately 3-5 times greater than that of Cu, Cd, and Zn ions (10-15%). Also, it was seen that although different dosages of jute fibers (0.5-2g) reached equilibrium at different times, same removal efficiency of Pb was achieved by all of them.

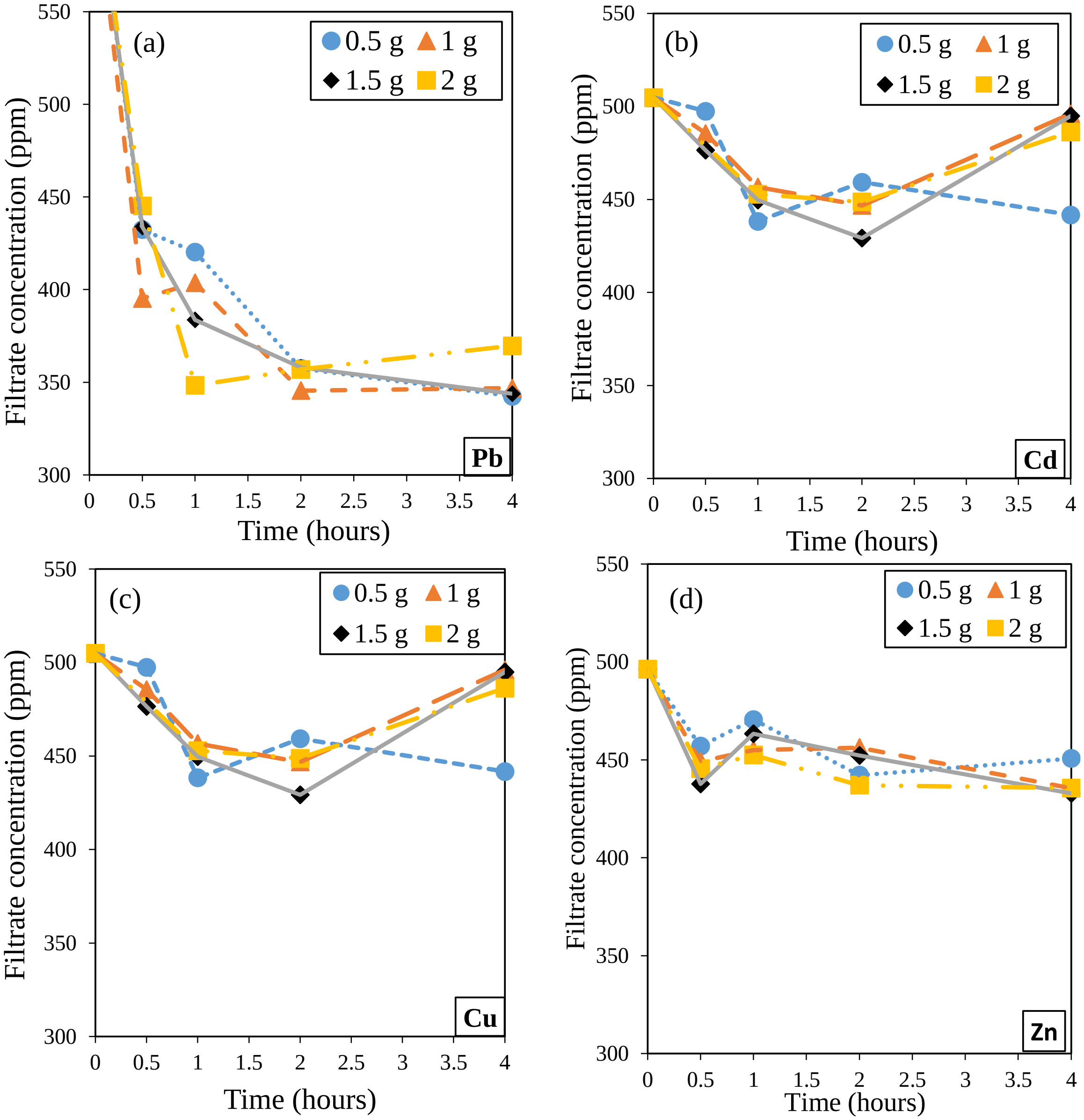

Figure 2.7 Kinetic study: Jute fibers (a) Adsorption of Pb, (b) Adsorption of Cd, (c) Adsorption of Cu, and (d) Adsorption of Zn

Table 2.4 Summary of percentages for all dosage removal of jute fibers

JUTE FIBERS	Amount (g)	Initial Concentration (ppm)	Equilibrium time (hours)	Equilibrium concentration (ppm)	Removal %
Pb	0.5	646.33	4	342.43	47.02
	1.0	646.33	4	346.43	46.56
	1.5	646.33	4	343.79	46.81
	2.0	646.33	2	348.34	46.11
Cd	0.5	496.33	2	442.18	10.91
	1.0	496.33	4	435.56	12.24
	1.5	496.33	4	432.96	12.77
	2.0	496.33	4	435.63	12.23
Cu	0.5	504.84	1	438.26	13.19
	1.0	504.84	2	446.78	11.50
	1.5	504.84	2	429.25	14.97
	2.0	504.84	2	448.71	11.12
Zn	0.5	519.75	2	462.92	10.93
	1.0	519.75	4	461.19	11.27
	1.5	519.75	4	448.72	13.67
	2.0	519.75	4	449.82	13.46

The adsorption of Pb, Cd, Cu , and Zn into kraft pulp are shown in Figures 2.8 (a), (b), (c), and (d), respectively. It can be seen from Figure 2.8 (a) that all dosage of kraft pulp except 0.5 g reached equilibrium at 2 hours, whereas 0.5 g took 4 hours to reach equilibrium for the adsorption of Pb. The adsorption increased with the increase in dosage of kraft pulp till 1.5 g and the maximum removal efficiency obtained was 28%. The removal efficiency of Pb achieved by kraft pulp was 10-20% lower than that of peanut hull and jute fibers (Refer Table 2.5). All dosage of kraft pulp reached equilibrium at 1 hour for the adsorption of Cd ions. The removal efficiency increased with the increase in dosage of kraft pulp with a maximum of 29% for the adsorption of Cd. It can be seen that all dosage of kraft pulp attained equilibrium at 1 hr for the adsorption of Cd.

In case of 2g kraft pulp dosage, the concentration of Cd in the filtrate increased after the equilibrium (Refer Figure 2.8 (b)). Kraft pulp exhibited better affinity to Cd compared to jute or peanut hull. The maximum removal efficiency of kraft pulp to Cd was 10-15% higher than that of jute fiber or peanut hull. All dosage of kraft pulp reached equilibrium at 2 hours for the adsorption of Cu, and except 0.5 g, the removal efficiency increased with the increase in dosage. The maximum removal efficiency of Cu was 28%, which is greater than that achieved by jute (14%) or peanut hull (20%). As seen in case of Cd and 2g dosage of kraft pulp, there was increase in the concentration of Cu after the equilibrium state of adsorption. The adsorption of different dosage of kraft pulp to Zn ions is shown in Figure 2.8 (d) and the results are summarized in Table 2.5. The equilibrium of adsorption of Zn by kraft pulp occurred much slower (2 hrs.) with the lower dosage (0.5g and 1g) than the higher dosage (1.5 g and 2g)**.** The adsorption capacity of kraft pulp to Zn increased with the increase in dosage except 1 g (Refer Table 2.5). Similar to the Cd ions, maximum removal efficiency of 30% of Zn was much higher than that achieved by jute fibers or peanut hull.

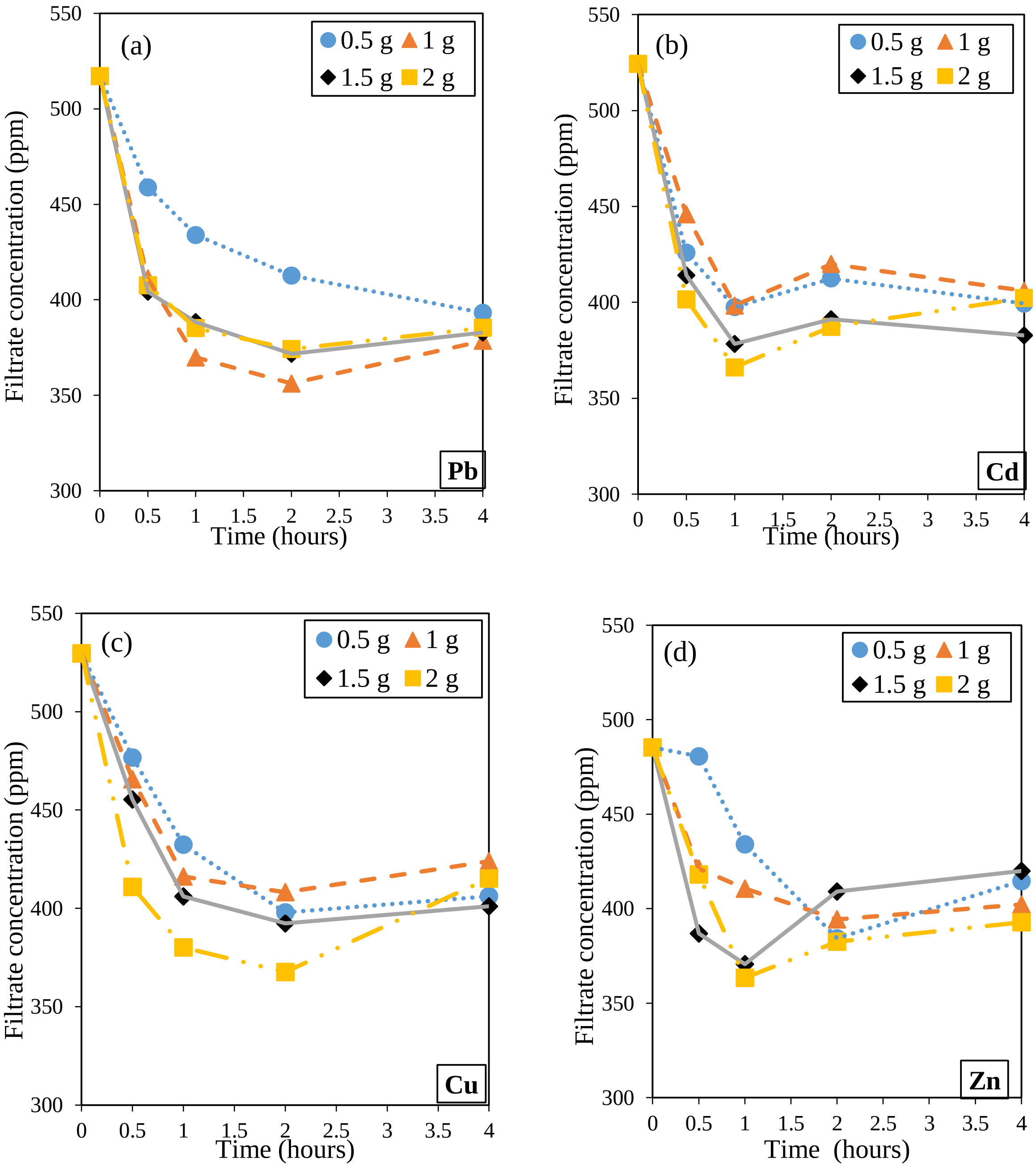

Figure 2.8 Kinetic study: Kraft Pulp (a) Adsorption of Pb, (b) Adsorption of Cd, (c) Adsorption of Cu, and (d) Adsorption of Zn

Table 2.5 Summary of removal percentages for all dosage of kraft pulp

KRAFT PULP	Amount (g)	Initial Concentration (ppm)	Equilibrium time (hours)	Equilibrium concentration (ppm)	Removal %
Pb	0.5	517.24	4	458.89	11.28
	1	517.24	2	411.19	20.50
	1.5	517.24	2	371.67	28.14
	2	517.24	2	374.17	27.66
Cd	0.5	517.24	1	397.49	23.15
	1	517.24	1	398.33	22.99
	1.5	517.24	1	378.37	26.85
	2	517.24	1	366.115	29.22
Cu	0.5	517.24	2	397.92	23.07
	1	517.24	2	408.23	21.08
	1.5	517.24	2	392.36	24.14
	2	517.24	2	367.63	28.92
Zn	0.5	517.24	2	384.29	25.70
	1	517.24	2	394.32	23.77
	1.5	517.24	1	370.64	28.34
	2	517.24	1	363.39	29.74

In general, it can be concluded from the kinetic study that all adsorbents exhibited high affinity for Pb with the removal efficiency between 30-50%. Jute and peanut hull did not show high affinity towards Cu, Cd, and Zn ions, and the removal efficiency varied between 15-20%. However, it can be seen that kraft pulp exhibited good affinity towards Cu, Cd, and Zn compared to jute fibers and peanut hull. The maximum removal efficiency as high as 30% was achieved by the kraft pulp for all metal ions.

2.4.2 Adsorption Isotherms

Adsorption isotherms are often used as empirical models which are mainly used to quantify adsorption parameters such as maximum adsorption capacity. They are obtained from measured data by means of regression analysis. The most frequently used isotherms are the linear isotherm, Freundlich isotherm, Langmuir isotherm, and the BET model. Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different sorbents (Langmuir 1916). In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites.

The adsorption data, for each combination of adsorbent and heavy metal, at each mixing time, was linearized using the Langmuir isotherm to quantify the adsorption capacity of each adsorbent. The linear form of the Langmuir equation is given by,

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} * K} + \frac{c_e}{q_{\max}}$$

where q_e is the amount of adsorbent at equilibrium (mg/g), K is the Langmuir constant (L/mg), q_{max} is the maximum adsorption capacity, c_e is the equilibrium solute concentration (mg/L). The Langmuir isotherm assumes that the adsorbent poses a homogenous surface with uniform adsorption potential (Argun et al. 2007). When $\frac{c_e}{q_e}$ is graphed versus c_e, a straight line plot should result with a slope of 1/ $q_{\max}$ (Tasar et al. 2014).

The summary of maximum adsorption capacities of peanut hull, jute fibers, and kraft pulp for four heavy metals have been shown in Table 2.6, 2.7, and 2.8 respectively. The plot of isotherms for peanut hull, jute fibers, and kraft pulp are shown in Figures 2.9, 2.10, and 2.11 respectively.

It can be seen from Table 2.6 and Figure 2.9 (a) that adsorption of Pb into peanut hulls fitted well into Langmuir isotherm with high regression coefficient of 0.98-0.99. The maximum adsorption capacity of peanut hull to Pb ranged from 11-23 mg/g. Brown et al. (2000) evaluated the adsorption capacity of 0.25 g peanut hull to Pb and other metals (Cu, Cd, Zn) by conducting a batch adsorption test on a 1000 mg/l metal solution equilibrated for 4 hours. They reported the maximum adsorption capacity of peanut hull to Pb to be 30 mg/g. The Langmuir isotherm plot of Cd into all dosage of peanut hull presented in Figure 2.9 (b) shows that a good fit was obtained with regression coefficients between 0.93-0.96. The maximum adsorption capacity of peanut hull to Cd ranged from 2.2-3.6 mg/g, which is very low compared to the adsorption of Pb. Brown et al. (2000) reported the adsorption capacity of peanut hull to Cd to be 6 mg/g, and the preference of the adsorbent to studied metal ion was Pb>Zn>Cu>Cd. Also, the adsorption of Cu into peanut hull fitted well into Langmuir isotherm with regression coefficients ranging between 0.95-0.98 and is shown in Figure 2.9 (c). The maximum adsorption capacity determined was 11.88 mg/g (Refer Table 2.7). It is slightly higher than the adsorption capacity reported by Brown et al. (2000) for the adsorption of Cu by peanut hull (8 mg/g). The adsorption of Zn into peanut hulls fitted using Langmuir isotherm (Refer Figure 2.9 (d)) produced a fair regression coefficient of 0.88-0.95, and the maximum adsorption capacity was 4.1 mg/g.

As shown in Figure 2.10 (a), the adsorption of Pb into jute perfectly fit the Langmuir isotherm with very high regression coefficient (0.99-1.00). Jute’s 100mg/g capcity for Pb adsorption is an order of magnitude greater than any other adsorption capacity observed during the testing. Shukla and Pai (2005b) reported the maximum adsorption capacity of 1 cm jute fibers to Pb to be 25.5 mg/g. However, the grinded jute fibers used in this study exhibited adsorption capcaity almost 4 times greater than that reported by them. The adsorption of Cd into jute fibers fit the Langmuir isotherm with fair regression coefficient (0.92-0.98) and is shown in Figure 2.10 (b). The maximum adsorption capcity of jute fibers to Cd ions was 2.69 mg/g. As the adsorption of Cu into jute fibers did not produce consistent data and couldnot be modeled using isotherm, hence the maximum adsorption capacity couldnot be reported. Similarly, the adsorption of Zn onto jute fibers produced a good linear fit with mamximum adsorption capacity of 4.10 mg/g (Refer Figure 2.10 (c)). Shukla and Pai (2005a) reported a similar adsorption capacity (3.55 mg/g) for the adsorption of Zn by jute fibers.

The summary of Langmuir isotherm parameters for adsorption of all metals into kraft pulp is shown in Table 2.8. It can be seen that the adsorption of Pb into kraft pulp fitted well into the Langmuir isotherm with high regression coefficeint of 0.94-0.99, and is shown in Figure 2.11 (a). The maximum adorption capacity of kraft pulp to Pb was16 mg/g, significantly lower than that of jute fibers. Kraft pulp exhibited better affinity towards Cd ions as the maximum adsorption capacity was 24 mg/g, higher than that of jute fiber and peanut hull and isotherm is shown in Figure 2.11 (b).Unlike jute, a good fit was obtained on adsorption of Cu into kraft pulp (Refer Figure 2.11 (c)) with maximum capacity of 13 mg/g. The adsorption of Zn into kraft pulp produced a good linear fit with regression coefficient of 0.96-0.99. The maximum adsorption capacity was 10.82 mg/g which is hgher than that of jute fibers and peanut hulls (Refer Figure 2.11 (d)).

Table 2.6 Maximum adsorption capacity for different dosage of peanut hull

PEANUT HULL	**Amount (g)**	**q_{max} (mg/g)**	**r^2**
Pb	**0.5**	21.69	0.98
	1	22.88	0.99
	1.5	11.57	0.98
	2	15.90	0.99
Cu	**0.5**	11.88	0.96
	1	5.05	0.98
	1.5	3.68	0.98
	2	2.78	0.99
Cd	**0.5**	3.16	0.96
	1	2.29	0.96
	1.5	3.62	0.93
	2	3.41	0.97
Zn	**0.5**	4.10	0.88
	1	2.69	0.88
	1.5	3.00	0.95
	2	2.21	0.94

Table 2.7 Maximum adsorption capacity for different dosage of jute fibers

JUTE FIBERS	**Amount (g)**	**q_{max} (mg/g)**	**r^2**
Pb	0.50	100.00	0.99
	1.00	56.18	1.00
	1.50	33.22	1.00
	2.00	22.52	0.99
Cd	0.50	2.69	0.92
	1.00	NA	NA
	1.50	1.85	0.93
	2.00	1.54	0.98
Zn	0.50	4.10	0.97
	1.00	2.50	0.96
	1.50	1.53	0.97
	2.00	1.54	0.98

Table 2.8 Maximum adsorption capacity for different dosage of kraft pulp

KRAFT PULP	Amount (g)	q_{max} (mg/g)	r^2
Pb	0.5	14.39	0.94
	1	16.13	0.99
	1.5	10.73	0.99
	2	7.44	0.99
Cu	0.5	13.00	0.96
	1	7.10	0.99
	1.5	6.18	0.99
	2	8.68	1.00
Cd	0.5	23.98	1.00
	1	9.30	0.98
	1.5	10.10	1.00
	2	9.15	1.00
Zn	0.5	10.82	0.96
	1	6.02	0.99
	1.5	5.20	0.98
	2	4.18	0.97

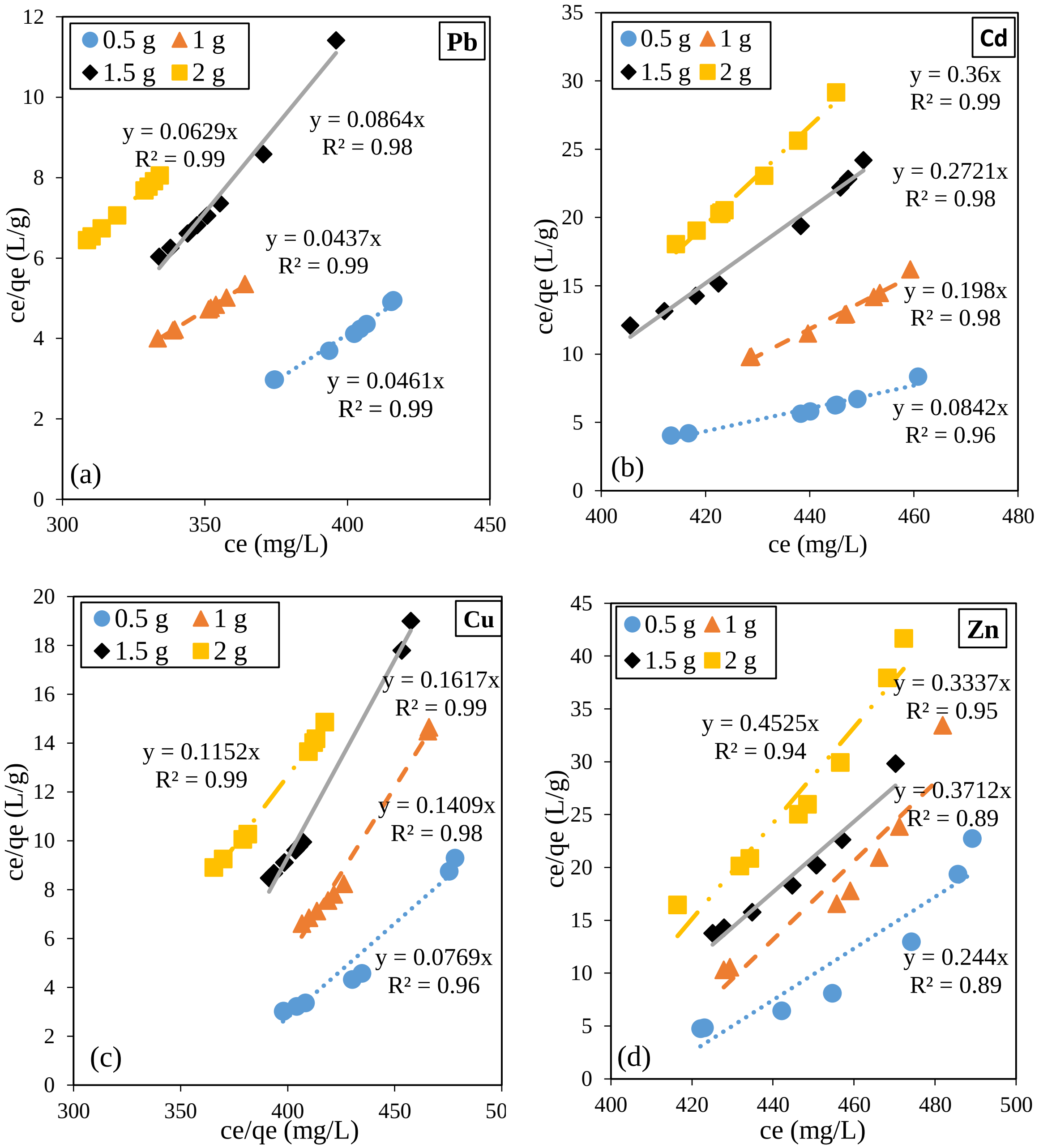

Figure 2.9 Langmuir isotherms: Peanut hulls (a) Adsorption of Pb, (b) Adsorption of Cd, (c) Adsorption of Cd, and (d) Adsorption of Zn

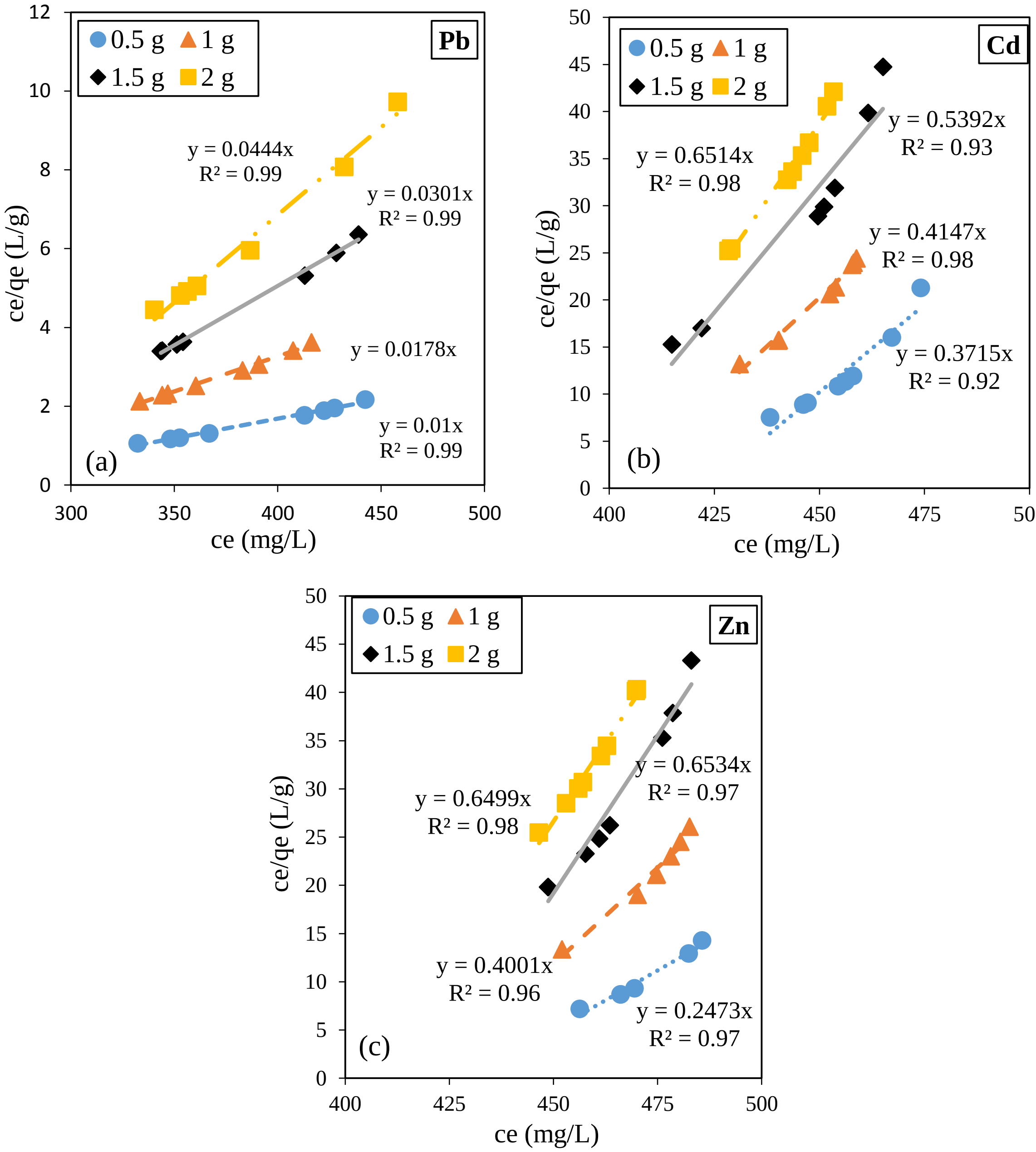

Figure 2.10 Langmuir isotherms: Jute fibers (a) Adsorption of Pb, (b) Adsorption of Cd, and (c) Adsorption of Zn

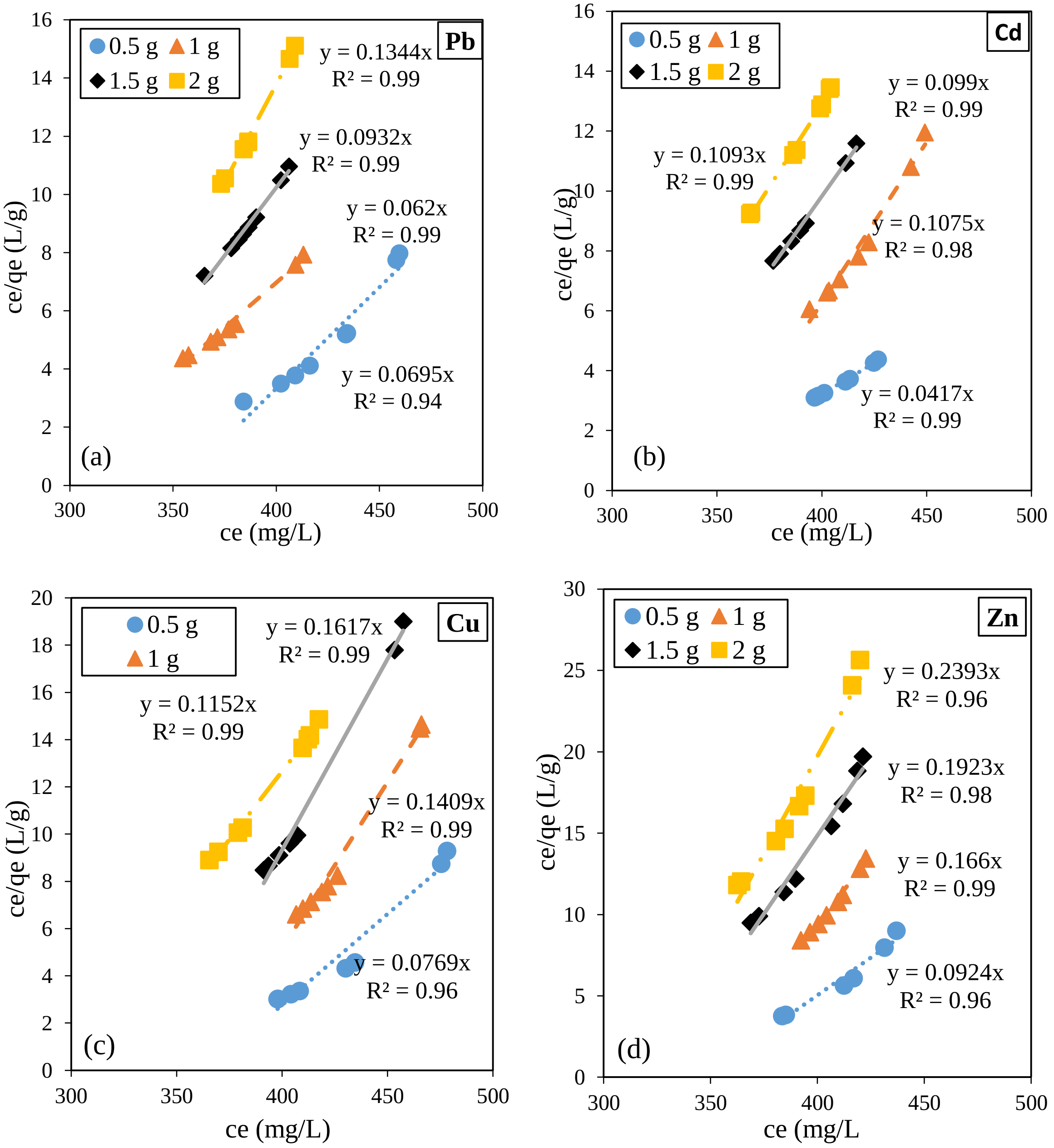

Figure 2.11 Langmuir isotherms: Peanut hulls (a) Adsorption of Pb (b) Adsorption of Cd (c) Adsorption of Cd (d) Adsorption of Zn

2.5 Conclusions

In this study, the efficacy of low cost cellulosic materials to adsorb selected heavy metal ions from aqueous medium was investigated using batch adsorption tests. Using peanut hull, grounded jute fibers, and kraft pulp as adsorbents, adsorption tests were run by varying the adsorbent amount from 0.5 to 2g each sampled at 0.5, 1, 2, and 4 hours adding up to 192 tests in total. All of the adsorbents tested in this study removed selected metal ions (Pb, Cu, Cd, Zn), but with varying degree and affinity. Based on the results and observations from batch adsorption test following conclusions can be drawn.

- All dosage of jute exhibited very high affinity towards Pb ion with a maximum removal of 47% attained at 4 hours. The removal efficiency of Pb did not correlate with the dosage of jute. The removal of Pb ions increased with the increase in dosage of peanut hull, and a maximum removal efficiency of 38% was achieved in equilibrium time of 2 hours. The adsorption of Pb ions increased with increase in dosage of kraft pulp from 0.5 to 1.5g, and its maximum removal efficiency of 28% was much lower than that of jute and peanut hull. The maximum adsorption capacity of jute, peanut hull and kraft pulp for adsorption of Pb ions, determined using Langmuir isotherms, were 100 mg/g, 23 mg/g, and 16 mg/g respectively.
- In case of adsorption of Cu, kraft pulp had the highest removal efficiency of 28% compared to 20% of peanut hull and 15% of jute. Also, different dosage of jute and peanut hull achieved equilibrium at different times unlike an equilibrium time of 2 hours for all dosage of kraft pulp. The removal efficiency of Cu could not be correlated with the dosages of jute fibers and peanut hull. However, the removal efficiency of Cu increased with the increase in dosage of kraft pulp from 0.5 to 1.5g. As seen in case of Pb, desorption of Cu ions took place beyond kraft pulp's dosage of 1.5g as indicated by the increase in metal concentration in the filtrate. The adsorption of Cu by jute fibers did not fit the Langmuir isotherm. The

maximum adsorption capacity of kraft pulp and peanut hull to Cu ions were 13 mg/g and 11.88 mg/g respectively.

- Kraft pulp exhibited high affinity to Cd ions compared to peanut hull and jute fibers. The maximum removal efficiency of 29% was attained at 1 hour. The removal efficiency of Cd ions increased with the increase in dosage of peanut and kraft pulp. However, no correlation was found in case of jute fibers. The maximum removal efficiencies achieved by peanut hull and jute fibers were 21% and 13% respectively. Langmuir adsorption capacities for jute fibers, peanut hull, and kraft pulp were 2.69 mg/g, 3.62 mg/g, and 23.98 mg/g respectively.
- The adsorption of Zn followed the same pattern as Cd with kraft pulp having the highest removal efficiency of 29%. The removal efficiency of Zn could not be correlated with the dosage for all adsorbents. The maximum adsorption capacity of jute fibers and peanut hull was 4.81 mg/g, whereas, kraft pulp had comparatively very high adsorption capacity of 10.82 mg/g.

Hence, it can be seen that the low cost materials rich in cellulose and lignin can be used to remove heavy metal ions like Pb, Cd, Cu, and Zn from the aqueous solution.

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CHAPTER 3

A STUDY ON ADSORPTION AND RETENTION OF HEAVY METALS ON SOIL AND SOIL CONSTITUENTS

3.1 Introduction

Many inland and coastal water bodies have been polluted with heavy metals as a result of discharge from industrial processes including mining operations, smelting, metal plating, tanning, and battery manufacturing and rubber manufacturing (Bailey et al.1999, Shukla et al.2002, Mackie et al. 2007). As a result of these toxic discharges, concentrations of heavy metals such as Pb, Cr, Cd, Cu, Zn, Co, Ni and Mn are often found to be elevated in suspended sediments, bed sediments and the water column.

Among the various components of environment such as air or water, soils have been found to possess higher metal adsorption and retention capacity. Soil being a three phase heterogeneous system consisting of solid phase (minerals and organic matters) and void phase (water and air), the heavy metals have higher possibility of spreading amongst these phases. Heavy metals have tendencies to react with soils, change oxidation states and precipitate (Fein et al.1999). Heavy metals are associated with soil components in several ways, (i) adsorption onto soil particle surfaces, (ii) co-precipitation with major hydroxide or carbonate phase, (iii) binding with organic matter, (iv) occlusion in iron or manganese hydroxides as coatings on soil particles, (v) binding in lattice positions in aluminosilicates (Patterson1987). As the behavior of heavy metals is controlled to some extent by surface reactions, clay and organic colloid matters can be the primary soil components affecting metal adsorption as well as retention (Sposito and Page 1984). The negative charge on clay particles, developed mostly by hydroxyl groups disposing hydrogen ion (pH dependent process), act as a perfect binding site for the heavy metal ions. The negative charge on clay particles can also be developed through pH independent isomorphous ion replacement (Si^{4+} is replaced by Al^{3+}) (Dube et al. 2001). The reactivity of clay particles to positively charged ions also depends upon whether the clay is 1:1 or 2:1. In 1:1 clays, 1 sheet of silicon and oxygen are joined to 1 sheet of aluminum and oxygen. The layers are joined by strong hydrogen bonding so the space between the layers is fixed. It is typical for kaolinite clay and its chemical formula is $Al_2 (OH)_4(Si_2O_5)$. They shrink or swell very little on drying and wetting. 2:1 clays are typical for clays montmorillonite and illite where the unit cell is built from two silica tetrahedral layers surrounding an aluminum octahedral layer. The layers are joined by weak oxygen to oxygen or oxygen to cation exchange which promotes the swelling when it comes in contact with water. As a result, 2:1 clays have higher surface area than 1:1 clays. 2:1 clays have higher negative charge and hence higher adsorption capacity than 1:1 clays (Brown 1998). A brief literature review on the factors affecting the adsorption capacity of selected heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}) ,commonly encountered in the contaminated sites, to soil constituents and minerals has been presented.

3.1.1 Literature review on adsorption of heavy metal ions on soil

The most important parameters controlling heavy metal adsorption and their distribution are soil type, metal concentration, soil pH, solid: solution mass ratio, and contact time (Cavallaro & McBride 1980, Stahl & James1991, Martinez & Motto 2000). In addition, the degree of retention and low solubility of metals from soils is affected by soil parameters such as soil mineralogy (Tiller et al.1963; Jenne1968; Kinniburgh et al.1976;

Cavallaro & McBride1984; Ziper et al.1988), cation exchange capacity (Ziper et al.1988), organic matter content (Elliot et al.1986), amount of metal (Garcia-Miragaya1984), pH (McBride and Blasiak 1979; Cavallaro and McBride1980).

In order to quantify the maximum adsorption capacity of soil to heavy metal ions, generally batch adsorption tests are carried out. The data from the adsorption tests are fitted using adsorption isotherms. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e, to the concentration of the solute in the liquid, c_e, with which it is in contact. It is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution. Among many available isotherm models, Langmuir and Freundlich isotherm models are most commonly used to find out the adsorption parameters such as maximum adsorption capacity and diffusion constants. The mathematical expression and the linear form of the Langmuir equation are given in Equations 3.1a and 3.1b respectively.

$$q_e = \frac{K * c_e}{1 + K c_e} \qquad \text{(Equation 3.1a)}$$

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} * K} + \frac{c_e}{q_{\max}} \qquad \text{(Equation 3.1b)}$$

where, q_e is the amount of adsorbent at equilibrium (mg/g), K is the Langmuir constant (L/mg), q_{max} is the maximum adsorption capacity (mg/g), c_e is the equilibrium solute concentration (mg/L). The inverse of the slope of linear Langmuir plot gives the maximum adsorption capacity in mg/g.

3.1.1.1 Adsorption of Pb

Lead (Pb^{2+}) is one of the most hazardous and common heavy metal which inhibits growth, reduces photosynthesis in plants, reduces water absorption, and promotes defoliation and ATP synthesis (USEPA 1979). The Pb concentration in soil is mainly dependent upon the clay fraction content, therefore the abundance of Pb is higher in argillaceous (clayey) soils compared to the sands and sandy soils (USEPA1986). Background levels of Pb in dry soils in the United States have been reported at 38 ppm in the east and 32 ppm in the west by U.S. EPA (Raji & Anirudhan1998). Clays, peats, Fe oxides and usual soils exhibit excellent affinity towards Pb ions (Basta & Tabatabai1992). The behavior of Pb is also significantly affected by the carbonate content in soils (Heike 2004). However, in noncalcareous soils, the solubility of Pb is controlled by lead hydroxides and phosphates (Elkhatib et al.1991).

Honging et al. (2000) investigated the adsorption of various heavy metals onto Kaolinite, Illite and Ca-montmorillonite. They found that at pH 3.10 the sorption ratio (adsorbed/added) was 7.72 and at pH 4.65 the sorption ratio increased to 25.67 for Illite. Similarly, the sorption ratio for Ca-montmorillonite was 35.84 at pH 3.06, 84.09 at pH 4.53, and 90.91 at pH 5.96. The selective adsorption of Kaolinite and Illite for heavy metals was Pb>Zn>Cu> Cd and Pb>Cu>Zn>Cd respectively. However for Ca-montmorillonite the trend was Cu>Zn>Cd>Pb. Naseem and Tahir (2001) investigated the adsorption of Pb ions on commercial grade Bentonite clay at a concentration of 20 mg of Pb per 1 g of Bentonite. It was found that Bentonite had high affinity to Pb ions and the adsorption followed Langmuir isotherm with a maximum adsorption capacity of 52.6 mg/g. The adsorption of Pb increased from 30 to 94.5% with an increase in pH of the solution from 1.4 to 3.4 and decreased to 40% at pH 5.0. They also found out that more than 96% Pb uptake by Bentonite occurred within 10 mins of interaction. Abollino et al. (2003) investigated the adsorption of heavy metals on Na-montmorillonite by studying the effect of pH and organic substances on adsorption. They concluded that the effect of pH is more pronounced on adsorption of Cu, Pb, and Cd ions because decreasing pH promotes protonation of aluminol (Al-O-H) and silanol (Si-O-H) groups present in clay minerals. Since Pb and Cd ions have larger ionic radius and lower charge density, they are more affected by protonation of the surface groups. Wahba and Zaghloul (2007) compared three different soil minerals (Montmorillonite, Kaolinite and Calcite) for their ability to adsorb heavy metals. They found out that the maximum Pb metal removed from the solution was found in Calcite by about 74.2% as compared to Cd or Zn. The increasing trend of adsorption capacity to these metals had the order Calcite> Montmorillonite > Kaolinite. Ming et al. (2010) investigated the adsorption of Pb, Cd, Ni, and Cu ions onto natural Kaolinite clay. They studied the effect of contact time, pH, initial concentration, competitive adsorption, and ionic strength on the adsorption. They found that 30 min mixing time was optimum for the adsorption as 92 % of Pb was adsorbed within that time. Also, it was reported that 98 % of Pb ions was adsorbed at pH 6.0 when the pH of the solution was increased from 2 to 8. The percentage removal of Pb ions decreased by increasing the initial metal concentration. The adsorption capacity of natural Kaolinite to Pb calculated from Langmuir isotherm was 2.35 mg/g. The adsorption capacity decreased to 1.35 mg/g for competitive adsorption (Pb-Cd-Ni-Cu). It can be seen that most of these studies have been focused on understanding the adsorption of Pb onto pure clay minerals. Also very few studies have studied the adsorption as well as retention of Pb ions by soil particles in presence of other heavy metal ions. Hence, this study aims to study the adsorption of Pb not only on commercial grade pure Kaolinite but also on natural soils.

3.1.1.2 Adsorption of Cu

The average total copper (Cu) contents in soils all over the world ranges between 20 and 30 mg/kg (Alloway 1995). The availability of Cu ions in soil depends upon cation exchange capacity, organic matter content and clay content, soil pH, and amorphous Fe, Al, Si and Mn oxides (Chen et al.1997). Omer et al. (2003) investigated the removal of Cu, Ni, Co and Mn from aqueous solution by Kaolinite. They studied the effect of equilibrium time and thermodynamics on adsorption of the studied heavy metals. The equilibrium time for Kaolinite was found to be 2 hours. Also, adsorption of Cu on raw Kaolinite was shown to follow Langmuir isotherm with a maximum adsorption capacity of 11.0 mg/g. Bhattacharyya and Gupta (2008) investigated the removal of Cu from aqueous solution by Kaolinite, Montmorillonite and their modified derivatives. They found the adsorption capacity of Kaolinite to be 4.4 mg/g. However, Montmorillonite had the high adsorption capacity for Cu of 25.5 mg/g. Sipos et al (2008) investigated the adsorption of Cu, Pb, and Zn on soil mineral phases. Four soils, 8% clay (60 % Vermiculite and 40% Illite), 15% clay (80% Vermiculite and 20 % Illite), 7% clay (75% Chlorite and 25% Illite), and 45% clay (90% Montmorillonite and 10% Illite) were spiked with heavy metal solutions. It was observed that sample containing significant Chlorite and Illite had the highest adsorption capacity (166 mg/g for Pb, 130.02 mg/g for Cu, and 68.76 mg/g for Zn). Wang et al. (2009) in their study found that the adsorption of Cu on natural Kaolinite was sensitive to pH over the range of 2 to 6. The removal efficiency at pH 2 was 38.46%, whereas it doubled (75.27%) at pH 6. Also, the adsorption capacity was found to decrease from 30.39 mg/g to 5.98 mg/g when the Kaolinite concentration was increased from 0.25 to 5 g/L. Ming et al. (2010) found that the maximum adsorption of Cu was observed within 30 mins for Kaolinite. Also, the removal percentage decreased with the increase in initial concentration of Cu in the solution. The adsorption capacity of 1.22 mg/g for Cu decreased to 0.50 mg/g for in presence of other metal ions (Pb-Cd-Ni-Cu).

3.1.1.3 Adsorption of Cd

Cadmium (Cd) exists as Cd^{2+}, $Cd(OH)_2$ (aq), $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$ and $CdCO_3$ and in various other organic and inorganic complexes in aquatic systems (Moore 1991). In soils, they occur as $CdCl^+$, $CdOH^+$ and $CdHCO3^+$ cations and anions such as $CdCl_3^-$, $Cd(OH)_4^{2-}$ and $Cd(HS)_4^{2-}$ (Merian et al. 2008). Like other heavy metal ions, Cd is retained in soils through adsorption and precipitation reactions. Adsorption of Cd increases with the increase in pH of the soil and hence mobility of Cd is greatest in acidic soils (Dijkstra et al. 2004). Bhattacharyya and Gupta (2007) used Kaolinite, Montmorillonite and their other derivatives for removal of Cd from water and concluded that the adsorption was influenced by pH and the amount adsorbed increased with decreasing acidity. For Kaolinite, there was an increase in removal efficiency from 4.3 to 29.5 % by increasing pH from 1 to 10. They found the adsorption capacity of Kaolinite to be 9.9 mg/g and Montmorillonite to be 32.7 mg/g.

3.1.1.4 Adsorption of Zn

The adsorption of zinc (Zn) on soil is a function of pH, clay content, CEC, soil organic matter and soil type. Abdelhamid and Chegrouche (1997) used natural Bentonite for the removal of Zn ions from the aqueous solution and found the Langmuir maximum adsorption capacity between 25.8 to 52.9 mg/g. Bayat (2002) investigated the adsorption of Zn ions by two Turkish fly ashes. It was found out that the fly ash with high calcium content was better adsorbent with the maximum adsorption capacity of 0.251 to 1.194 mg/g in the pH range of 3 to 6. The adsorption capacity of local soil (pH=7.40, 1.81% organic matter, 65% sand, 12.8% silt, 21 % clay) had maximum adsorption capacity of 8.26 mg/g. Sanchez et al. (2003) used Na-bentonite and Ca-bentonite for the adsorption of Zn ions and found that the adsorption followed the Langmuir isotherm model with maximum adsorption capacity of 23.1 mg/g for Na-bentonite and 5.8 mg/g for Ca-bentonite.

The majority of studies on heavy metal adsorption are conducted on pure clay minerals such as Kaolinite, Bentonite, Illite, Chlorite, Vermiculite, and/or mixtures of clay to heavy metal ions. The studies have shown that these minerals have varying preferences to heavy metal ions. It has also been shown that among other heavy metal ions, Pb and Cu are most readily adsorbed and retained in the clay minerals. These studies have confirmed that adsorption of heavy metal ions on soil is highly dependent on pH. However, each heavy metal ion has its own range of pH for maximum adsorption and the range seems to be quite wide as reported by many studies. Also, since the contaminant solution generally encountered in the field contains many metal ions rather than individual ions, hence controlling pH to a single value is not feasible. Hence, in this study the all the tests have been conducted without manipulating or controlling the pH. Among the many mathematical models available to model the adsorption of heavy metals in soils, Langmuir isotherm model have been commonly used. These models by linearizing the adsorption data helps to quantify the maximum adsorption capacity of the metal ions on the soil.

3.2 Objectives

Dewatering high water content contaminated sediment slurries using geotextile tubes has gained huge popularity especially in the United States because of its effectiveness in dewatering and containment. This technology is used in conjunction with wastewater treatment technologies like adsorption using activated carbon, sand filtration, and others as the filtrate coming out from the tubes need further treatment before they can be discharged to natural water bodies. In recent years, some studies have focused in investigating low cost amendment strategies in order to reduce the cost incurred during the post treatment of the effluent from geotextile tubes. Koerner and Huang (2005) investigated the use of charcoal and phosphoric rock to adsorb organic and inorganic contaminants inside the geotextile tubes and have reported only preliminary results showing that more than 90% containment of these contaminants was achieved with the use of those materials. The overall objective of our study is to investigate effective and low-cost materials to contain heavy metal ions inside the geotextile tube. The effectiveness of these materials in enhancing the dewatering performance is also investigated. In order to have better understanding of the dewatering of heavy metal contaminated sediment slurries, it is imperative to understand the adsorption and retention capacity of soils to metal ions under varying conditions such as contact time and initial concentrations. The understanding of the dewatering behavior of such sediments will not only help to design efficient treatment strategies, it will also help to optimize the amount of flocculants and coagulants to be used in dewatering operations.

Although researchers have investigated the role of pure clay minerals in adsorption and retention of heavy metal ions from aqueous solutions, few studies have focused on the capacity of naturally available sediments. Also, very few studies have been performed to understand the adsorption behavior in an environment that contains mixture of heavy metals rather than just individual metal ions. The dredged sediment in most of the geotextile dewatering projects generally contain particles of varying soil sizes (medium to fine sands, silts, clays, and organics).Hence, in order to better represent to the field conditions, this study is focused on investigating the role of natural sediments and pure Kaolinite for individual as well as competitive adsorption and retention of heavy metal ions. For this purpose, sediments collected from a local quarry at Tully, New York (Tully coarse and Tully fines) and commercial grade Kaolinite were used to adsorb four commonly encountered heavy metals in contaminated sediments and wastewater Pb, Cu, Cd, and Zn. Stock solutions of the test reagents were made by dissolving $Pb (NO_3)_2$, $Cu (NO_3)_2.3H_2O$, $Zn (NO_3)_2.6H_2O$, $Cd (NO_3)_2.4H_2O$ in de-ionized water.

3.3 Materials and Reagents

3.3.1 Soils

The soils used for this study were obtained from Clarks Aggregate, a local quarry located at Tully, NY. The coarse soil, identified as Tully coarse (TC), was prepared by removing fractions coarser than US sieve No. 4. Fine soil, identified as Tully fines (TF), was prepared by wet-sieving through a US sieve No. 200 and oven drying the passing fraction. The Kaolinite clay was purchased from Sigma Aldrich. The Scanning Electron Microscope (SEM) image of the Tully coarse, Tully fines, and kaolinite are shown in Figures 3.1(a), 3.1(b) and 3.1(c), respectively.

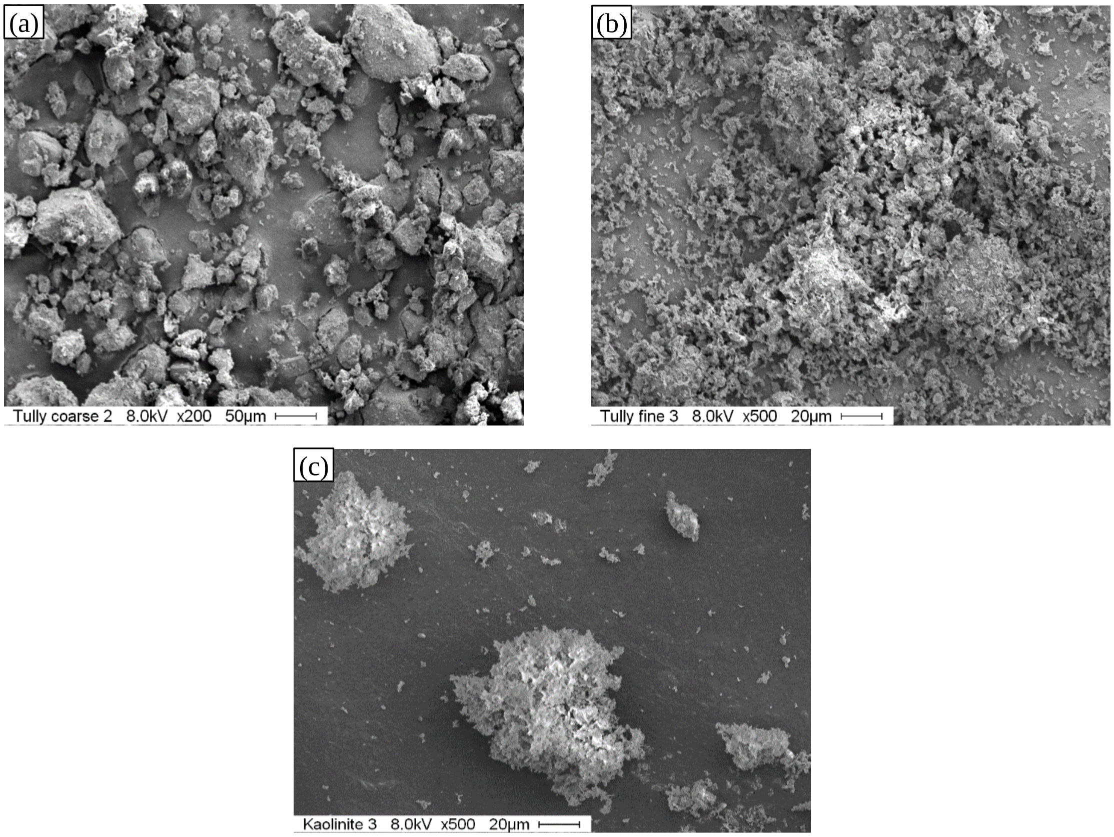


Figure 3.1 SEM image of (a) Tully coarse, (b) Tully fines, and (c) Kaolinite

3.3.2 Characterization of soils

3.3.2.1 Particle size distribution, Atterberg limits, Mineral composition, and Specific gravity

The particle size distribution of soils was carried out using sieve and hydrometer analysis following ASTM D6913-04 and D422-63.The particle size distribution of the soils is shown in Figure 3.2. It can be seen that Tully coarse is compsoed of 55 % coarse fractions (>0.075 mm) and 45% fine fractions with 39% silt and 6 % clay. Tully fines is 100% fines (<0.075 mm) with 85% silt and 15% clay whereas kaolinite is 100% fines with 70% clay size.

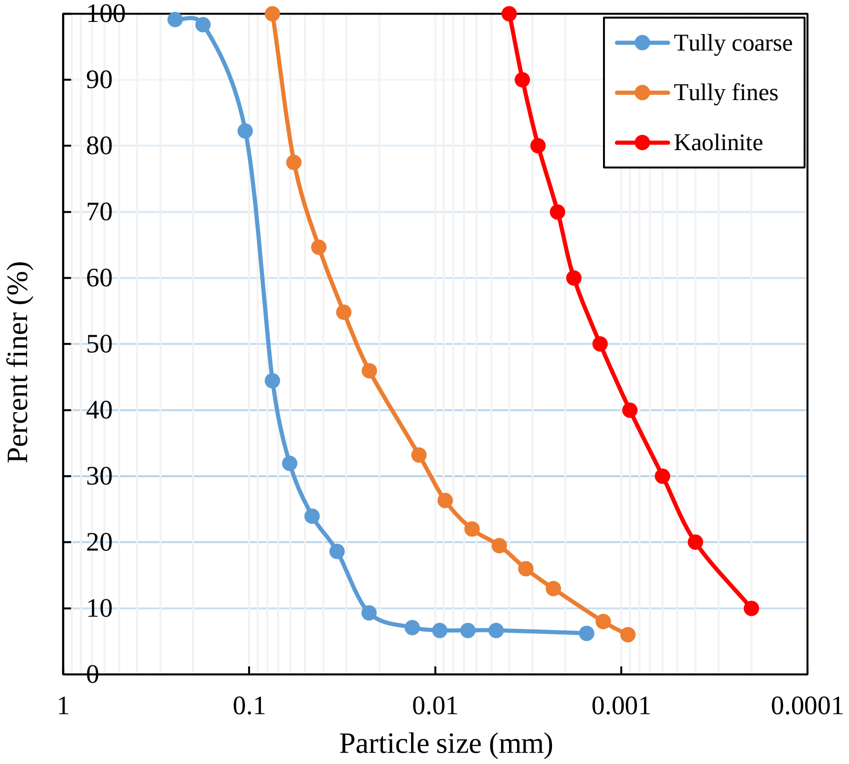


Figure 3.2 Grain size distribution of soils

The plasticity of Tully fines was determined following ASTM D4318-10. Since the particle size distribution and composition of Kaolinite is very similar to that used by Maher and Ho (1994), the physical and chemical properties reported by them have been used in this study.

The mineralogical composition of the soils was determined using X-ray diffraction (XRD) at University of Wisconsin, Madison. For Tully coarse and Tully fines, normal clay analyses were performed (3 patterns: air dry, glycol, heated) for the extracted clay minerals (soaked in water). For Kaolinite, XRD was measured for bulk powder sample The result of the quantitative analyses for Tully coarse, Tully fines and Kaolinite is shown in Figure 3.3(a), 3.3(b), and 3.3(c), respectively. The specific gravity of the soils was determined following ASTM D854-14.

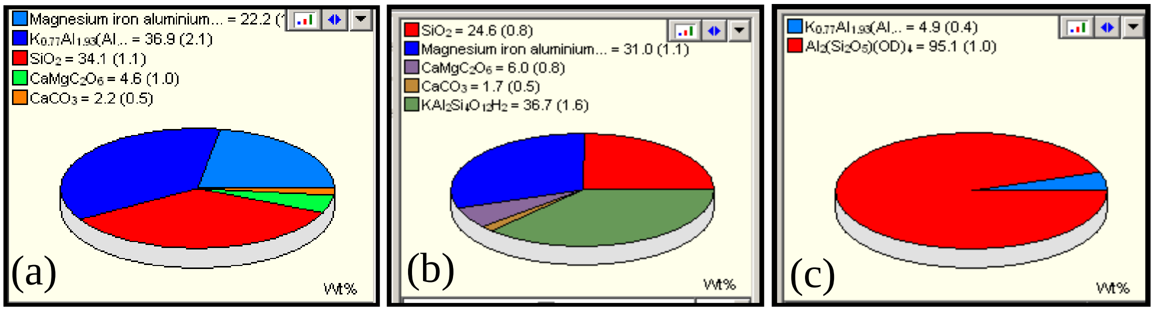


Figure 3.3 Mineral composition of (a) Tully coarse, (b) Tully fines, and (c) Kaolinite

3.3.2.2 Permeability

ASTM D2434-68, used to determine permeability of coarse grained soil employing constant head method was followed to find the permeability of Tully fines and Tully coarse.

3.3.2.3 Surface Charge

The amount of charge in soils (specific charge density) was determined using Mutek PCD 02 Particle Charge Detector by performing polyelectrolyte titration. The titrant used was Potassium Polyvinyl Sulfate solution (N/400). The endpoint was identified when the steaming potential reaches 0 mV. The average volume of titrant from three trials to attain isoelectric point (0 mV) was used to calculate the specific charge density. The test setup is shown in Figure 3.4. The charge density of Kaolinite could not be determined with this method.

Figure 3.4 Measurement of charge density in the PCD 02 setup

3.3.2.4 Organic Content

The organic content is the ratio, expressed as percentage, of the mass of organic matter in a given mass of soil to the mass of the dry soil solids. The organic contents in soils was determined using ASTM D 2974.

3.3.2.5 pH

The pH of the soils were measured in a distilled water. Approximately 10 g of air dried soils were placed into a glass jar containing 10 mL of distilled water. It was mixed and the pH was taken after 1 hour. The properties of the soils have been summarized and given in Table 3.1.

Table 3.1 Properties of the soils

Properties	**Tully coarse**	**Tully fines**	**Kaolinite**
Atterberg limit	Not applicable	LL: 26%, PL: 14%, PI: 12*	LL: 35%, PL: 19%, PI: 16*
USCS Classification	SP-SM	CL	CL
Mineral composition	Illite:36.9%, Chlorite: 22.2%, Quartz: 34.1%, Dolomite: 4.6%, Calcite: 2.2%	Illite:36.7%, Chlorite: 31%, Quartz: 24.6%, Dolomite: 6.8%, Calcite: 1.7%	Kaolinite: 95.1%, Illite: 4.9%
Specific gravity	2.71	2.63	2.65
Permeability (cm/sec)	8.2E-4	1.68E-5	3.6E-8
Surface charge (meqµg^{-1})	11.36	36.23	Couldn't be measured
Organic content (%)	0.49	0.83	0.00
pH	6.5	7.2	4.5

3.3.3 Reagents

All the compounds used to prepare reagent solutions were of analytic grade. The reagents were purchased from Sigma Aldrich. Stock solutions of the test reagents were made by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$ in de-ionized water.

3.4 Method

Stock solution of heavy metal was prepared by adding metal salt in de-ionized water. The solution was mixed for 30 minutes to ensure complete solubility of the metal salt. Batch adsorption test was carried out by mixing soil-metal solution. The typical initial solids concentration of the dredged sediments during geotextile dewatering varies between 10-14% (Lawson 2008). In this study, a 15% solid concentration slurry was made by mixing 75 grams of soil to 425 mL of the metal solution. It was allowed to mix in a shaker using magnetic stirrer for 1 hour. After mixing, three samples were collected in a 15 mL vial by filtering the slurry through a 2 micron filter paper. The filtered samples were centrifuged for 1 hour at 1600 rpm to settle the soil particles that passed the filter paper. It was again filtered and the filtrate was tested in ICP-OES at SUNY ESF to determine the concentration of metal ions in the filtrate. For each heavy metal, Pb, Cu, Cd, Zn, metal solution with concentration of 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm, and 2500 ppm were prepared and mixed with 15% sediments of Tully coarse, Tully fine and Kaolinite.

Generally, in the field, a mixture of metal ions are found rather than the individual ions. Hence, an aqueous solution containing mixture of the studied metal ions were prepared. For this purpose, metal solution was prepared by mixing equal volumes (106.25mL) of 1000 ppm Pb and 500 ppm each of Cu, Cd and Zn. The higher adsorption of Pb ions compared to other studied metal ions by soils was seen from individual adsorption tests. Therefore, higher concentration of Pb ions was used for the competitive adsorption tests. The slurry was mixed for four hours and sampling was done at 0.5, 1, 2 and 4 hours. At each sampling point, two samples were collected in a similar way as was done for individual adsorption test. The test setup is shown in Figure 3.5. The test combinations for individual adsorption of metal ions is shown in Table 3.2.

Table 3.2 Test combinations for individual and competitive adsorption

Soils	**Individual adsorption initial concentrations (ppm)**				**Competitive adsorption initial concentrations (ppm)**
Tully coarse	**Pb**	**Cu**	**Cd**	**Zn**	1000 ppm Pb+ 500 ppm Cu+ 500 ppm Cd+ 500 ppm Zn
	500	500	500	500	
	1000	1000	1000	1000	
	1500	1500	1500	1500	
	2000	2000	2000	2000	
	2500	2500	2500	2500	
Tully fines	**Pb**	**Cu**	**Cd**	**Zn**	1000 ppm Pb+ 500 ppm Cu+ 500 ppm Cd+ 500 ppm Zn
	500	500	500	500	
	1000	1000	1000	1000	
	1500	1500	1500	1500	
	2000	2000	2000	2000	
	2500	2500	2500	2500	
Kaolinite	**Pb**	**Cu**	**Cd**	**Zn**	Not performed
	500	500	500	500	
	1000	1000	1000	1000	
	1500	1500	1500	1500	
	2000	2000	2000	2000	
	2500	2500	2500	2500	

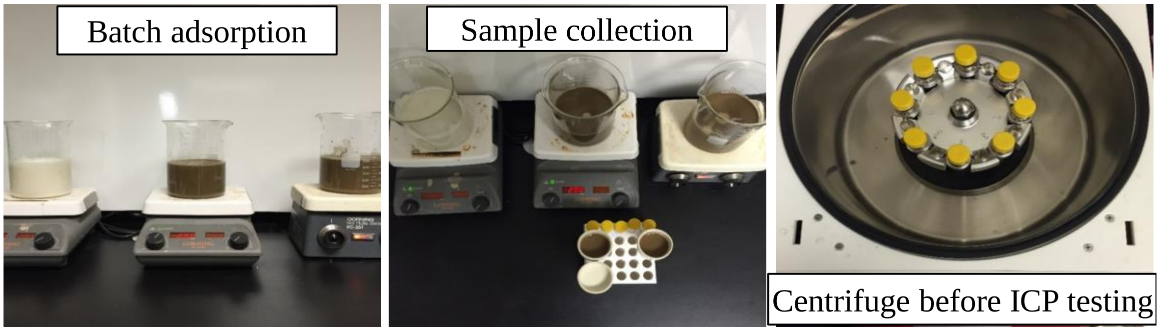


Figure 3.5 Test setup

3.5 Results and Discussion

To quantify the maximum adsorption capacity of soils to the individual metal ions, the adsorption data has been fitted using Langmuir isotherm. The Langmuir adsorption isotherm of soils to single metal ions over the range of initial concentrations is presented and discussed. The effect of initial concentration of single metal ion on its adsorption and retention is also discussed. Lastly, the effect of time on the competitive adsorption of metal ions in a slurry is presented.

3.5.1 Adsorption of lead (Pb)

The adsorption of Pb on Tully coarse soils followed Langmuir isotherm (shown in Figure 3.6 a). The maximum adsorption capacity of Tully coarse to Pb ions calculated from Langmuir isotherm was 33.1 mg/g. The high affinity of Tully coarse soil to Pb ions can also be attributed to its mineralogical composition, charge density, and particle size distribution. Tully coarse soil is very similar to Tully fines in mineralogical composition except it contains less fines (45%) and calcite content than the Tully fines soil. Also, Tully coarse is slightly acidic (pH 6.5) than Tully fines (pH 7.2). Hence, the adsorption capacity of Tully coarse soil was observed to be less than the Tully fines.

The adsorption of Pb was excessively high on Tully fines soil. At all initial concentrations (500 ppm to 2500 ppm), almost all the Pb ions were adsorbed by Tully fines. The maximum removal capacity of more than 99% was achieved by Tully fines for all initial concentrations. Hence, the adsorption of Pb into Tully fines did not follow Langmuir isotherm models. Instead, the adsorption of Pb into Tully fines was perfectly linear meaning a linear relationship was established between initial and final concentrations (see Figure 3.6 b). One of the main reasons for such high adsorption and retention of Pb ions by Tully fines is the pH range. Kinniburgh and Jackson (1981) reported the critical pH ranges for the adsorption of divalent metal ions on hydrous iron and aluminum oxides and is shown in Table 3.3. It can be seen that the critical pH range for maximum adsorption of Pb is 3-5. The pH was measured for all initial concentrations of Pb before the test and it was found that the pH ranged from 3.7 to 4.9. Since the pH was within the critical range, maximum adsorption of Pb ions was achieved by Tully fines soil. Other reason for high adsorption could be attributed to the presence of high amount (31%) of chlorite or hydrous oxides of iron, magnesium and aluminum. Jenne (1968) and Jenne (1977) reported that among the other factors responsible for adsorption of metal ions into soils and sediments, presence of hydrous oxides of iron and aluminum play the most predominant role in sorption and retention of heavy metal ions. The other factor contributing to such a high adsorption of Pb by Tully fines is the presence of very reactive Illite mineral (36.7%). Sposito (1984) and Ranville and Schmiermund (1999) based on their investigation concluded that metal adsorption by soils and sediments generally increase with decreasing grain size. As the grain size decreases, the specific surface area of the particle increases, hence for finer particles more adsorption sites are available for adsorption of metals. Tully fines is predominantly fines and hence possess large surface area for adsorption of metal ions. Tully fines soil has a surface area of 11.83 m^2/gm and high surface charge density of 36.23meq/µg, which are one of the dominant factors for adsorption of metal ions.

The adsorption of Pb ions into kaolinite also followed Langmuir isotherm model with a maximum adsorption capacity of 14.9 mg/g (see Figure 3.6(c)). The primary reason for low adsorption capacity of kaolinite compared to Tully fines and coarse is due to its low reactivity and molecular stability. Kaolinite is non-expanding and least reactive clay unlike Illite and Smectite (Suraj et al.1998). Because of its high molecular stability, isomorphous substitution is limited or even non-existing (Mitchell 1993).

Table 3.3 Critical pH ranges for adsorption of divalent metal cations on hydrous iron and aluminum oxides (after Kinniburgh and Jackson1981)

Cation	**pH range**
Pb, Cu, Hg	3-5
Zn, Cd, Ni, Co	5-6.5

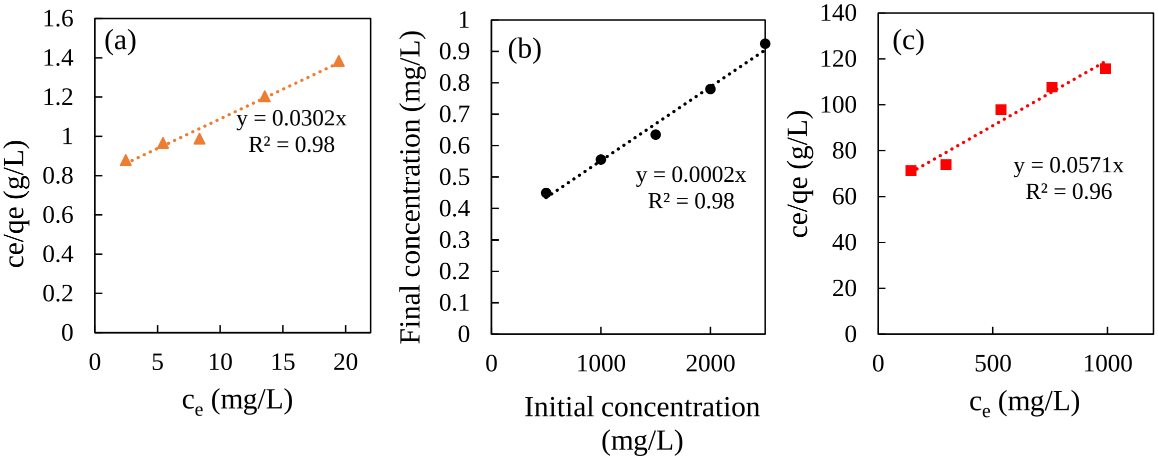


Figure 3.6 Langmuir and linear isotherm for adsorption of Pb into (a) Tully coarse, (b) Tully fines (Linear), and (c) Kaolinite

3.5.2 Adsorption of copper (Cu)

The adsorption of Cu into Tully coarse soil is shown in Figure 3. 7 (a). The adsorption followed Langmuir isotherm and the maximum adsorption capacity was 6.54 mg/g. The adsorption of Cu into Tully fines followed the Langmuir isotherm and is shown in Figure 3.7 (b). The adsorption capacity of Tully fines to Cu was not as high as Pb. The maximum adsorption capacity of Tully fines to Cu was 6.55 mg/g. It can be seen that both Tully fines and Tully coarse soils had same adsorption capacity for Cu unlike Pb.

The adsorption of Cu into Kaolinite is shown in Figure 3.7(c). It can be seen the adsorption followed Langmuir isotherm with maximum adsorption capacity of 1.99 mg/g. As seen in case of Pb, adsorption capacity of Kaolinite to Cu was low compared to both Tully soils.

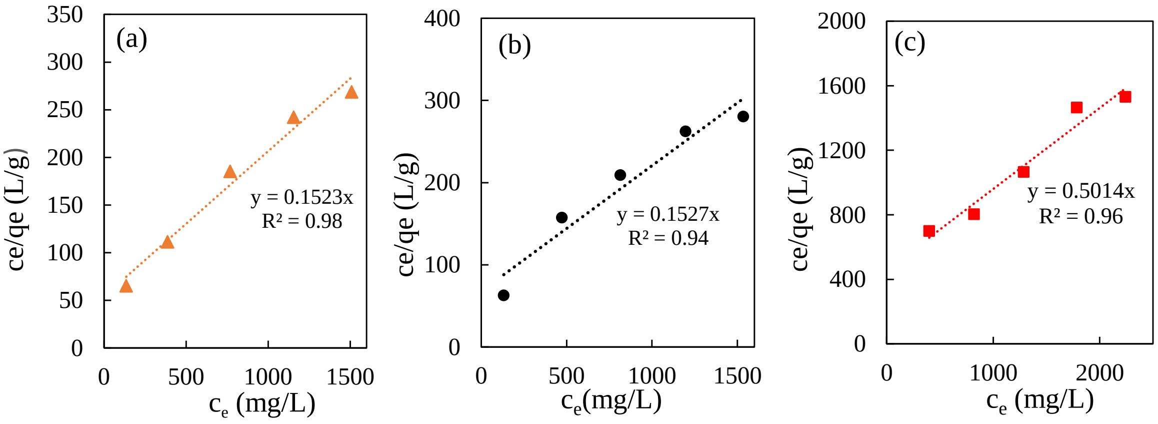


Figure 3.7 Langmuir isotherm for adsorption of Cu on (a) Tully coarse, (b) Tully fines, and (c) Kaolinite

3.5.3 Adsorption of cadmium (Cd)

The adsorption of Cd by all soils followed Langmuir isotherm. The adsorption of Cd by Tully coarse, Tully fines, and Kaolinite are shown in Figures 3.8 (a), 3.8 (b) and 3.8 (c) respectively. It can be seen that Kaolinite exhibited higher affinity towards Cd ions than both Tully soils. The maximum adsorption capacity of Kaolinite for Cd was 7.32 mg/g, whereas that of Tully fines and Tully coarse were 2.11 and 1.74 mg/g. Hence, it can be seen that although kaolinite had lower affinity for Pb and Cu ions, it had fair affinity to Cd. Jiang et al (2010) from their study on adsorption of Pb, Cd, Ni, and Cu onto Kaolinite clay concluded that the relative affinity of Kaolinite towards studied metal ions was in order of Pb>Ni>Cd>Cu. Although similar results were observed in this study in terms of adsorption of Cd and Cu by Kaolinite, the adsorption of Pb did not follow the same order as reported by Jiang et al. (2010).

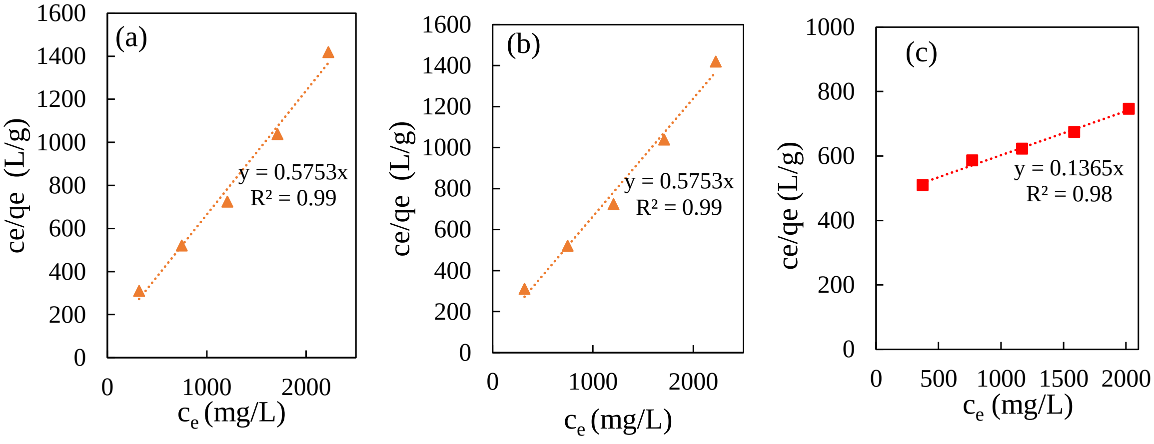


Figure 3.8 Langmuir isotherm for adsorption of Cd on (a) Tully coarse, (b) Tully fines, and (c) Kaolinite

3.5.4 Adsorption of Zinc (Zn)

The adsorption capacity of Tully coarse followed Langmuir isotherm with good regression coefficient and is shown in Figure 3.9 (a). The maximum adsorption capacity of Tully coarse to Zn was 4.65 mg/g. The adsorption of Zn ions on Tully fine soils also followed Langmuir isotherm and is shown in Figure 3.9 (b). The maximum adsorption capacity of Tully fines to Zn was 3.64 mg/g which is slightly lower than that of Tully coarse. Kaolinite had the least affinity for Zn ions with a maximum adsorption capacity of 1.30 mg/g (Refer Figure 3.9 (c)). The adsorption capacity of Kaolinite to Zn of 1.30 mg/g is in the range reported by Kounau et al. (2015) (0.31 mg/g) and Mishra and Patel (2009) (3.05 mg/g).

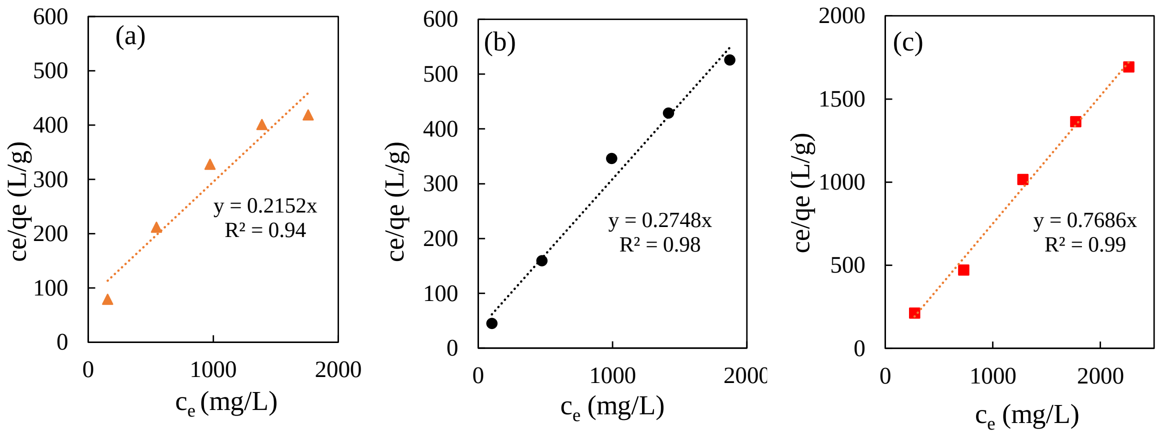
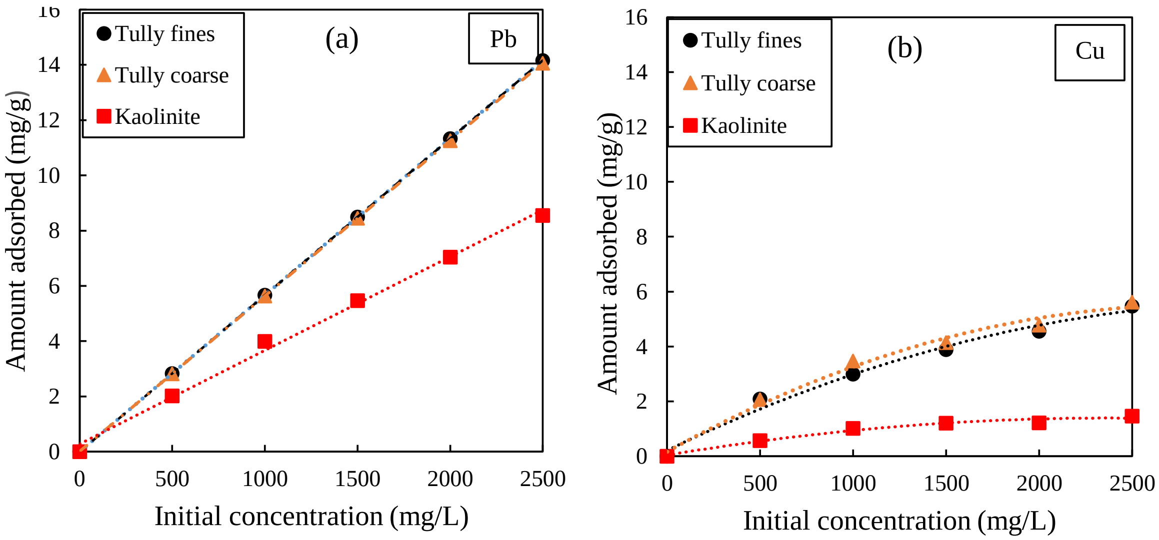


Figure 3.9 Langmuir isotherm for adsorption of Zn on (a) Tully coarse, (b) Tully fines, and (c) Kaolinite

3.5.5 Effect of initial concentration on adsorbed amount

The concentration of heavy metal ion present varies significantly in site specific basis and often a wide range of concentration has been observed and reported. In order to assess the suitability of the soils to adsorb and retain heavy metal ions, it is imperative to have better understanding of its adsorption capacity at different initial concentrations of the metal ions. Keeping mixing time of 1 hour and soil solids content of 15% as a constant, the concentration of all the metals are varied from 500 ppm to 2500 ppm. It can be seen from Figure 3.10(a) that the amount of Pb adsorbed by all soils increased linearly with increase in its concentration in the slurry. However, nonlinear relationship was observed between the initial concentration and the adsorbed amount by all soils in case of Cu ions as shown in Figure 3.10(b). It can also be seen that the adsorption of Cu by Kaolinite did not increase beyond 1500 ppm meaning it is completely saturated around that concentration. However, no such saturation could be observed on both Tully soils as the adsorbed amount of Cu kept on increasing till 2500 ppm. The effect of initial concentration of Cd and Zn on its adsorption by all three soils are shown in Figure

3.10(c) and 3.10(d) respectively. It can be seen that the adsorption of Cd ions by Kaolinite increased linearly with increase in its initial concentration, and could not be saturated till 2500 ppm. Also, the adsorption capacity was higher than both Tully soils. Tully soils got saturated with Cd ions as there was no significant change in their adsorption capacity beyond initial concentration of 1500 ppm. It can be seen from Figure 3.13 that the adsorption of Zn on Kaolinite increased with increase in initial concentration till 1000 ppm. Beyond 1000 ppm, Kaolinite got saturated with Zn ions and the adsorbed amount did not change beyond that concentration. However, the adsorption capacity of both Tully soils kept on increasing and could not be saturated till 2500 ppm.



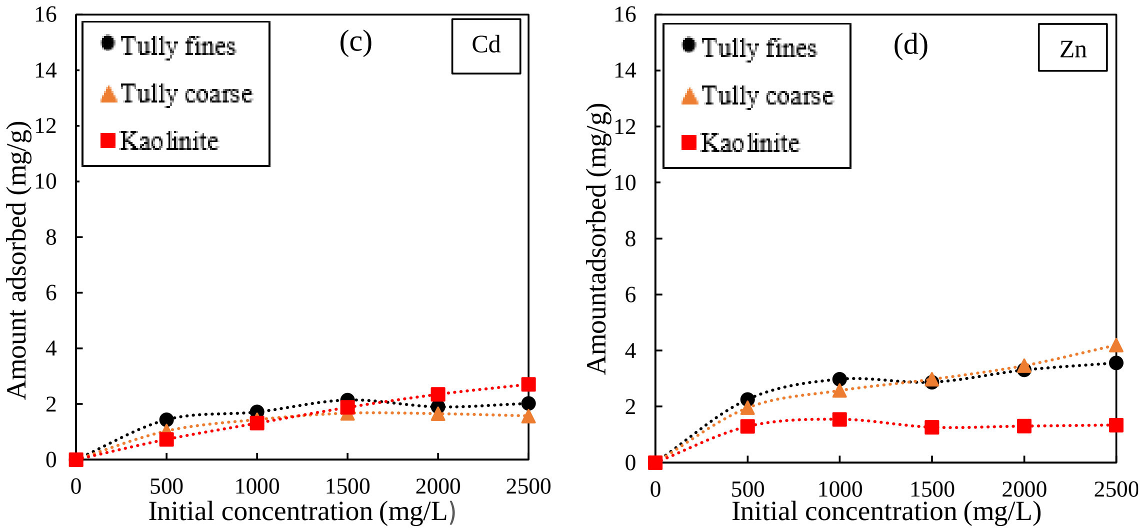


Figure 3.10 Effect of initial concentration on adsorption of (a) Pb, (b) Cu, (c) Cd, and (d) Zn

3.5.6 Competitive adsorption of metal ions

The competitive adsorption of metal ions was carried out with Tully fines and Tully coarse soils only. It was seen from the individual adsorption tests that kaolinite doesn’t possess adsorption capacity comparable to other studied soils especially for Pb and Cu ions. Hence, kaolinite was not included in the competitive adsorption study. For competitive adsorption test; equal volumes (106.25 mL) of the metal ions were mixed together. The initial concentration of the metal ions chosen for competitive adsorption test was 1000 ppm Pb and 500 ppm Cu, Cd, and Zn each. The slurries (15% concentration) were prepared in the same manner as the individual adsorption test. However rather than equilibrating for just one hour, the slurry was mixed for 4 hours during competitive adsorption study. The sampling was performed at 0.5 hr, 1hr, 2 hr and 4 hr. At each sampling point, three samples were collected and measured for metal ion concentration using ICP-OES.

The adsorption of Pb and Cu ions on Tully fines is shown in Figure 3.11(a) while that of Cd and Zn is shown in Figure 3.11(b). It can be seen from these Figures that most of the adsorption of metal ions occurred within 30 mins of mixing. Beyond 30 minutes, the adsorption of these ions proceeded slowly and have been related to time by power relationship. As seen in case of individual adsorption study, Pb and Cu ions were adsorbed in much higher amounts than Cd or Zn. However, the adsorption capacity of Tully fines to Pb decreased in presence of other metal ions. The relative preference of Tully fines to the metal ions from competitive adsorption tests followed the order Pb>Cu>Cd>Zn. The competitive adsorption of Pb and Cu by Tully coarse is shown in Figure 3.12(a), and that of Cu and Cd is shown in Figure 3.12(b). As seen with Tully fines, the maximum adsorption of all metal ions occurred within 30 minutes with higher affinity for Pb and Cu than Cd or Zn ions. However, the adsorption capacity of Tully coarse soil was lower than the Tully fines for all metal ions as seen during individual adsorption.

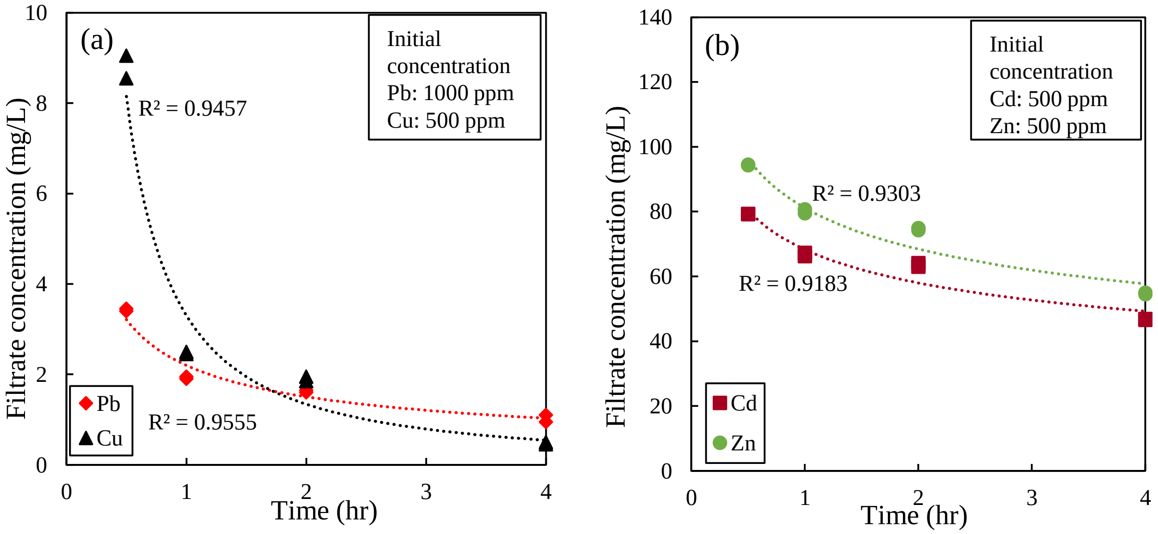


Figure 3.11 Competitive adsorption of (a) Pb and Cu and (b) Cd and Zn, by Tully fines

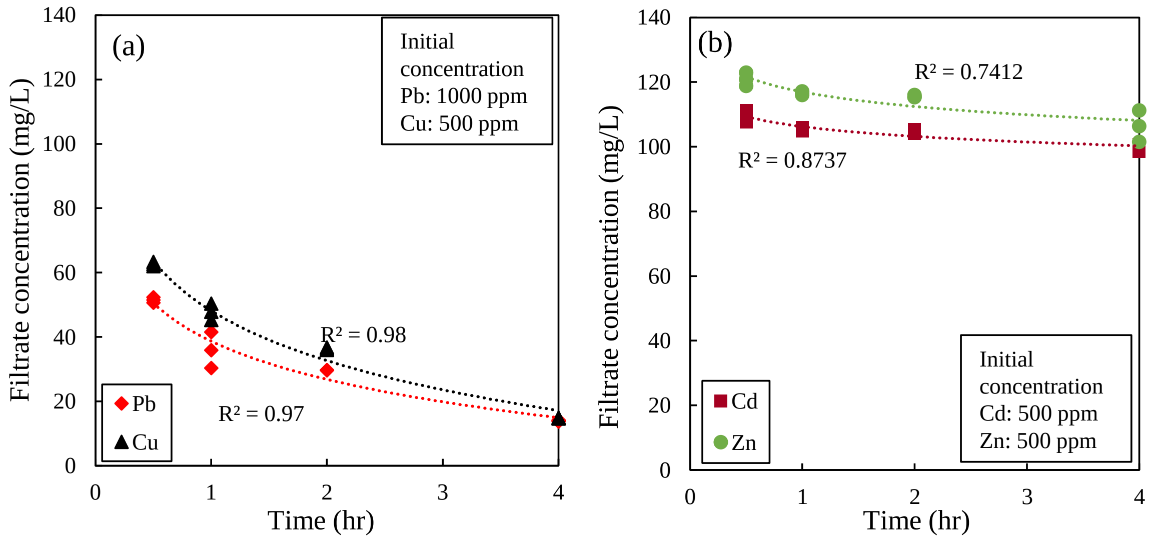


Figure 3.12 Competitive adsorption of (a) Pb and Cu and (b) Cd and Zn, by Tully coarse

3.6 Conclusions

In order to design amendment strategies to effectively contain heavy metal contaminated slurries inside a geotextile tube, it is very important to understand the interaction between sediments and heavy metal ions in a slurry. The adsorption and retention of Pb, Cu, Cd, and Zn individually as well as in a competitive environment was studied using batch adsorption test in this study. For the study of single ion adsorption, three sediments (Tully fines, Tully coarse, Kaolinite) were used to prepare 15% slurry containing heavy metal solution with initial concentrations of 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm, and 2500 ppm. For competitive adsorption study, only Tully fines and Tully coarse sediments were used to prepare 15 % slurry containing 1000 ppm Pb, 500 ppm Cu, 500 ppm Cd, and 500 ppm Zn. Based on the findings of this investigations following conclusions can be drawn.

- Tully fines which has 100% fines exhibited very high affinity towards Pb ions. For all initial concentrations of Pb ions in the slurry, more than 99% adsorption as well as retention was achieved by Tully fines soil. In addition to being predominantly fines, it contains more than 10% clay minerals such as Illite and Chlorite. These clays are known to form strong bond surface complexes with Pb ions in aqueous solution. Tully coarse also had fair affinity to Pb. The maximum adsorption capacity of 33.1 mg/g was achieved by Tully coarse soils to Pb. Tully coarse (55% coarse and 45% fines) also contains Illite, Dolomite, and Chlorite clay minerals. Kaolinite although having more than 70% clay size had least affinity to Pb ions (maximum adsorption capacity of 14.9 mg/g) compared to both Tully soils. Studies have shown that compared to other clay minerals, Kaolinite is considered less reactive because of its high molecular stability (Sposito 1989). .

- The maximum adsorption capacity of both Tully soils to Cu was 6.5 mg/g, which is significantly lower than that of Pb. Similarly, Kaolinite also had lower affinity to Cu ions than Pb. The maximum adsorption capacity of kaolinite to Cu was 1.99 mg/g. The lower affinity of all soils to Cu compared to Pb could be difference in atomic radius. The ionic radius of Pb^{2+} (119 pm) being higher than Cu^{2+} (73 pm), adsorption of Pb could have been more favorable than Cu.
- Unlike the adsorption of Pb and Cu, the highest affinity to Cd ions was exhibited by Kaolinite. When maximum adsorption capacity of Kaolinite to Cd was 7.32 mg/g, Tully fines and Tully coarse had maximum adsorption capacity of 2.11 mg/g and 1.74 mg/g respectively. Based on these results, it can be seen that adsorption of Cd was more favorable on Kaolinite clay than other clays like Illite or Calcite present in Tully soils.

- The maximum adsorption capacity of Tully fines and Tully coarse to Zn was observed to be higher than Kaolinite. The adsorption capacity of Tully coarse (4.65 mg/g) was slightly higher than Tully fines (3.64 mg/g). The maximum adsorption capacity of Kaolinite to Zn was 1.30 mg/g.
- It was seen from the competitive adsorption tests that the capacity of all metal ions to get adsorbed to a soil surface decreased in presence of other metal ions in the solution.
- It was seen that for all soils, the amount of adsorption of Pb increased linearly with increase in its initial concentration. The amount of Cu adsorbed by both Tully soils increased non-linearly with the increase in its concentration in the slurry. However, Kaolinite got saturated with Cu around 15000 ppm.
- The adsorption of Cd by Kaolinite increased linearly with the increase in its concentration in the slurry. However, for Tully soils the adsorption of Cd did not increase beyond 1000 ppm suggesting their complete saturation around that concentration. The adsorption of Zn increased non-linearly with increase in its concentration in Tully coarse slurry. However, Tully fines and Kaolinite got saturated with Zn ions around 1500 ppm.

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CHAPTER 4

A STUDY ON CONTAINMENT AND DEWATERING OF HEAVY METAL CONTAMINATED SLURRIES USING CELLULISIC MATERIALS

4.1 Introduction

With the rapid industrialization and municipal activities over the last fifty years and limited stringent legislation on the disposal of the wastes, many water bodies have been polluted with harmful metals, and organic and inorganic pollutants. Krizek (2000) states that approximately one billion cubic meters of contaminated slurries are produced annually from industrial, municipal, and marine activities in the United States. According to Lawson (2008), such a large volume of wastes especially in slurry form poses a serious environmental threat and require cleaning to remove the sediments and sludge so that the impoundments can accept further flows. Over the last 20 years, geotextile tubes have gained rapid popularity to contain and dewater high water content contaminated slurries, mine tailings, municipal wastes and sludge (Moo-Young et al. 2002; Liao and Bhatia 2005; Cetin et al. 2014; Lawson 2008).Containment and consolidation of fine-grained sediments in geotextile tubes have had success in the municipal, industrial, and environmental dredging markets with recent innovations in chemical conditioning products (Mastin and Lebster 2006; Mastin and Lebster 2007). Since 80's, hundreds geotextile tube dewatering projects have been used in many parts of Europe, Asia, Australia, and the United States to contain and dewater high water content slurries.

Generally the remediation of contaminated sediments using geotextile tube involves further step/s in conjunction with dewatering. The effluent is collected from the lined gravel drainage area beneath the geotextile tubes and pumped into the water treatment plant. Therefore, water treatment plant has been an essential step in geotextile dewatering project to treat the effluents before they are discharged into water course. In recent years, there has been an interest to investigate a more sustainable solution to treat contaminated sediments using geotextile tubes. The addition of low cost adsorbents such as clay minerals, cellulose adsorbents, bio adsorbents and other reactive materials have been effective in wastewater treatment to treat heavy metal contaminated sludge. Although many studies have been conducted on geotextile tube dewatering, however there are limited studies on dewatering behavior and performance of heavy metal contaminated sediment slurries and the use of low cost adsorbents and cellulose adsorbents. In addition, very few studies have focused on investigating amendment strategies for the geotextile tube dewatering project to treat heavy metal contaminated slurries. A short review of the case studies on geotextile dewatering of contaminated sediments has been presented.

Approximately 55000 yd^3 of contaminated sediment was dredged and successfully contained in forty four geotextile containers from Marina Del Rey, Los Angeles, CA in 2008 (Risko 1995) . The dredged sediments had 7 to 8 percent fines and was contaminated with a number of heavy metals such as lead, zinc and copper. The dredged materials also contained polychlorinated biphenyls (PCB), polynuclear aromatic hydrocarbons (PAH’s), oil and grease, hydrocarbons, sulfides, and ammonia. For this project, the heavy metals in the sediments were above acceptable limits as opposed to other contaminates. The concentration of heavy metals in sediment sample was 138 ppm

Cu, 400 ppm Pb, and 380 ppm Zn. The concentration of the metals in the effluent was 5 ppm Cu, 1.3 ppm Pb, and 10 ppm Zn. Further dilution of the effluent was made to make sure the effluent meets the water quality criteria before they were discharged.

The Ottawa River Remediation Project, performed in Toledo, Ohio in 2010, successfully dredged 242,000 yd^3 of PCB contaminated sediments from the Ottawa River (Cretens 2011). The dredged materials (226,000 $yd^{3)}$ were dewatered with geotextile tubes placed in a landfill facility and capped later in place for disposal. Remaining 16,000 $yd^3$of sediments exceeded 50 ppm total PCBs and were therefore dewatered separately and hauled off-site for disposal in a Toxic Substance Control Act (TSCA) permitted landfill. Non TSCA sediments were screened, thickened, treated with chemical conditioner, and dewatered in geotextile tubes. About 38,000 linear feet of geotextile tubes stacked in five layers were used. However, TSCA sediments were directly pumped into the geotextile bags (2150 linear feet stacked in two layers) without prior screening or thickening. Effluent from dewatering process had to be collected and treated on site in a water treatment plant, and eventually discharged to the Ottawa River. The treatment plant incorporated three processes: flocculation, coagulation and settling, two step filtration: and Granular Activated Carbon (GAC) adsorption.

Ashtabula River lying in Northeast Ohio had been subjected to heavy industrial development and unregulated discharge from the 1940’s to late 1970’s (Cretens 2012). This led the sediments along the river to be highly contaminated with heavy metals such as lead, zinc, chromium, mercury and organic compounds such as PCB’s, PAH’s and small traces of radionuclides. The navigation was restricted for years because of this high buildup of contaminated sediments. A remediation plan involving dredging of 523181

yd^3 contaminated sediments and pumping the slurry to a geotextile tube dewatering facility was made. The dewatering facility was designed to be permanent contaminated sediment disposal facility. The effluent water was collected in a pit and was fed to water treatment plant before being discharged into the river. The water treatment by sand filtration and activated carbon filtration was employed to remove any residual concentration of organic and inorganic contaminants on the effluent. It was estimated that a total of 14000 kg of PCB's and other contaminants were removed from the river bed.

Waukegan harbor is a man-made channel located along the sea horse drive in Waukegan, about forty miles north of Chicago. The U.S. EPA had documented PCB contaminant level exceeding 1000 ppm in the sediment in a study conducted in 1981. EPA had reported that about 50,000 yd^3 of sediment had contaminated above 50 ppm PCBs with even higher volume containing PCBs at 10 ppm or higher. Infrastructure Alternatives, Inc. removed about 117,278 yd^3 of Polychlorinated biphenyls (PCB) contaminated sediments by hydraulically dredging from the harbor and transferring them to the landfill facility for disposal. Prior to geotextile tube dewatering, the sediment was processed using a large screen for debris removal and slurry thickener in a gravity thickener. 75-82 feet circumference geotextile tubes were stacked in three layers over the containment facility. A separate water treatment plant was constructed to treat the dewatered effluents. The water treatment plant was configured with lamella inclined plate clarifiers, pressurized multi-media filter, bag filters and granular activated carbon (GAC) vessels. The treated effluent met the target concentration of 0.2 ppm PCB.

It can be seen from these case studies that the effluent collected from geotextile tubes require some sort of post treatment or dilution before they can be discharged into water bodies. It can also be seen that most of the post treatment methods are designed to treat organic contaminants such as PCBs and PAHs. Although a lot of studies have been conducted on treating organic contaminants either through pretreatment or post treatment methods, there is a shortage of literature on the dewatering of heavy metal contaminated slurries using geotextile tubes. Significant number of heavy metal contaminated sites around the world requires cleanup and. Hence, in order to use geotextile tube technology to contain and dewater such slurries, a proper understanding of metal ion with the sediments is essential. Moreover, to increase its effectiveness, it is important to investigate amendment strategies that will help to prevent heavy metal ions leaching from the tubes.

The primary objective of this study is to investigate the dewatering behavior of heavy metal contaminated slurries and evaluate the effectiveness of low cost adsorbents in geotextile tube not only to adsorb the heavy metals but also to enhance the dewatering performance. To study the dewatering behavior of heavy metal contaminated slurries,, a slurry prepared by mixing soil sediments rich in minerals such as Illite, Chlorite, quartz and cellulose adsorbents (Peanut hull, jute fibers, kraft pulp) was investigated using the Pressure Filtration Test (PFT) in the lab.

4.2 Materials

4.2.1 Soil

The soils used in this study are Tully coarse and Tully fines. The soils were obtained from Clark’s aggregate pit located at Tully, NY. The properties of the soil sediments are given in Table 4.1.

Table 4.1 Properties of the soils

Soil	**D_{10} (μm)**	**D_{50} (μm)**	**C_u**	**pH**	**Minerals (in descending order)**	**Surface charge (meqμg^{-1})**	**Organic content (%wt.)**
Tully coarse	22	80	3.52	6.5	Illite, quartz, chlorite, calcite, dolomite	11.36	0.59
Tully fines	1.8	29	27.1	7.2	Illite, chlorite, quartz, dolomite, calcite	24.90	0.81

4.2.2 Cellulose Materials

Three different types of cellulosic materials investigated in this study are peanut hulls, jute fibers, and kraft pulp. Peanut husks were obtained from Birdsong Peanuts, a peanut shelling company out of Suffolk, VA. The jute fibers 1 cm in length were imported from Korea through Bast Fibers LLC, headquartered in Cresskill, NJ. Kraft pulp was obtained from Kraft pulping process at SUNY College of Environmental Science and Forestry (SUNY-ESF), NY. All the adsorbents were ground to make the mixing with slurry more homogenous and also to increase its specific surface area. The percentages of cellulose and lignin for the selected adsorbents are given in Table 4.2. The adsorbents have been shown in Figure 4.1.

Figure 4.1 Cellulose adsorbents (a) Peanut hulls, (b) Jute fibers, and(c) Kraft pulp

Table 4.2 Cellulose and lignin content in the adsorbents

Materials	% Cellulose	% Lignin
Peanut hull	55.1	27.6
Jute fibers	85-88	12-15
Kraft pulp	98	2.7

4.2.3 Geotextile

A composite geotextile (woven/non-woven) having an Apparent Opening Size (AOS) of 100 microns and bubble point of 98 microns was used in this study. The properties of the geotextile is given in Table 4.3.

Table 4.3 Basic Properties of the geotextile

Fabric and Polymer type	**Hydraulic Properties**		**Mechanical Properties**		
	Apparent Opening Size (AOS) (μm)	Permittivity (sec^{-1})	Wide-width tensile strength CD (kN/m)	Grab tensile strength CD (N)	Puncture (N)
Polypropylene	100	0.23	625	NR	2000

Note: CD = cross machine direction, NR = Not Reported

4.3 Test Methods

The soil slurry preparation and testing has the following four steps, (1) preparation of heavy metal solution (2) mixing heavy metal solution with soil sediments to prepare 15% solid slurry (3) mixing cellulose adsorbents with the prepared slurry (4) performing pressure filtration tests. For this study, metal solution was prepared by mixing equal volumes of1000 ppm Pb, 500 ppm Cu, 500 ppb Cd, and 500 ppm Zn. After the preparation of metal solution, soil sediment was added to form 15% solid slurry, and it was mixed for one hour. After the contaminated soil slurry was prepared, cellulosic adsorbent (2% weight of soil) was added and mixed for further one hour. During the mixing of adsorbents to the soil slurry, kraft pulp formed chunks of 300 µm and larger and did not mix well. A glass rod was used frequently to break the chunks while mixing. The jute fibers mixed well in the slurry and the fibers got dispersed almost homogenously. Peanut hull being fine powder mixed well and formed the perfect slurry mix .After the mix was ready, PFT tests were conducted under an air pressure of 1.5 psi, and the filtrate was tested for metal concentration using ICP-OES. Pressure filtration tests were performed to simulate the geotextile tube dewatering in the field with both kind of soils. The test was stopped when the dewatering rate dropped to 1 ml per 3 minutes. The dewatering rate was recorded using a digital scale coupled with the computer. After the test, total collected filtrate was stirred and the turbidity measurements were taken using 2100N Turbidimeter. Also, the solid content and height of the filter cake were measured. The tests were also conducted on uncontaminated slurries (slurry prepared with DI water rather than heavy metal solution) with and without cellulosic materials. The test schematic and setup have been shown in Figures 4.2 and 4.3, respectively.

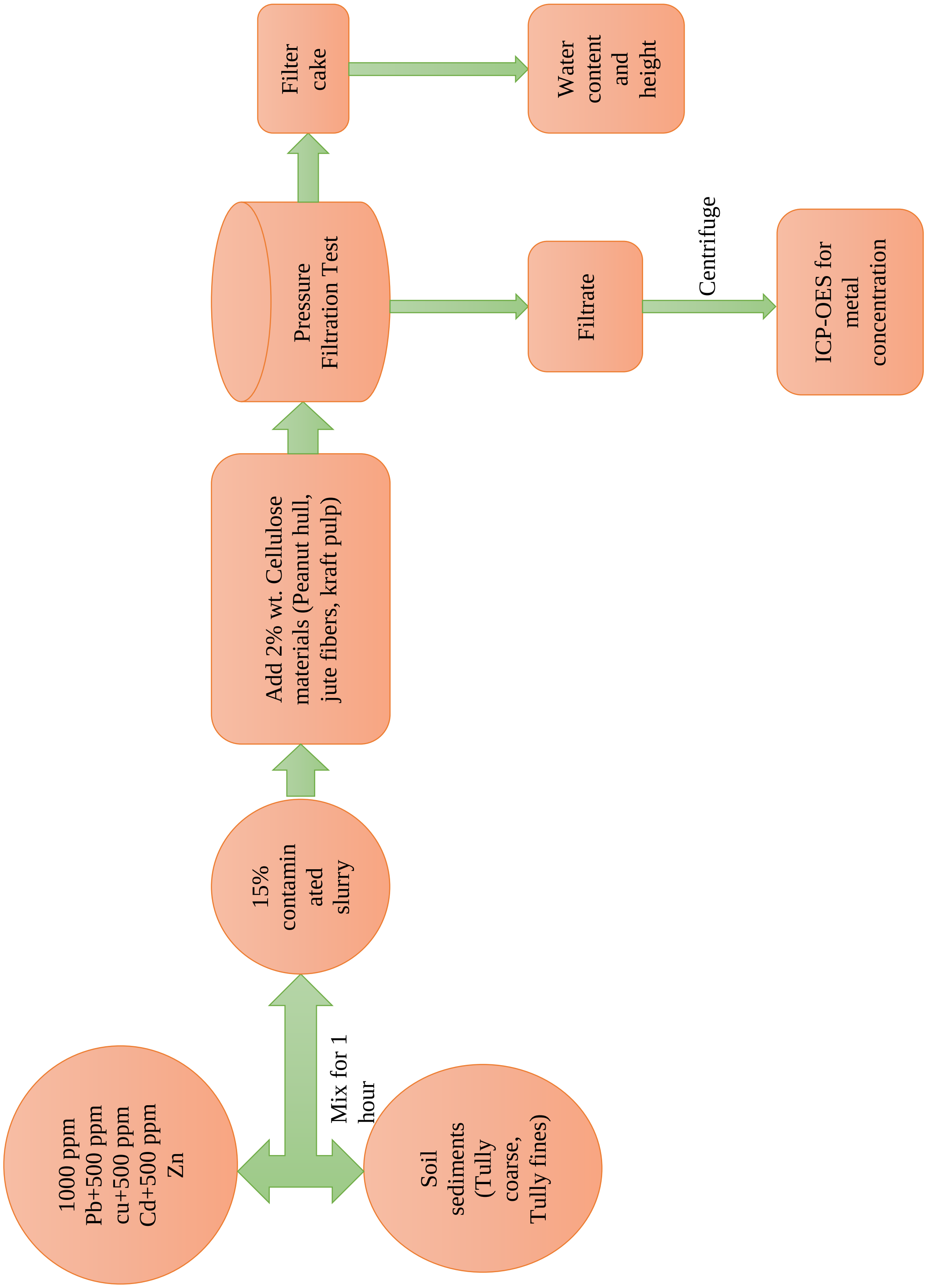


Figure 4.2 Experimental steps

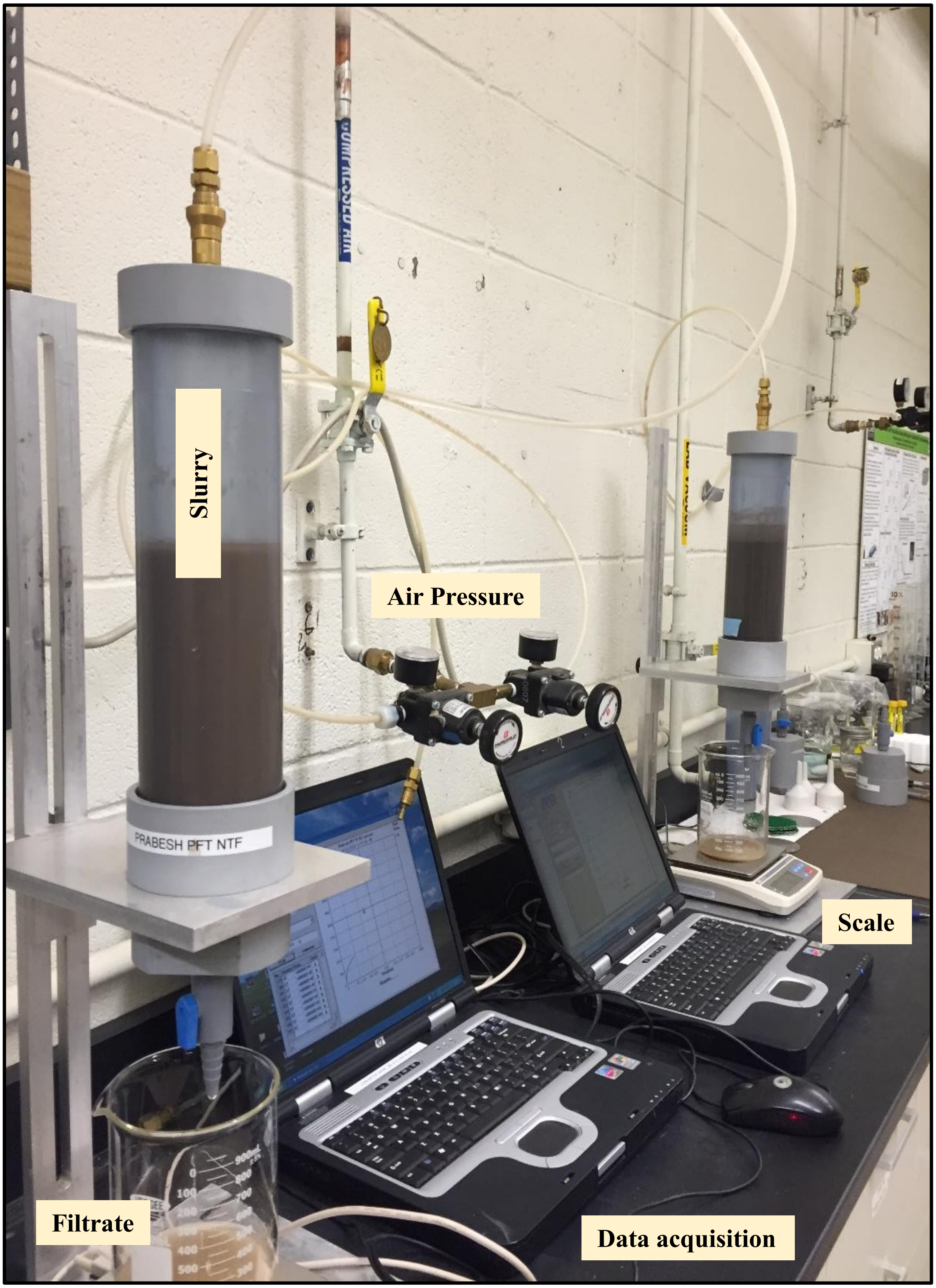


Figure 4.3 Pressure Filtration Test setup

4.4 Results and Discussion

4.4.1 Dewatering rate and performance

4.4.1.1 Polymer optimum dose

Jar tests were conducted on the uncontaminated and contaminated Tully coarse and Tully fine soils to quantify the effect of contamination on the optimum dose of the polymer to be added to the slurry. The dosage of polymer was determined to be optimum when the turbidity was lower than 20 NTU. Two cationic polymers, zetag 8115 (very low cationic charge) and zetag 8185 (very high cationic charge), and two high molecular weight anionic polymers, magnafloc 155 and magnafloc 336 were used for the study. The jar test results for uncontaminated and contaminated Tully coarse slurries is shown in Figures 4.3 and 4.4 respectively. The results are summarized in Table 4.4. It can be seen that for both uncontaminated and contaminated Tully coarse sediments, cationic polymers (zetag 8115 and 8185) are more efficient than the anionic polymers (magnafloc 155 and 336). It can also be seen that the optimum dose required for contaminated Tully coarse sediments is much lower than the uncontaminated sediments. When uncontaminated sediments required 3.82 ppm of zetag 8185, the optimum dose for contaminated Tully coarse was 1.7 ppm. For all polymers studied, contaminated Tully coarse required less polymer dosing than the uncontaminated ones. The results of jar test for uncontaminated and contaminated Tully fines is shown in Figures 4.5 and 4.6 respectively and the summary is presented in Table 4.5. As observed in case of Tully coarse sediments, cationic polymers were much more effective than the anionic ones for both contaminated and uncontaminated Tully fine sediments. Also, the optimum dose of these polymers were very low for contaminated Tully fines than the uncontaminated ones. Since the Tully fines has more fines content (15%), the polymer dosage was higher than that required for the Tully coarse sediments. It was observed that the optimum dose of polymer for metal contaminated slurries was lower than the uncontaminated sediments. Since, zetag 8185, a cationic polymer was most effective for all the slurries, it was selected for the tests.

Table 4.4 Optimum dose for uncontaminated and contaminated Tully coarse sediments

Slurries	**Polymers**	**Optimum dose (ppm)**
Uncontaminated Tully coarse	Magnafloc 155	> 8
	Magnafloc 336	> 29
	Zetag 8115	4.41
	Zetag 8185	**3.82**
Contaminated Tully coarse	Magnafloc 155	1.76
	Magnafloc 336	17.64
	Zetag 8115	1.76
	Zetag 8185	**1.17**

Table 4.5 Optimum dose for uncontaminated and contaminated Tully fine sediments

Slurries	**Polymers**	**Optimum dose (ppm)**
Uncontaminated Tully fines	Magnafloc 155	>29
	Magnafloc 336	>58
	Zetag 8115	41.8
	Zetag 8185	**25**
Contaminated Tully fines	Magnafloc 155	26
	Magnafloc 336	41.2
	Zetag 8115	27.9
	Zetag 8185	**16.2**

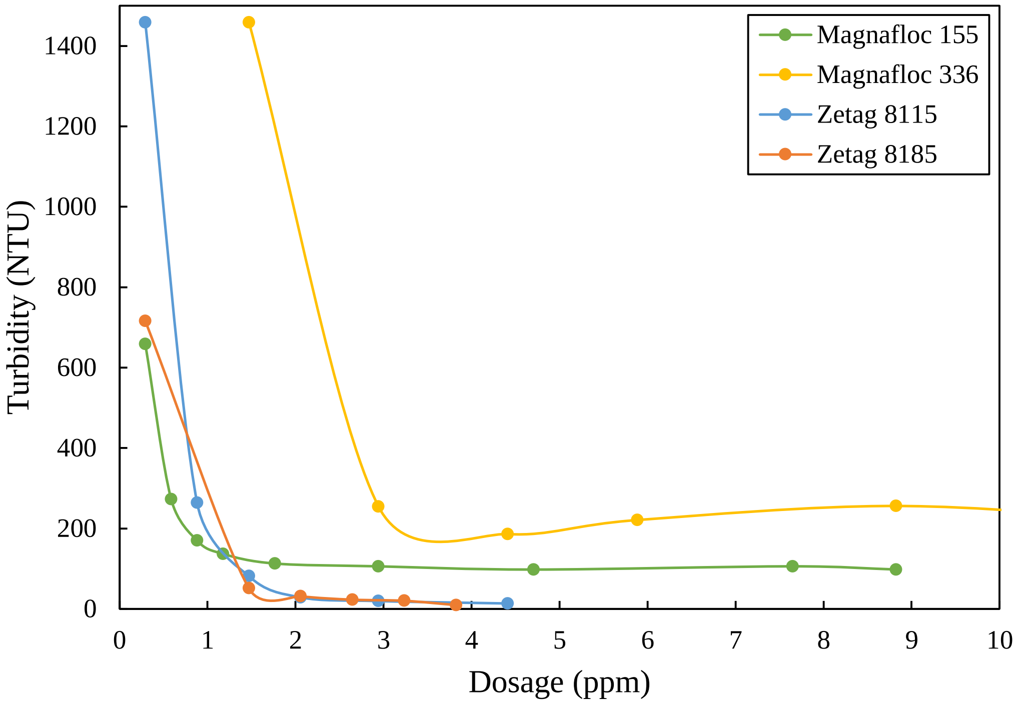


Figure 4.4 Optimum dose for uncontaminated Tully coarse

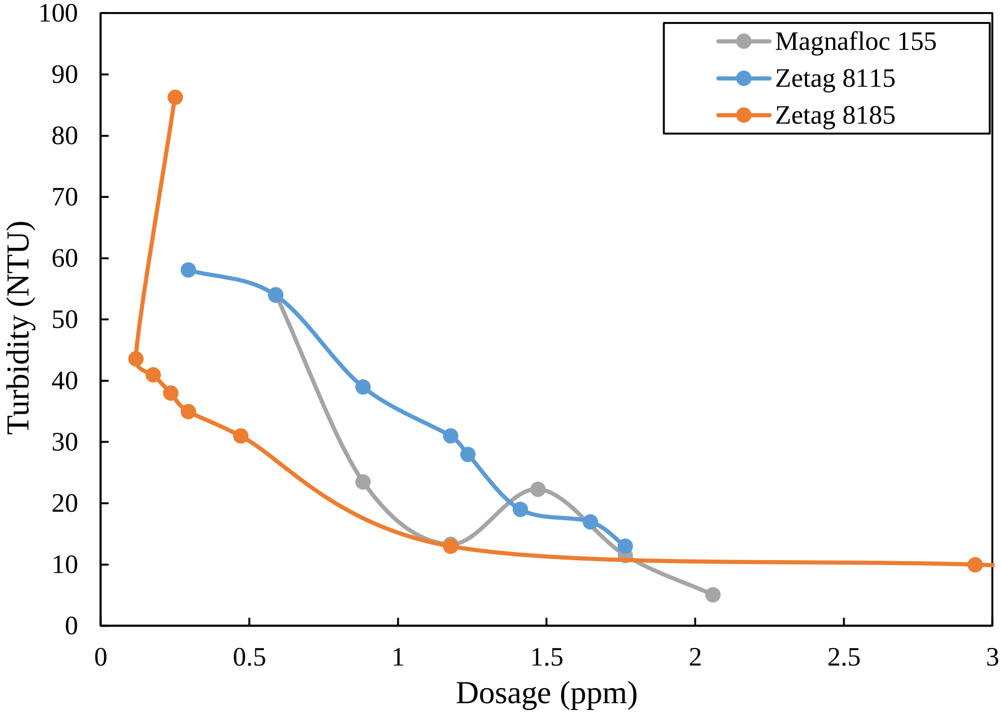


Figure 4.5 Optimum dose for contaminated Tully coarse

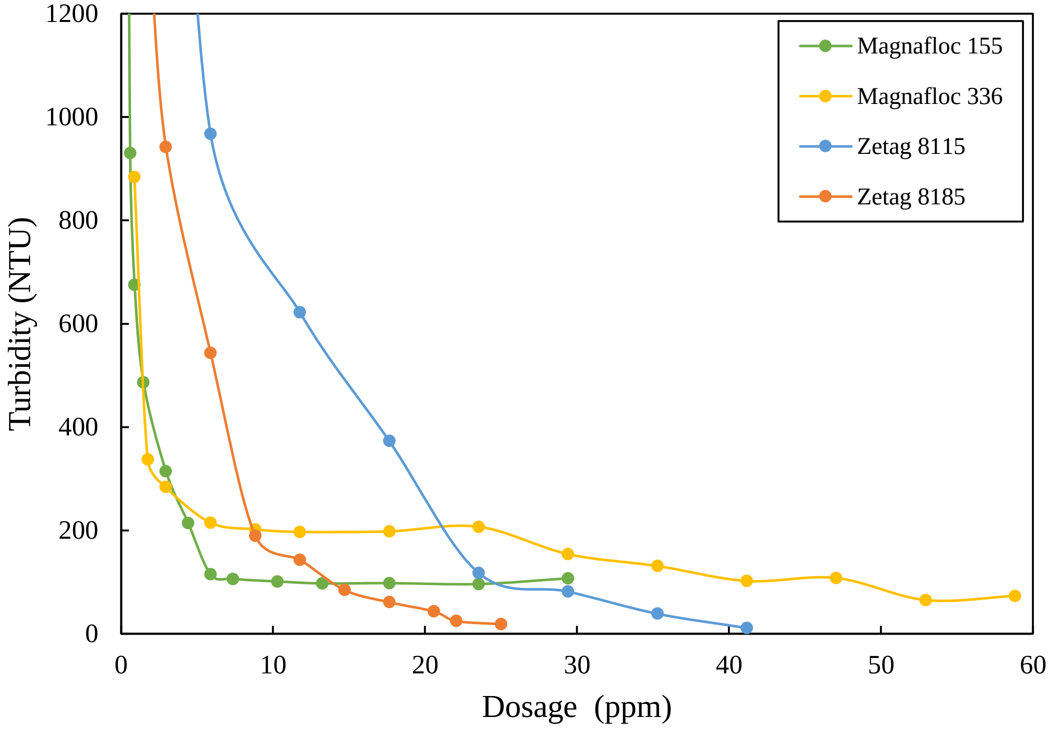


Figure 4.6 Optimum dose for uncontaminated Tully fines

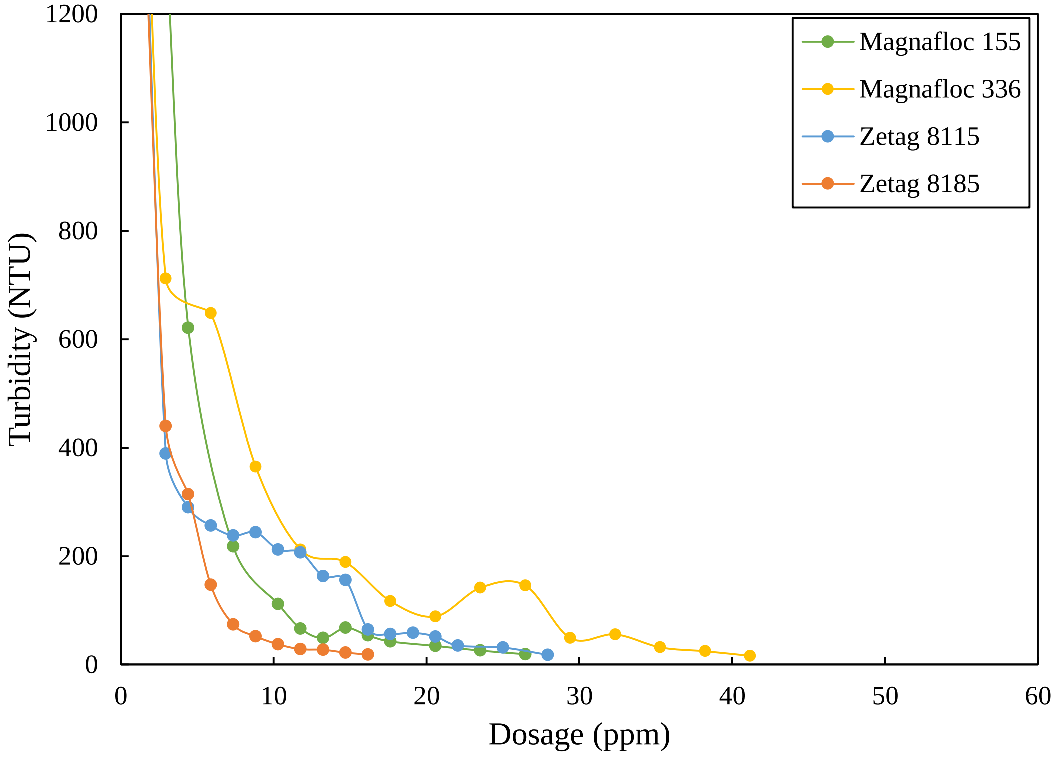


Figure 4.7 Optimum dose for contaminated Tully fines

4.4.1.2 Pressure Filtration Tests (PFT) Results: Uncontaminated and contaminated slurries without cellulose and polymer

PFT tests were conducted on contaminated and uncontaminated slurries of both Tully fines and Tully coarse to compare their dewatering rate, filter cake properties and filtrate quality in terms of turbidity and heavy metals. Typical test results of dewatering of uncontaminated and contaminated Tully coarse is shown in Figure 4.8. It can be seen that the contaminated Tully coarse dewatered much faster than the uncontaminated ones. It took uncontaminated Tully coarse 70 minutes to dewater whereas the contaminated slurry dewatered in approximately 1/3 rd the time (20 minutes). This reduction in dewatering time in contaminated sediment is due to the fact that as metal ions get adsorbed on the soil particles, negative charges in the soils (due to presence of clay minerals) neutralize and flocculation of soil particles takes place. Because of such flocculation, the clayey fraction in the soil slurries settled quickly and the dewatering rate was much faster. The results of solid content and turbidity is given in Table 4.6. It was observed that the solid content of the contaminated Tully coarse filter cake (74%) was 2-3% higher than the uncontaminated (71%) sediments. Also, turbidity of the filtrate from the dewatering of contaminated Tully coarse (32-39 NTU) was found to be much lower than the uncontaminated sediment (249-263 NTU).

The dewatering of contaminated and uncontaminated Tully fines is shown in Figure 4.9. As seen with the Tully coarse slurries, contaminated Tully fines also dewatered much faster than the uncontaminated fines. While it took uncontaminated Tully fines 1800 minutes to dewater, the contaminated Tully fines dewatered much faster i.e. around $1/6^{th}$ the time it took for uncontaminated ones (340 minutes). The solid content of the uncontaminated Tully fine filter cake was as high as 67%. The solid content of the contaminated Tully fine filter cake increased to 70%. Also, significant reduction in turbidity from 1384 NTU to 612 NTU was observed (Refer Table 4.6). Since the soil loss especially during the initial stage of dewatering was very minimal for contaminated slurry of both soils, the turbidity was significantly low and the solid content was higher. Due to high water content of uncontaminated filter cakes of both Tully fines and Tully coarse sediments, filter cake heights couldn’t be measured.

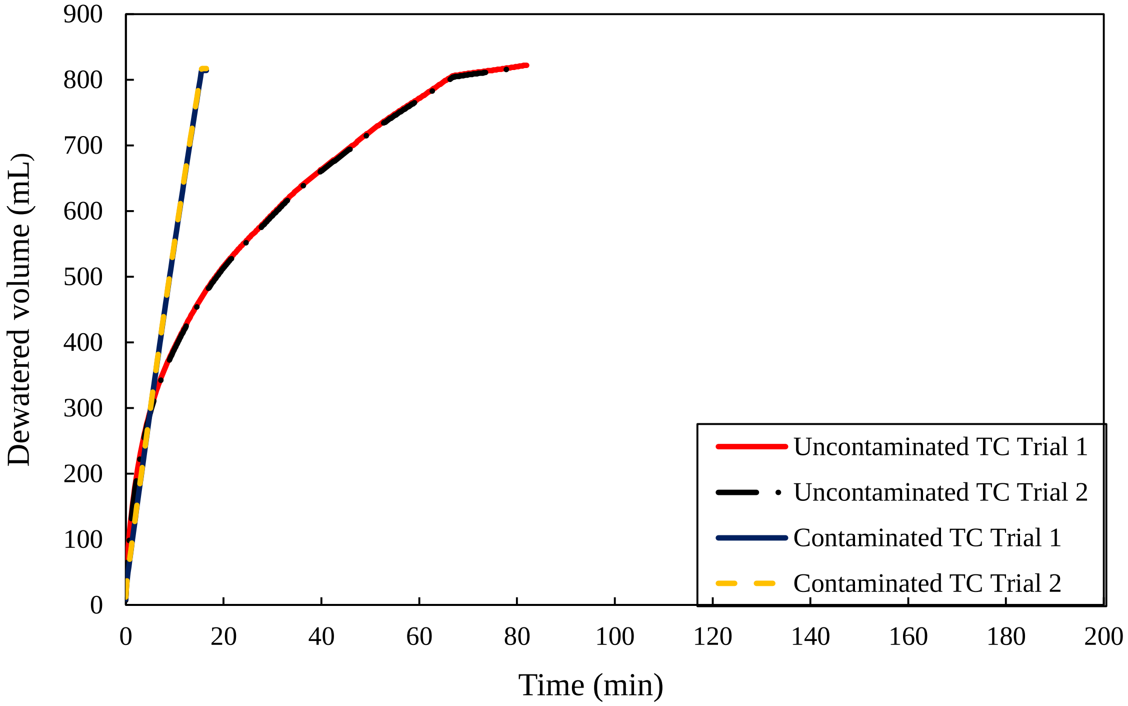


Figure 4.8 Dewatering of contaminated and uncontaminated Tully coarse

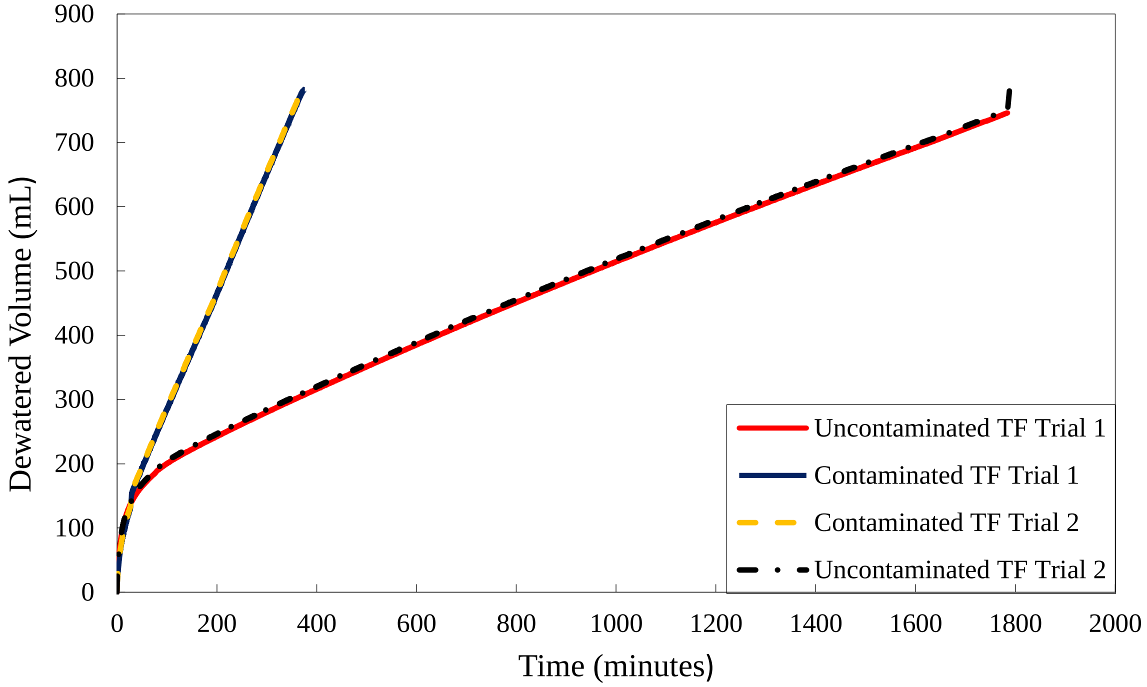


Figure 4.9 Dewatering of contaminated and uncontaminated Tully fines

Table 4.6 Summary of dewatering parameters without cellulose and polymer

Test Conditions	**Trials**	**Overall turbidity (NTU)**	**Solid content of filter cake (%)**	**Filter cake height (mm)**
Uncontaminated Tully coarse	Trial 1	249	71.9	
	Trial 2	263	72.7	
Contaminated Tully coarse	Trial 1	39	74.5	22.36
	Trial 2	32	74	22.17
Uncontaminated Tully fines	Trial 1	862	66.9	
	Trial 2	834	67.3	
Contaminated Tully fines	Trial 1	48.78	70.3	24.84
	Trial 2	45.4	70.7	23.15

4.4.1.3 PFT Results: Uncontaminated and contaminated slurries with cellulose fibers and without polymers

Cellulosic materials (2% weight of soil) were added to the contaminated and uncontaminated slurries and were mixed for one hour to prepare a homogenous soil-fiber slurry. After the preparation of soil-fiber slurries, they were transferred to the PFT setup and dewatering test was carried out under air pressure of 1.5 psi.

The dewatering behavior of uncontaminated Tully coarse with cellulosic materials is shown in Figure 4.10. It can be seen that the uncontaminated Tully coarse without any cellulosic materials took 80 minutes to dewater. No signification reduction in dewatering time was observed with the addition of jute fibers or kraft pulp. However, dewatering time reduced by almost 40% with the use of peanut hull. The kraft pulp being clumpy and fibrous in nature did not form a homogenous mix with the sediment slurries. Few small clumps of these fibers were observed during the dewatering test. These clumps contributed to form blinding or clogging spots in the filter cake. As a result, no reduction in dewatering time was observed with the use of kraft pulp.

The dewatering of contaminated Tully coarse is shown in Figure 4.11. It can be seen that as opposed to a case in uncontaminated Tully coarse, all the cellulosic fibers slightly reduced the dewatering time with the fastest achieved with the use of peanut hull. The summary of solid content of the filter cake and turbidity is given in Table 4.7. It can be seen that there is a significant benefit of using peanut hull and jute fibers since they helped to increase the solid content of the filter cake from 72% to 77% and 79% respectively. Since the jute fibers and especially peanut hull were almost in particulate form, they mixed properly to form homogenous slurry and eventually formed a uniform filter cake. Solid content was generally lower with the use of kraft pulp by almost 10% than peanut hulls or jute fibers. As the fibers of kraft pulp have high capacity to adsorb water and swell when mixed in a slurry, filter cakes had lower solid contents (or higher water contents). One of the measure of success of a dewatering project is the solid content of the filter cake. Generally a high percentage solids is targeted in the field. Although all adsorbents were able to reduce the turbidity of the filtrate, a reduction in turbidity as much as 80% was achieved with the addition of peanut hulls. It was also noticed during dewatering tests that some of the pulp and jute fibers escaped through the pores of geotextile and contributed to the turbidity. However, no loss of peanut hull were noticed under any testing conditions. The results of the dewatering performance (turbidity and solids content of the filter cake) of uncontaminated and contaminated Tully coarse with cellulose materials have been shown using a bar diagram in Figures 4.12 and 4.13, respectively.

The dewatering of uncontaminated Tully fines with and without cellulosic materials is shown in Figure 4.14. It can be seen that jute fibers and peanut hull were efficient in reducing the dewatering time from 1800 mins to 1000 mins. A slight increase in solid content of the filter cake was also observed with the use of these materials. However, the solid content of the filter cake decreased with the addition of kraft pulp as it has the capacity to adsorb and retain water (Refer Table 4.8). The solid content of the uncontaminated Tully fine filter cake was 4-5% higher with the use of peanut hulls and jute fibers than the kraft pulp. The dewatering of contaminated Tully fines with and without fibers is shown in Figure 4.15. It can be seen that among the cellulose materials, peanut hull and jute fibers were more efficient in reducing the dewatering time. The solid content of the filter cake increased from 70% to 75% and 73.5% with the addition of jute fibers and peanut hull respectively. However, no change in solid content of the filter cake was seen with the use of kraft pulp. The addition of all the adsorbents reduced the turbidity significantly as it dropped from 38 NTU to 2-8 NTU. The results of the dewatering performance (turbidity and solids content of the filter cake) of uncontaminated and contaminated Tully fines with cellulose materials have been shown using a bar diagram in Figures 4.16 and 4.17 respectively.

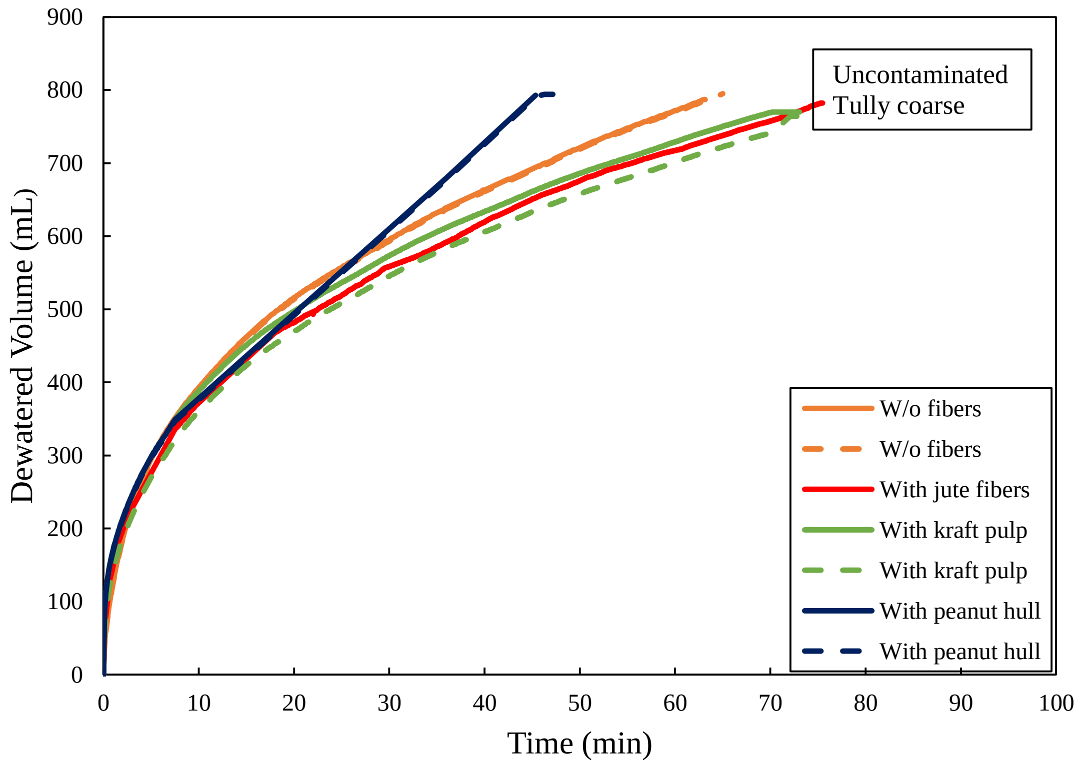


Figure 4.10 Dewatering of uncontaminated Tully coarse with cellulose and without polymer

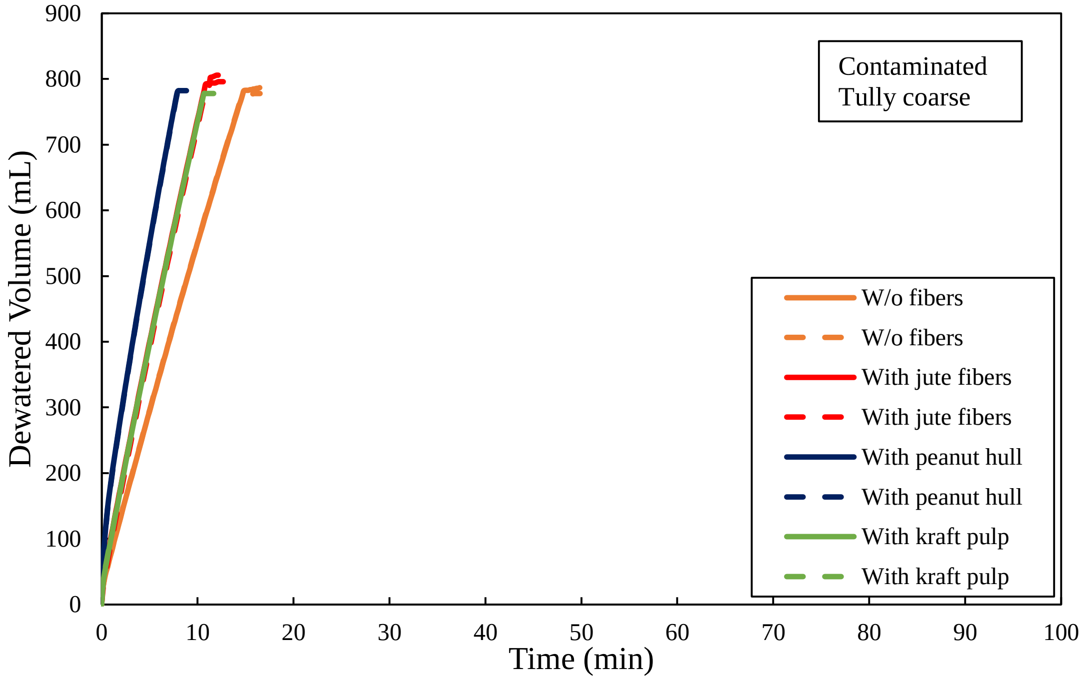


Figure 4.11 Dewatering of contaminated Tully coarse with cellulose and without polymer

Table 4.7 Summary of dewatering parameters of Tully coarse with cellulose and without polymer

Test Conditions	**Trials**	**Overall turbidity (NTU)**	**Solid content of the filter cake (%)**	**Filter cake height (mm)**
Uncontaminated Tully coarse with kraft pulp	Trial 1	202	70.8	24.6
	Trial 2	186	69.7	23.1
Uncontaminated Tully coarse with jute fibers	Trial 1	86	73.7	24.2
	Trial 2	94	74.5	25.3
Uncontaminated Tully coarse with peanut hulls	Trial 1	64	72.8	22.4
	Trial 2	71	73.7	23.8
Contaminated Tully coarse with kraft pulp	Trial 1	27	71.2	26.32
	Trial 2	28	70.7	26.64
Contaminated Tully coarse with jute fibers	Trial 1	8	78.4	27.21
	Trial 2	8	79.2	27.08
Contaminated Tully coarse with peanut hulls	Trial 1	23	77.2	26.84
	Trial 2	24	76.5	25.74

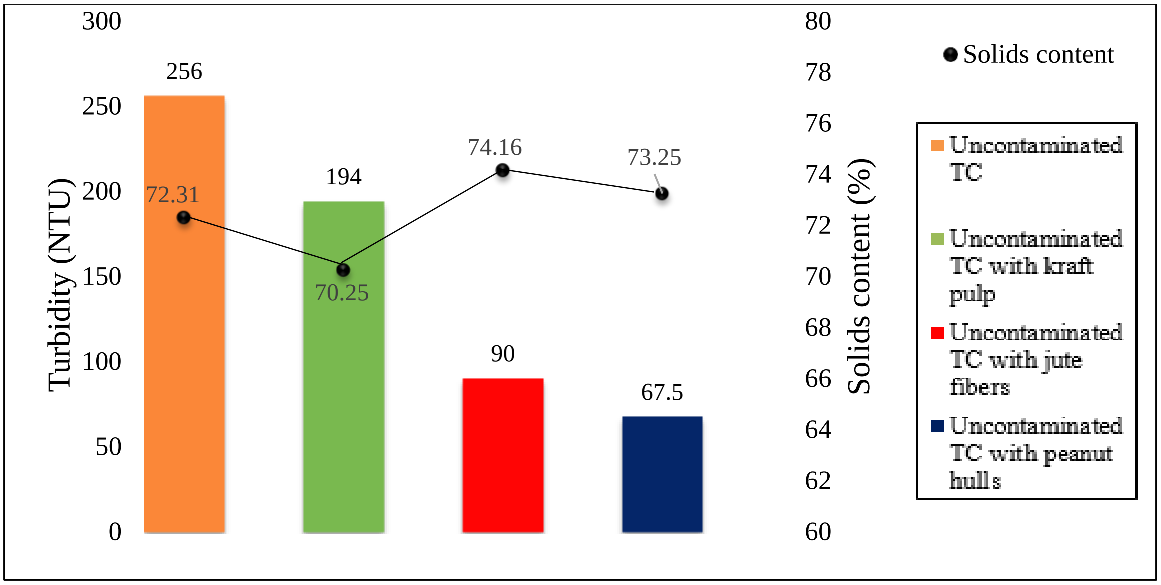


Figure 4.12 Dewatering parameters (turbidity and solids content) of uncontaminated Tully coarse with cellulose materials and without polymer

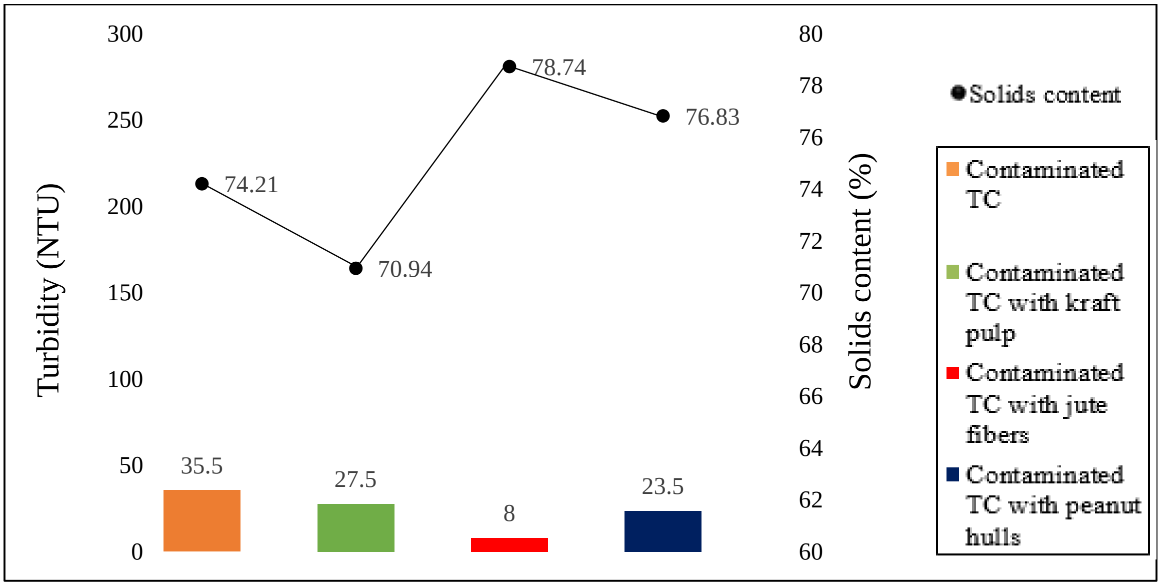


Figure 4.13 Dewatering parameters (turbidity and solids content) of contaminated Tully coarse with cellulose materials and without polymer

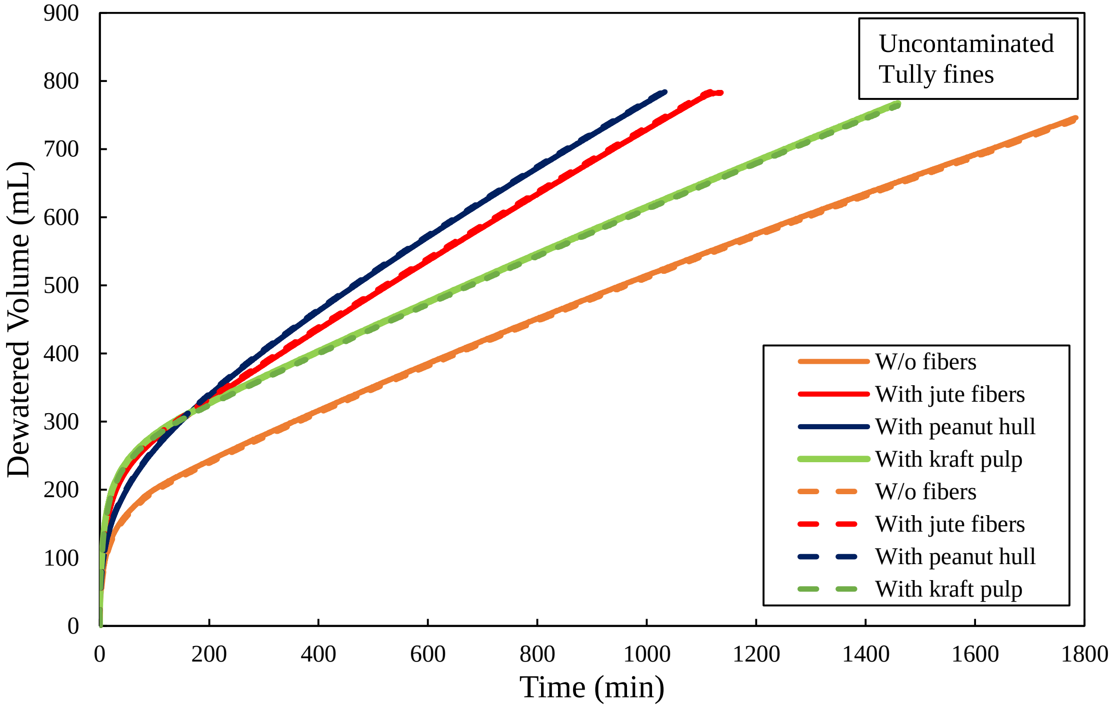


Figure 4.14 Dewatering of uncontaminated Tully fines with cellulose and without polymer

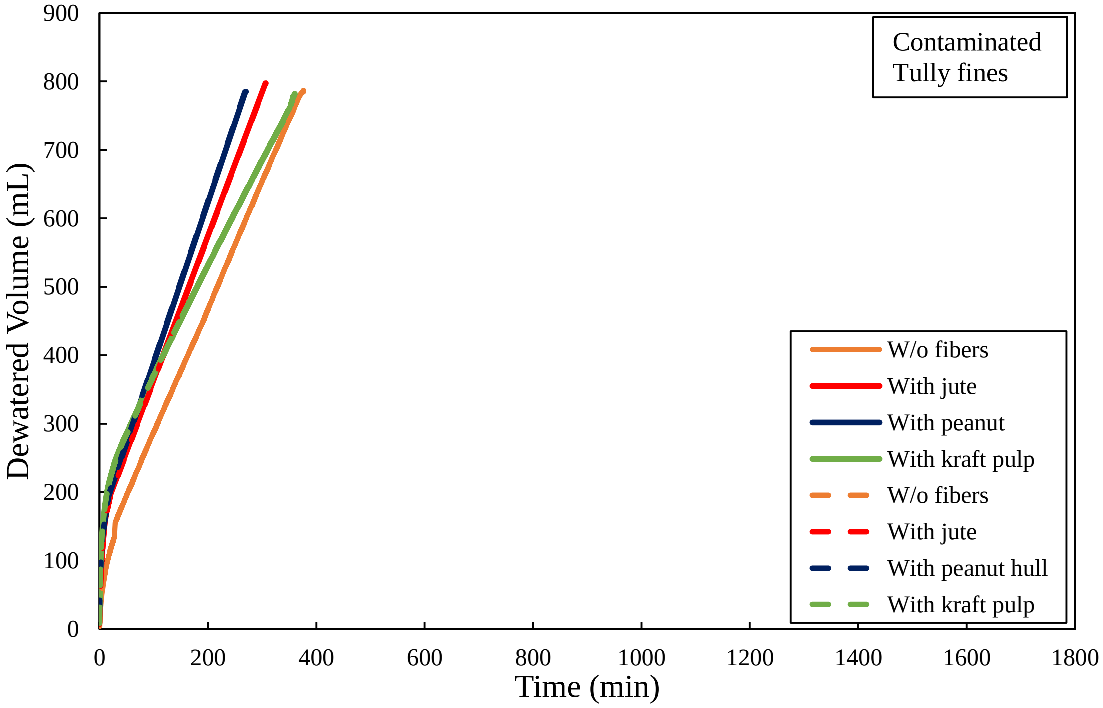


Figure 4.15 Dewatering of contaminated Tully fines with cellulose and without polymer

Table 4.8 Summary of dewatering parameters of Tully fines with cellulose and without polymer

Conditions	**Trials**	**Overall turbidity (NTU)**	**Solid content of the filter cake (%)**	**Filter cake height (mm)**
Uncontaminated Tully fines with kraft pulp	Trial 1	317	66.13	23.7
	Trial 2	329	65.53	22.9
Uncontaminated Tully fines with jute fibers	Trial 1	107	69.83	25.4
	Trial 2	124	70.52	24.3
Uncontaminated Tully fines with peanut hulls	Trial 1	113	68.36	22.6
	Trial 2	129	70.11	21.8
Contaminated Tully fines with kraft pulp	Trial 1	11.74	71.23	24.09
	Trial 2	11.89	70.81	24.12
Contaminated Tully fines with jute fibers	Trial 1	2.54	74.16	27.94
	Trial 2	2.65	73.59	28.89
Contaminated Tully fines with peanut hulls	Trial 1	8.62	71.68	25.43
	Trial 2	8.28	72.07	24.62

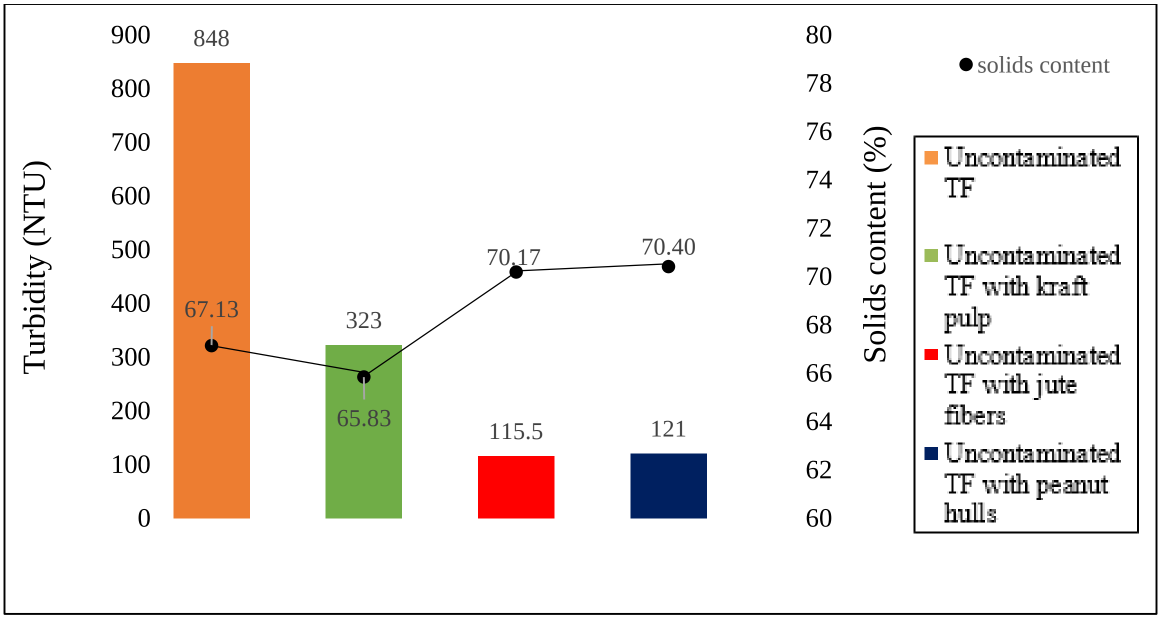


Figure 4.16 Dewatering parameters (turbidity and solids content) of uncontaminated Tully fines with cellulose materials and without polymer

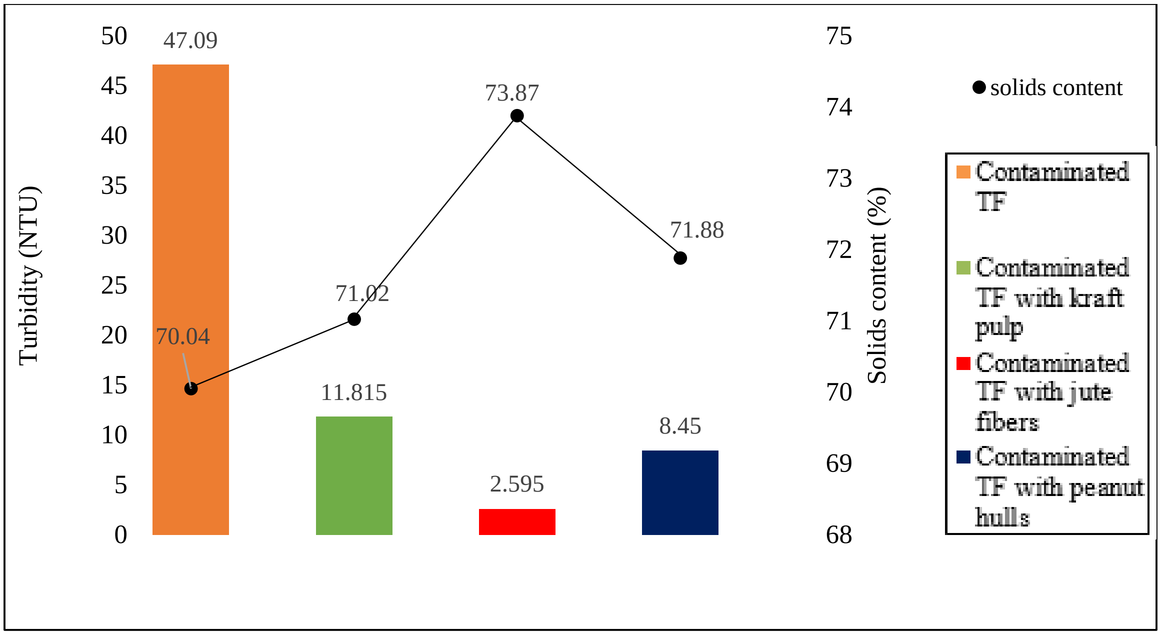


Figure 4.17 Dewatering parameters (turbidity and solids content) of contaminated Tully fines with cellulose materials and without polymer

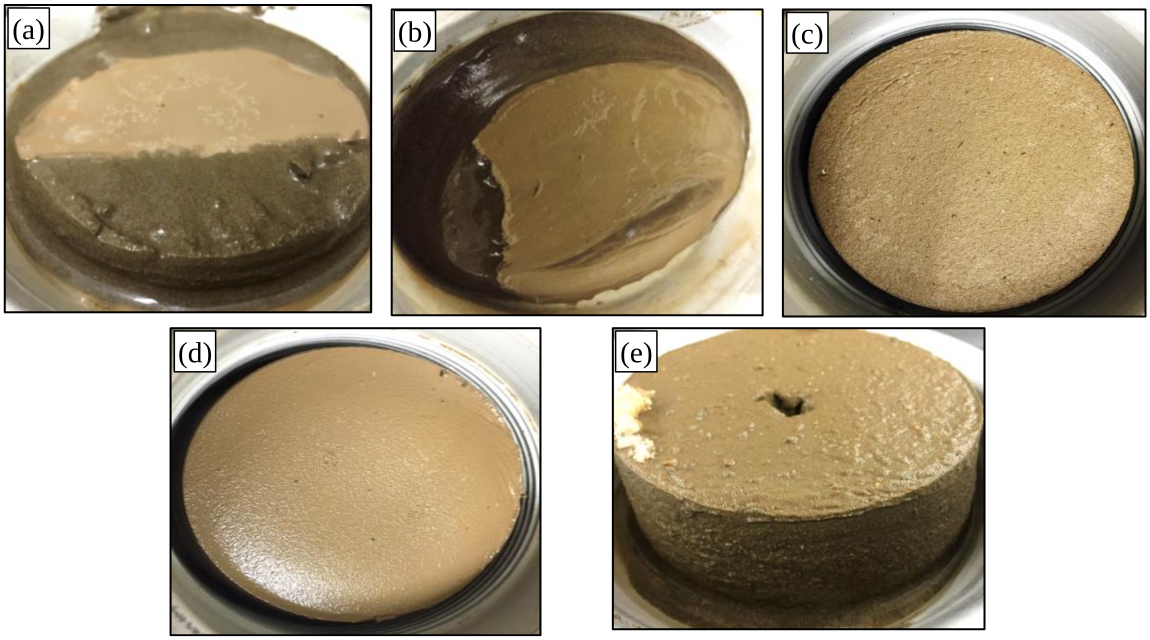
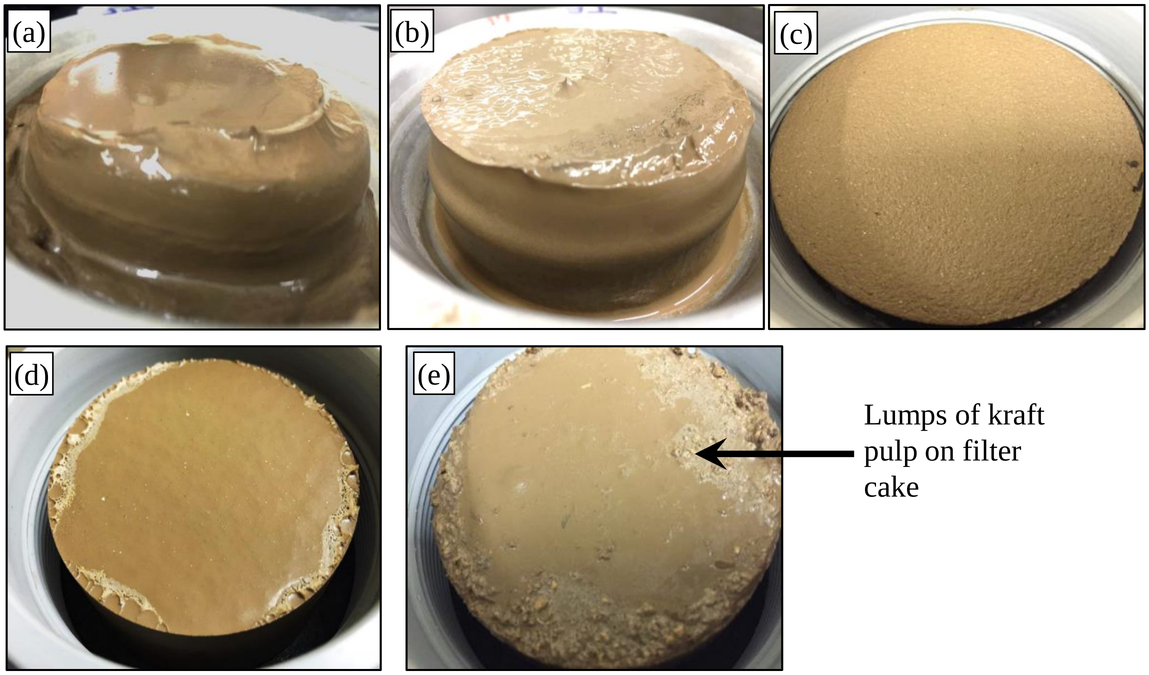


Figure 4.18 Filter cake of Tully coarse without polymer (a) Uncontaminated, (b) Contaminated, (c) Contaminated with jute fibers, (d) Contaminated with peanut hull, and (e) Contaminated with kraft pulp



Lumps of kraft pulp on filter cake

Figure 4.19 Filter cake of Tully fines without polymer (a) Uncontaminated, (b) Contaminated, (c) Contaminated with jute fibers, (d) Contaminated with peanut hull, and (e) Contaminated with kraft pulp

4.4.1.4 PFT Results: Contaminated slurries with cellulose fibers and polymer

In almost all geotextile dewatering projects, dredged sediments are treated with polymers in order to promote flocculation and coagulation of fines to speed up the dewatering as well as reduce the turbidity. Hence, the dewatering of contaminated Tully soils in presence of cellulose materials were carried by treating the slurries with the optimum dose of zetag 8185 determined from the jar test which were 1.17 ppm for Tully coarse and 16.2 ppm for Tully fines. The dewatering of contaminated Tully coarse and Tully fines with cellulose materials and polymer is shown in Figures 4.20 and 4.21, respectively. As expected, the dewatering rate increased significantly with the addition of polymer. It can be seen from Figure 4.20 that with the addition of polymer and cellulose materials in contaminated Tully coarse slurry, the dewatering completed within 3-5 minutes. The summary of the solids content of the Tully coarse filter cake and turbidity is given in Table 4.9. It can be seen that with the addition of polymer, the turbidity with all cellulose materials was very low (3-5 NTU). However, the solids content of the filter cakes decreased with the addition of polymer in case of all cellulose materials by 5.-8%. It can be seen from Figure 4.21 that the addition of polymer on a Tully fine contaminated slurry with cellulose materials reduced the dewatering time from approximately 200-400 minutes to 25-80 minutes. The summary of solids content and turbidity is given in Table 4.10. As observed in case of Tully coarse, the addition of polymer reduced the solids content of the filter cake. The results of the dewatering performance (turbidity and solids content of the filter cake) of uncontaminated and contaminated Tully fines with cellulose materials have been shown using a bar diagram in Figures 4.22 and 4.23, respectively.

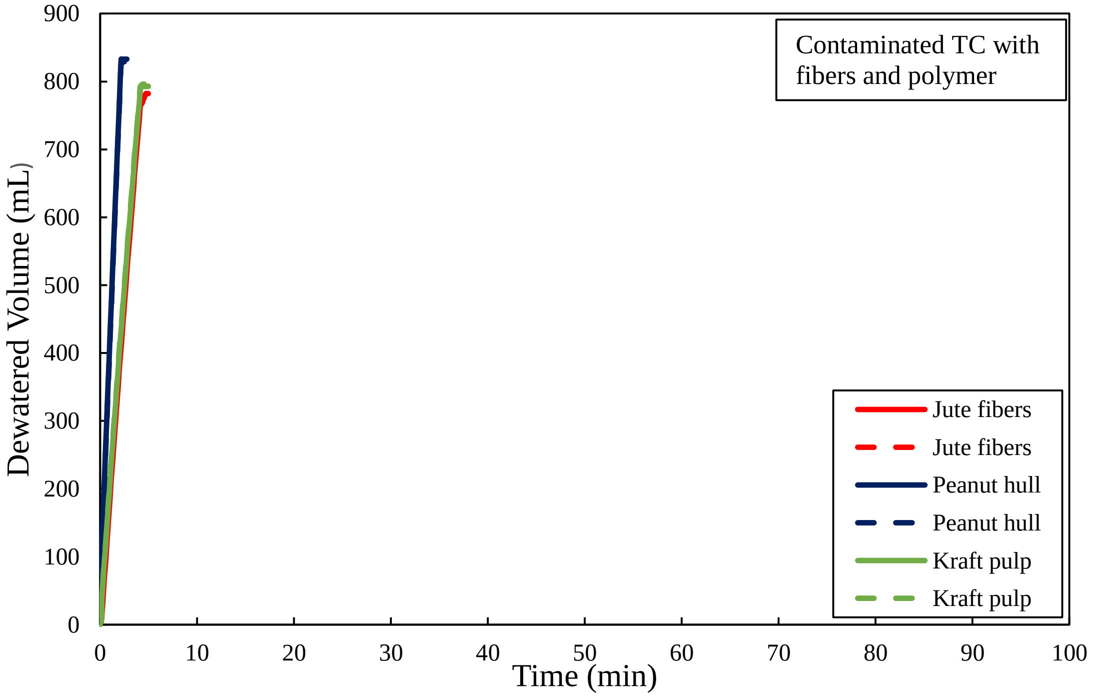


Figure 4.20 Dewatering of contaminated Tully coarse with cellulose and polymer

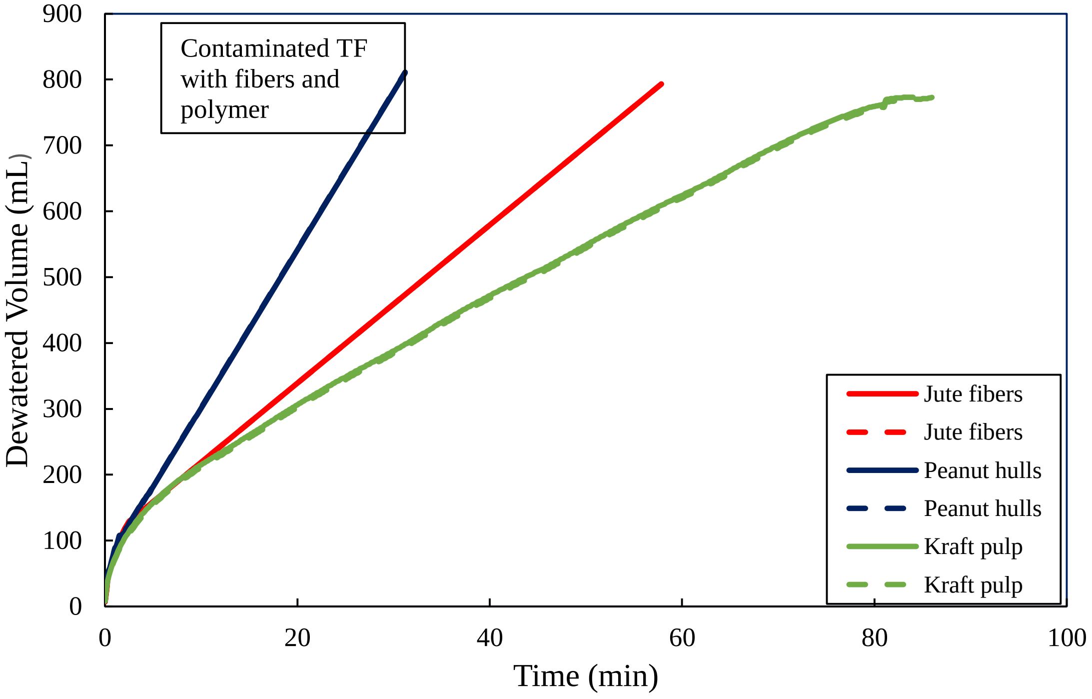


Figure 4.21 Dewatering of contaminated Tully fines with cellulose and polymer

Table 4.9 Summary of dewatering parameters of contaminated Tully coarse with cellulose and polymer

Conditions	**Trials**	**Overall turbidity (NTU)**	**Solids content of the filter cake (%)**	**Filter cake height (mm)**
Contaminated Tully coarse with kraft pulp and polymer	Trial 1	2.96	69.87	28.8
	Trial 2	2.21	69.80	29.56
Contaminated Tully coarse with jute fibers and polymer	Trial 1	3.89	70.78	31.14
	Trial 2	3.45	70.06	32.19
Contaminated Tully coarse with peanut hulls and polymer	Trial 1	5.00	69.41	27.98
	Trial 2	4.38	69.31	27.67

Table 4.10 Summary of dewatering parameters of contaminated Tully fines with cellulose and polymer

Conditions	Trials	Overall turbidity (NTU)	Solids content of the filter cake (%)	Filter cake height (mm)
Contaminated Tully fines with kraft pulp and polymer	Trial 1	7.62	67.43	32.79
	Trial 2	8.37	66.82	32.84
Contaminated Tully fines with jute fibers and polymer	Trial 1	4.12	68.36	34.13
	Trial 2	3.24	68.82	33.27
Contaminated Tully fines with peanut hulls and polymer	Trial 1	4.29	65.96	30.79
	Trial 2	6.19	66.33	29.43

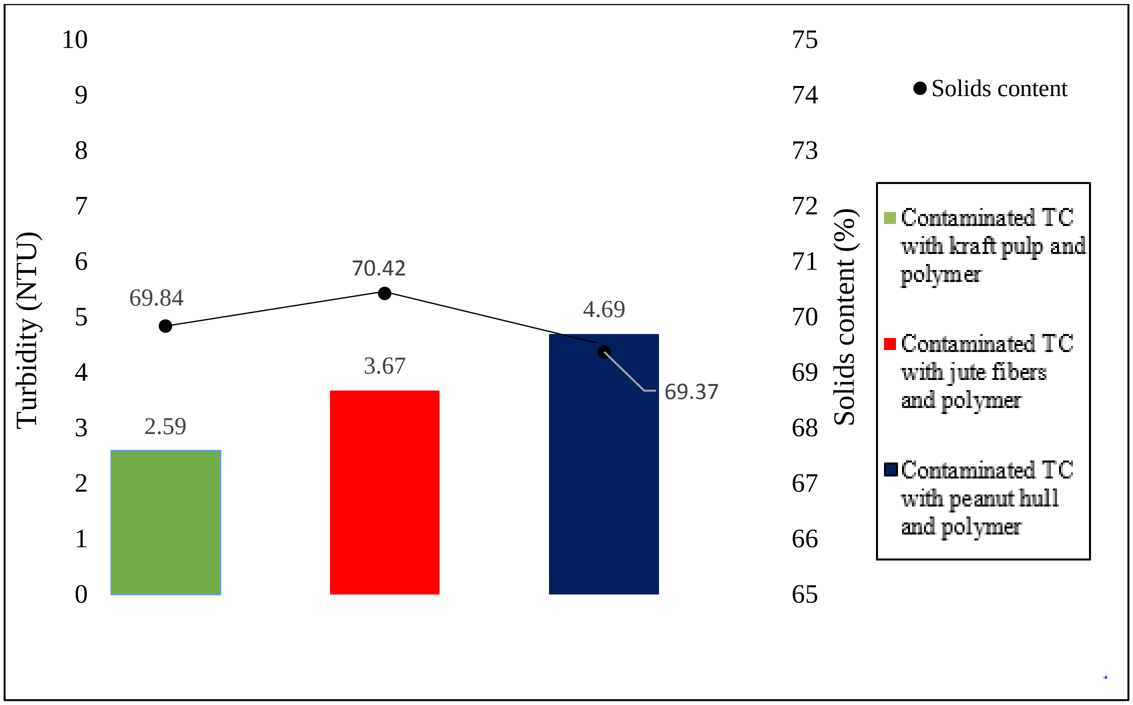


Figure 4.22 Dewatering parameters (turbidity and solids content) of contaminated Tully coarse with cellulose materials and polymer

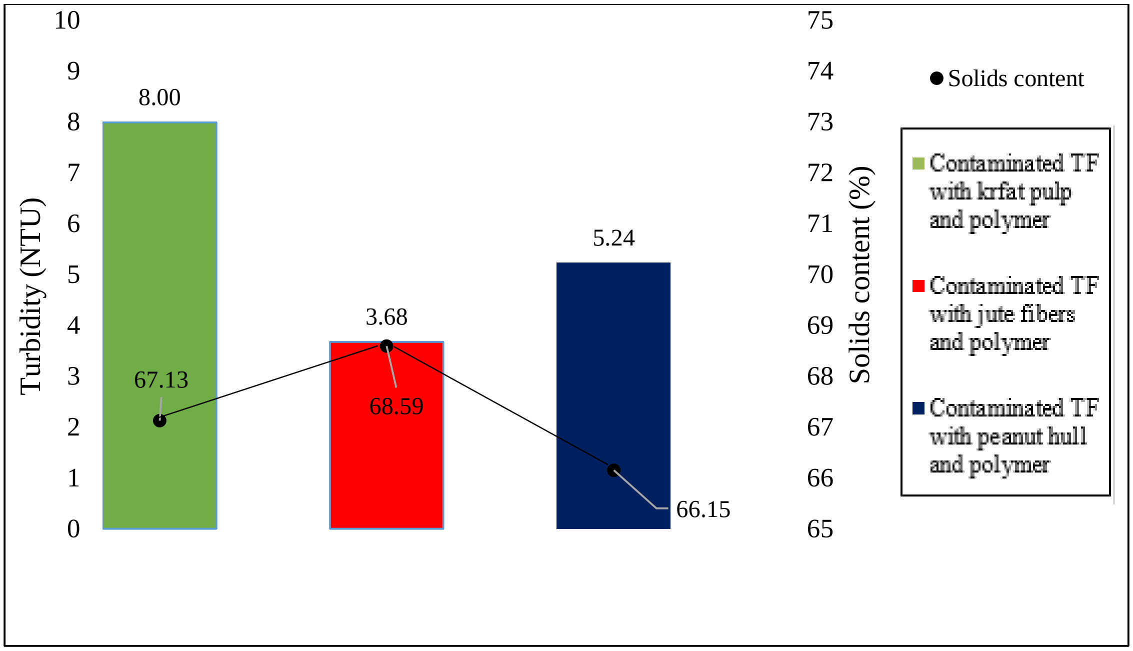


Figure 4.23 Dewatering parameters (turbidity and solids content) of contaminated Tully fines with cellulose materials and polymer

4.4.2 Metal concentration in the filtrate and removal efficiency:

For all PFT tests, the dewatered effluents were collected and tested for metal concentration using ICP OES. All the samples were made and tested in triplets. The removal efficiency of heavy metal ions in the PFT is given by:

$$\text{Removal Efficiency (\%)} = \frac{C_i - C_f}{C_i} * 100\%$$

where, C_i and C_f are initial and final concentrations of heavy metals in the slurry and filtrate respectively. The summary of removal efficiencies under different conditions for Tully coarse and Tully fines are presented in Tables 4.11 and 4.12 respectively. Both sediment slurries had an initial concentration of 1000 ppm Pb, 500 ppm Cu, 500 ppm Cd, and 500 ppm Zn. It can be seen from Table 11 that Tully coarse was able to adsorb 96 % Pb, 89% Cu, 81% Cd, and 76% Zn even without the cellulose adsorbents. It can also be seen from that the addition of cellulose materials was able to adsorb even higher amount of all heavy metals expect Cd. The addition of cellulose materials in contaminated Tully coarse had no role in adsorption of Cd. The addition of jute fibers was more beneficial in terms of adsorption of Cu as the removal efficiency increased form 90% to 99%. Also, all the cellulose materials were able to adsorb Pb with their addition in contaminated Tully coarse slurry. The adsorption of 99% Pb, 98% Cu, 86% Cd, and 83% Zn was achieved by Tully fines without any adsorbents (see Table 4.12). Among many reasons for such high adsorption capacity of both soils, is the presence of high amount of very reactive clay minerals such as Illite, Chlorite, and calcite in the Tully fine sediments. Since these minerals have high adsorption and retention capacity, they are also commonly used as soil amendment. The addition of cellulose materials in contaminated Tully fine sediment slurry was more effective in adsorption of Zn unlike in Tully coarse. Although the adsorption of heavy metals was very high even without the addition of cellulose materials, the cellulose materials had significant benefit for the dewatering performance. Also, independent tests conducted on the studied cellulose materials have confirmed that they have good adsorption capacity to the heavy metals. In cases where there are non-reactive soil sediments in a slurry, the addition of cellulose materials might have more pronounced effect in metal adsorption and retention. Addition of cellulose reduced dewatering time, increased solid content of the filter cake, and decreased turbidity of the filtrate in addition to adsorption heavy metal ions.

Table 4.11 Summary of % removal by Tully coarse with and without cellulose (without polymer)

Conditions	% Removal			
	Pb	Cu	Cd	Zn
Contaminated Tully coarse without adsorbents	95.98	89.94	81.41	76.34
Contaminated Tully coarse with peanut hulls	98.35	95.51	80.61	78.73
Contaminated Tully coarse with kraft pulp	97.04	93.41	80.95	78.10
Contaminated Tully coarse with jute fibers	99.37	98.37	80.22	81.59

Table 4.12 Summary of % removal by Tully fines with and without cellulose (without polymer)

Conditions	% Removal			
	Pb	Cu	Cd	Zn
Contaminated Tully fines without adsorbents	99.74	98.92	88.06	83.83
Contaminated Tully fines with peanut hulls	99.93	99.46	92.07	87.07
Contaminated Tully fines with kraft pulp	99.88	99.56	89.08	86.03
Contaminated Tully fines with jute fibers	99.94	99.75	91.30	87.76

4.5 Conclusions

This study aimed at addressing the issue of sustainable and effective containment of heavy metal contaminated slurries by investigating few low cost cellulose adsorbents not only to contain heavy metal contaminated sediments but also to improve the dewatering performance. Based on the results and observations from the PFT tests, following conclusions can be drawn.

- The optimum dose required for heavy metal contaminated sediments is very low compared to the non-contaminated sediment slurries. The primary reason is the presence of few charged surfaces on soils as a result of adsorption of metal ions from the contaminated slurry. A reduction in polymer dosage of as much as 50% was observed for the heavy metal contaminated sediment slurries. The PFT tests conducted show that the contaminated slurries dewater much faster than the uncontaminated slurries because of the flocculation of soil particles with metal ions.

- In both sediment slurries, the addition of cellulose adsorbents except kraft pulp significantly increased the dewatering rate irrespective of the contamination. However, profound effect of jute fibers and peanut hull on increasing dewatering rate was observed in case of contaminated slurries.
- A significant reduction in turbidity was achieved with the addition of the cellulose materials. A reduction in turbidity of more than 80% was observed with the addition of jute fibers. Peanut and kraft pulp were successful in reducing the turbidity by 78 and 69% respectively. Some cellulose materials like jute provided additional benefit in dewatering by increasing the solid content of the filter cake. A higher solid content of the filter cake is one indication of successful dewatering project. Addition of peanut and jute on contaminated Tully coarse increased the solid content by approximately 33% and 46% respectively. However, in case of contaminated Tully fines a minor increase of 12% was achieved with the addition of jute. The addition of kraft pulp had no significant effect in the solids content.
- The concentration of heavy metal ions in the filtrate from dewatering of contaminated slurries mainly depends upon the type of soil, its grain size and mineral composition. The filtrate collected from PFT tests were analyzed using ICP OES for metal concentration. It was observed that there is extremely high adsorption and retention of Pb and Cu ions by both of these soils. The filtrates collected from dewatering of contaminated Tully fines showed that approximately

98-99% of Cu and Pb was retained, whereas, in Tully coarse soils 89% Cu and 96% Pb were retained. Tully soils are essentially composed of active clay minerals like Illite, Chlorite and quartz. These clay minerals have very good adsorption and retention capacity of metal ions especially Pb. Although not very high adsorption, both Tully soils were able to retain more than 75% Cd and Zn. Hence, it can be concluded that to enhance the dewatering performance and heavy metal retention inside geotextile tubes, addition of reactive minerals like Illite, Chlorite and quartz could provide a viable solution.

4.6 References

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CHAPTER 5

CONCLUSION AND FUTURE WORK

5.1 Conclusion

The purpose of this study was to investigate effective and sustainable amendment strategies to contain and dewater heavy metal contaminated sediment slurries using geotextile tubes. For this purpose, three cellulosic materials (Peanut hulls, jute fibers, and kraft pulp) were chosen to be added to the slurry, which was dewatered using Pressure Filtration Test (PFT) in the lab. The sediment slurries were prepared using natural sediments, Tully coarse and Tully fines obtained from Clark's aggregate pit located at Tully, NY. The obtained soil from the quarry was used to prepare two batches of soil sediments. Tully coarse was prepared by removing fractions coarser than US sieve No. 4, and contains 55% coarse fractions (>75 µm) and 45% fine fractions (<75 µm). Tully fines were prepared by wet sieving through a US sieve No. 200 and oven drying the passing fraction. As a result, Tully fines contain 100% fine fractions. The reason behind choosing two sediments is to represent various soil sediments encountered in the dredging. The mineral composition of both soils, determined using X-ray diffraction showed that these soils are rich in clay minerals such as Illite, Chlorite, Dolomite, and quartz. Inorder to design effective amendment strategies for geotextile tube applications, it was important to understand the role of sediments in the adsorption and retention of heavy metals. Hence, adsorption studies were conducted where both soil sediments were mixed with heavy metal ions (Pb, Cu, Cd, and Zn). Moreover, Kaolinite clay was also used in this sub study. Both Tully soils were able to adsorb and retain more than 90% Pb and Cu, whereas Kaolinite clay being less reactive had lesser affinity towards those metal ions. Since both Tully soils had significant fines, very reactive clay minerals, and oxides and hydroxides of iron and aluminum they exhibited excessively high affinity towards Pb and Cu. However, Kaolinite had better adsorption for Cd than both Tully soils. Based on the results of these tests, it can be concluded that the type of clay minerals and grain size distribution play a dominant role in metal adsorption and retention. It can also be concluded that the abovementioned clay minerals have the potential to be an effective and viable additive materials to adsorb and retain Pb and Cu from slurries during geotextile dewatering process. Since, most of the studied heavy metal ions were adsorbed by Tully soils, an independent study was conducted to investigate the efficacy of cellulosic materials to the heavy metal ions. For this purpose, batch adsorption tests were carried on a 500 ppm metal solutions by varying the amount of cellulose materials from 0.5 g to 2g, and mixed for 4 hrs. This study was conducted not only to investigate the capacity of these materials to adsorb heavy metal ions, it was also conducted to quantify optimum mixing time and amount to be added to the slurry. It was observed from these tests that all of the studied materials had adsorption capacity to the heavy metals ions, but with varying degree. Jute fibers, peanut hulls and kraft pulp were able to adsorb more than 28-47% Pb, 15-28% Cu, 13-29% Cd, and 13-30%Zn. The materials rich in cellulose and lignin have been widely used in wastewater treatment technologies to adsorb different pollutants. It was determined from these tests that 1.5 g dosage and 1 hr mixing with the slurry was optimum. After the thorough knowledge of the role of sediments and cellulose materials in heavy metal adsorption, PFT tests were conducted on a slurry of both soils with cellulose materials to understand the their role in dewatering performance. PFT tests were conducted on a 15% solids concentration slurry with cellulose materials

(2% wt. solids) under an air pressure of 1.5 psi. It was observed from these tests that the addition of cellulose materials significantly increased the dewatering rate expect kraft pulp. Since kraft pulp was clumpy in nature and did not mix well with the soil slurry, it had no effect in dewatering rate. The addition of cellulose materials aided to reduce the turbidity of the filtrate. Jute fibers and peanut hull were able to reduce the overall turbidity of the filtrate by 78-80%, whereas kraft pulp helped to reduce overall turbidity by 69%. Added advantage of using jute fibers and peanut hulls were also seen in the final solids concentration of the filter cake. Their addition increased the solids content by approximately 12-46%. Reduction in solids content with the use of kraft pulp was observed. Also, the filtrate collected from the PFT tests had less than 2% Pb and Cu, and 15% Cd and Zn. Hence it can be concluded that these materials along with some reactive clay minerals like Illite and Chlorite can be added inside geotextile tubes not only to adsorb heavy metals but also to improve dewatering performance.

5.2 Future work and recommendations

With the help of batch adsorption and pressure filtration tests, it was observed that the addition of cellulosic materials not only aid in adsorbing and containing heavy metals inside geotextile tubes, it also helps in improving the dewatering performance. However, it has been seen that most of the contaminated sites requiring cleanup and remediation contains organic contaminants such as PCBs and PAHs in addition to the heavy metal. Hence, it is equally important to investigate amendment strategies that will aid in containment of organic as well as inorganic pollutants inside the geotextile tube. In this study, clean sediments obtained from local quarry has been used to prepare heavy metal contaminated slurries. But the dredged sediments in most of the geotextile dewatering projects contain mixture of sediments with significant amount of organics. Hence, it is important to test the real dredged soils so that the results would be more representative of the field condition and it will also help to develop more effective amendment strategies. Also, to use these findings to develop methodology to treat heavy metal contaminated slurries using geotextile tubes, it requires testing in large scale.

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Objective:

To obtain an entry level geotechnical engineering position in a progressive organization, that offers varied responsibility and experience which will deploy both my technical skills and persistent work ethic.

Education:

Syracuse University, Syracuse, New York
MS: Civil Engineering *(Geotechnical focus)*
Expected Graduation: May 2016, GPA: 3.83

Institute of Engineering, Pulchowk Engineering College, Lalitpur, Nepal
BS: Civil Engineering
Graduation: February 2010

Work Experience:

Teaching Assistant, Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York

• *Geotechnical Engineering* • *Soil Dynamics* • *Civil Engineering Materials* • *Designing with Geosynthetics*

August 2013 – May 2016

Planned geotechnical lab experiments, assisted in preparing lab manuals and recorded videos illustrating procedure to perform tests on soils following ASTM standard.

- Train and evaluate students on lab tests in soil, concrete and steel (compressive and tensile strength)
- Train students on DEEPSOIL and SHAKE to perform linear as well as nonlinear site response analysis.
- Grade lab reports and assignments, conduct recitations and office hours.

Assistant Project Manager, Bacha Construction Pvt. Ltd., Kathmandu, Nepal
March 2010- June 2013

Worked alongside project manager on site investigations, layout surveys, construction planning and scheduling. Oversaw overall construction of 400 m^3 concrete overhead water tank and four story corporate building.

- Planned and evaluated excavations, sand fillings and stone soling, brickwork and concrete mix according to the specifications.
- Collected and dispatched samples for lab testing, prepared reports and corresponded with clients.
- Delegated work among employees to ensure quality and completion of projects.
- Managed subcontractors and vendors, prepared bills.
- Prepared detailed work progress reports and AutoCAD drawings.
- Trained and evaluated potential new employees on equipment and company operations.

Research Experience:

Graduate Student, A study on geotextile dewatering of heavy metal contaminated sediments using reactive soil minerals and cellulosic materials, Syracuse University
May 2014- February 2016

Worked to design sustainable conceptual methodology to effectively contain heavy metal contaminated sediments inside geotextile tubes inorder to reduce additional cost incurred during post treatment. The work was funded by National Science Foundations (NSF).

- Performed geotechnical lab tests on soils such as grainsize, plasticity, compaction, consolidation, permeability, direct shear, vane shear, and triaxial tests.
- Performed series of batch adsorption tests with different sediments and cellulosic fibers.
- Performed Pressure Filtration Tests to quantify the dewatering pattern of different contaminated sediment slurries.
- Collected and analyzed data, prepared plots, drew conclusions, and wrote a paper for GeoChicago 2016 conference.

Graduate Student, Geotextile Tubes for Sustainable Dewatering, Syracuse University
August 2015 – May 2016
Contributed to the developing of set-ups for small and large scale pilot testing for the study of green flocculants as a substitute for synthetic polymers in geotube dewatering projects, as well as the study of a fiber additive and deformation behavior in the filling stage. The project was funded by National Science Foundation (NSF) and worked in partnership with Water Solve LLC and TenCate.

- Assisted in designing a system that measures the dewatering rate from the geotube through the use of a digital scale to measure the mass collection rate of the filtrate.
- Assisted in designing a system that measures the geotubes cross-sectional geometry at different stages of filling through the application of a 1-D laser sensor, positioned by a belt driven linear actuator, and controlled by a programmable stepper motor.
- Performed small scale tests at a project site in Sayreville, NJ where highly contaminated dredged river sediments were dewatered through geotubes.
- Preformed small and large scale pilot tests at a Stone Harbor Maintenance Dredging site located in Stone Harbor, NJ.
- Reported to weekly meetings to discuss progress and project scheduling.

Certifications:

- Passed Fundamentals of Engineering Exam (February 2016)
- OSHA 40 Hour HAZWOPER (November 2015)

Relevant Course Work:

- Advanced Soil Mechanics
- Foundation Design
- Seepage and Earth Dam Design
- Finite Element Analysis
- Geomorphology
- Designing With Geofoam
- Designing with Geosynthetics
- Independent study: Consolidation and permeability of fine grained sediments during multiple filling of geotextile tubes

Software Experience:

Proficient In: AutoCAD, GEOStudio, ANSYS, DEEPSOIL, Excel, Word, Mathcad
Experience In: PLAXIS, SHAKE, REAME, FLAC, ArcGIS