

Removal of Chromium (VI) from water by using

Lanthanum based Hybrid Materials

A Dissertation

Submitted in partial fulfilment for the degree of
MASTER OF SCIENCE IN CHEMISTRY



By

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UNDER THE SUPERVISION

Of

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Dedicated to My

Parents.....

DECLARATION

The work embodied in this report is an original investigation carried out by the author, on the topic entitled, “Removal of Chromium (VI) from water by using Lanthanum based Hybrid Materials”, for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma.

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CERTIFICATE

This is to certify that the project report entitled, “Removal of Chromium (VI) from water by using Lanthanum based Hybrid Materials”, is being submitted by Johny Langkam ,Roll number 409cy2014 in partial fulfilment of the Master degree in Science (Chemistry) , NIT Rourkela, is an original work carried out under my guidance and supervision. This has not been submitted by him for any other degree to any other Institution or University.

The present study is a valuable contribution for the advancement of knowledge in the field of material chemistry and its environmental application.

In habit and character, **Mr. Johny Langkam** is quite a fit and proper person for the further research work.

Prof. R.K. PATEL

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Johny Langkam

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ABSTRACT

In various studies it is found that contamination of Chromium (VI) in water posed severe health problems throughout the world. Several methods are available to remove chromium from the aqueous environment but they are not feasible in all places and conditions due to various reasons. Some of the process are electrochemical precipitation, ion exchange, activated carbon adsorption, solvent extraction, reverse osmosis, etc., from contaminated water. The development of low cost adsorbent is essential for the benefit of the common people.

In this present work, Cr (VI) has been removed from water by a synthesized Lanthanum based hybrid material as adsorbent. The removal of fluoride was 98.50 % at optimum condition from the synthetic solution having initial Cr(VI) concentration of 100 mg/L The extend of adsorption was investigated as a function of solution pH, contact time, adsorbent concentration, reaction temperature, Langmuir and Freundlich isotherm were used to model the adsorption equilibrium data.

Keywords: Chromium, ion-exchange, XRD, AAS

CHAPTER-1

*INTRODUCTION
AND
LITERATURE REVIEW*

1.1. Environmental effects of chromium

Chromium exists in food, air, water and soil, mostly in the Cr -III form. It is only as a result of human activities that substantial amounts of Cr -VI become present. Cr- III is comparatively insoluble while Cr -VI is quite soluble and is readily leached from soil to groundwater or surface water. Chromium (III): Chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat. Chromium (VI): Breathing high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted.

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities.

The main human activity that causes to increase the concentrations of chromium (III) in environment is steel, leather and textile industries. The main human activities that increase chromium (VI) concentrations in environment are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils. Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water, chromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve. Chromium (III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer.

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur. Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumour formation.

1.2 Chromium related Health hazard

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The most common forms of chromium in the environment are trivalent chromium (chromium-III), hexavalent chromium (chromium-VI) and the metal form of chromium (chromium-0). Chromium-III occurs naturally in many vegetables, fruits, meats and grains, and in yeast. It is an essential nutritional element for humans and is often added to vitamins as a dietary supplement. Chromium-III has relatively low toxicity. Hexavalent chromium is used for chrome plating and the production of stainless steel as well as leather tanning, wood preservation, textile dyes and pigments. Hexavalent chromium is also used in anti-corrosion and conversion coatings.

Hexavalent chromium is recognized as a human carcinogen when it is inhaled. Chronic inhalation of hexavalent chromium has been shown to increase risk of lung cancer and may also damage the small capillaries in kidneys and intestines. Other adverse health effects associated with hexavalent chromium exposure, according to the National Institute for Occupational Safety and Health (NIOSH), include skin irritation or ulceration, allergic contact dermatitis, occupational asthma, nasal irritation and ulceration, perforated nasal septa, rhinitis, nosebleed, respiratory irritation, nasal cancer, sinus cancer, eye irritation and damage, perforated eardrums, kidney damage, liver damage, pulmonary congestion and edema, epigastric pain, and erosion and discoloration of one's teeth.

Chromium (III) is an essential nutrient for humans and shortages may cause disrupted heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes and other diseases. Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in, chromium (VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium (VI) are:

1. Skin rashes
2. Upset stomachs and ulcers
3. Respiratory problems
4. Weakened immune systems
5. Kidney and liver damage
6. Alteration of genetic material
7. Lung cancer
8. Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. There are various reports of adverse effects of the hexavalent form. Because of these health effects, World Health Organisation (WHO), established a guideline of maximum permissible limit which is 1.5 mg/L

1.3 Adsorption Techniques for Removal of Chromium

The technique adopted in chromium removal is to adsorb chromium from chromium-bearing aqueous media to a phase (usually a solid) that can be separated from the water. A number of methods are reported for removal of chromium such as membrane techniques, reverse osmosis, Nano-filtration, dialysis, Nano-filtration and adsorption. Although many of these methods have successfully reduced chromium concentration to acceptable levels, surface adsorption, in which

chromium is adsorbed on to a bed packed with resin or other material particles, retains a major place in chromium removal research and practice because of its greater accessibility and lower cost, especially in countries where the problem of excessive chromium in available drinking water is very high. Thus even in the past decade, many workers have continued to explore the development of low-cost and effective adsorbents and to improve the efficiency of all adsorbents. In this report Lanthanum based hybrid materials were used to study the removal of chromium from contaminated water samples through adsorption.

1.4 Aims and Objective of the Present Work

The aim of this work is to study the adsorption of chromium by a synthesized La-hybrid material for remediation of chromium with the following objective.

- To synthesis and characterize the Lanthanum based hybrid materials.
- To utilize the material to know the removal efficiency of Cr-VI
- To find the optimum condition for removal of Cr-VI
- To formulate a process for field application.

CHAPTER- 2

EXPERIMENTAL METHODS

EXPERIMENTAL SECTION

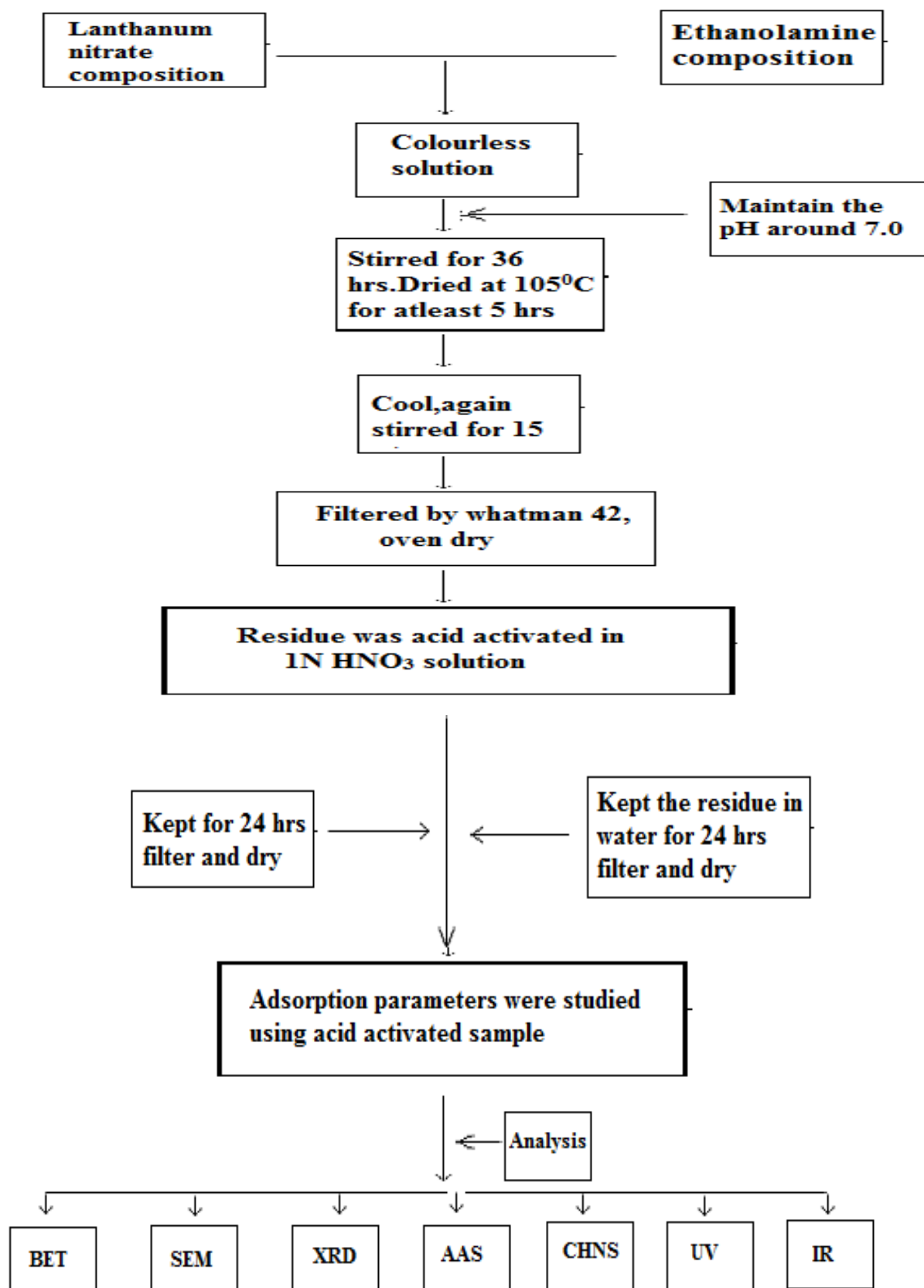
2.1 Materials and Methods:

All chemicals used for this study was of AR grade. All glassware like measuring cylinder, volumetric flask, conical flask, etc., were of borosil and tarson make Lanthanum nitrate and Ethanolamine (E.Merck) were used for the synthesis of the hybrid material. Standard solution of chromium was prepared from potassium chromate (K_2CrO_4). Nitric acid (HNO_3) and Ammonium Hydroxide (NH_4OH) were used to vary the pH. The other instruments used in this study are pH meter (elico), AAS (Perkin Elmer PE Analyst Atomic Absorption Spectroscopy), XRD (Phillips Powder Diffract meter Model PW 1830), SEM (JEOL, jXA-8100).

2.2 Synthesis and analysis of Lanthanum based hybrid material

Lanthanum based hybrid material was prepared by mixing aqueous solution of lanthanum nitrate with aqueous solution of ethanolamine of various concentration in the ratio 1:2(detailed are given below).The desired pH was adjusted by adding required amount of dilute nitric acid or ammonium hydroxide dropwise. The white gel so obtained was allowed to stand overnight at room temperature and was then filtered, washed with demineralised water to remove excess reagent till the filtrate attains a pH value of 6 or 7,then dried at 105^0c at least for 5 hours. The material is collected and then converted to H^+ form by treating it with 1.0 M HNO_3 for 24 to 30 hours with occasional shaking which was filtered washed with water several time and dried in room temperature for 36 hours. The materials were kept in an air tight container for further use. The chromium concentration was measured by AAS (Perkin Elmer PE Analyst Atomic Absorption Spectroscopy).The X-ray diffraction (XRD) analysis were done over a range of 10 to 80^0 using Phillips Powder Diffractometer Model PW 1830 at a scan speed of $2^0/min$.The surface morphology of the hybrid material were studied using scanning electron microscope (JEOL, jXA-8100).

2.3. Flowchart for preparation of Lanthanum based hybrid material



2.4: Adsorption experiments

The Cr (VI) sorption experiments from its aqueous solution on lanthanum based hybrid material were carried out using standard 100 mg/L Cr (VI) solution in absence of other competing ions. The adsorption experiments were carried out in 250mL glass conical flask with stopper by adding 0.2, 0.4, 0.6, 0.8 and 1.0 g of lanthanum based hybrid material in 100mL of synthetic Cr (VI) solution. Stoppers were provided to avoid change in concentration due to evaporation. All the adsorption experiments were carried out at ambient temperature (25 ± 2 °C). After continuous stirring over a magnetic stirrer at about 400 rpm for a predetermined time interval, the solid was separated by filtration through Whatman-42 filter paper and the remaining Cr (VI) concentration was determined by Perkin- Elmer Atomic Absorption Spectrophotometer (AAS). Measurement was done by taking 50mL of each standard and sample into separate 150mL beaker by standard procedure followed in AAS. All the sample and standards were maintained at same temperature to avoid interference due to difference in temperature, pH of the solution was maintained when needed, by addition of nitric acid (1.0 N) or ammonium hydroxide solution (1.0 M) and was measured with a elico pH meter.. A number of parameters such as contact time, mass of adsorbent concentration of adsorbate, pH, affecting the removal of chromium ion have been varied widely in order to optimize the adsorption process. All the three composition of lanthanum based hybrid material prepared were used for the removal of chromium but the composition-2 was found to have maximum removal efficiency and used in further studies.

2. 5 Adsorptions Theory

2.5.1. Adsorption isotherm model equations

Adsorption isotherms help in determining the properties of the adsorbents such as pore volume, pore size or energy distribution and specific surface area. The isotherm curve can also be utilized to obtain information concerning the desorption mechanism strictly connected with interaction between the adsorbent and adsorbate molecules. Therefore, the efficiency of an industrial adsorbent can be assessed through this curve. The correct interpretation of the experimental adsorption isotherm can be realized in terms of some mathematical equations called adsorption isotherm model

equations. Such equations are derived assuming an ideal physical model for the adsorption system. The model assumptions are usually a result of experimental observations. The experimental results allow for the formulation of hypothesis about the character of the adsorption process. This hypothesis can be tested experimentally and if found suitable, could be developed into a theory, i.e. a suitable adsorption isotherm equation. The adsorption isotherm thus developed provides useful information for estimating performance in a full scale process stream. Firstly, they help to determine, the possibility to reach a desired purity level for a given adsorbent. This is important when multiple impurities are present and one or more impurities are poorly adsorbed. Secondly, the isotherm allows calculation of uptake at equilibrium, which has a major impact on the process economy. It can also be used to predict the relative performance of different types of adsorbents.

Prior to 1914 only a few theoretical interpretations of adsorption isotherms were in use. But thereafter, a number of isotherm equations were proposed by different investigators. Some of those in frequent use are:

- Freundlich adsorption isotherm
- Langmuir adsorption isotherm

2.5.1.1. Freundlich adsorption isotherm

Freundlich adsorption isotherm was proposed by Boedecker¹ in 1895 as an empirical equation. Later Freundlich² made some useful modifications as a result of which, it assumed great importance. The Freundlich adsorption equation can be written as:

$$q_e = K_f C_e^{\frac{1}{n_f}} \quad (2.1)$$

Taking logarithm on both sides,

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (2.2)$$

Where 'q_e' is equilibrium adsorption capacity (mg g⁻¹), 'C_e' is the equilibrium concentration of the adsorbate in solution, K_f and n_f are constants related to the adsorption process such as adsorption capacity and intensity respectively.

2.5.1.2. Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the following assumptions:

- There are fixed number of adsorption sites at equilibrium. At any temperature, a fraction of the adsorbent surface sites (θ_s) is occupied by adsorbed molecules and rest ($1 - \theta_s$) is free
- All adsorption processes are homogeneous
- There is only one adsorbate
- One adsorbate molecule will react with only one active site
- No interaction between the adsorbate species
- A monolayer surface phase is formed

The equation proposed by Longmuir is universally applicable to chemisorptions with some restrictions involving physical adsorption. This equation is applicable to the physical or chemical adsorption on solid surface with one type of adsorption active centre. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for adsorption behaviour in different adsorbate-adsorbent systems or for varied conditions within any given system. Linear form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2.3)$$

Where ' C_e ' is the equilibrium concentration and ' q_e ' is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg g^{-1}); ' q_m ' and ' b ' are Langmuir constants related to the maximum adsorption capacity and intensity respectively.

2.5.2. Adsorption kinetic models

The study of adsorption kinetics of wastewater is significant as it provides valuable insight into the reaction pathways and into the mechanism of reaction. Further, it is important to predict the time at which the adsorbate is removed from the aqueous solution in order to design an appropriate adsorption treatment plant. Any adsorption process is normally controlled by three diffusive transport processes for the adsorbate:

- From the bulk solution to the film surrounding the adsorbent
- From the film to the adsorbent

- From the surface to the internal sites and binding of the metal ions onto the active sites.

But in kinetic modelling, all these three steps are grouped together and it is assumed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for adsorption. Further, it is established from the experimental observations that at optimum agitation speed, the external boundaries have hardly any effect. So application of kinetic model depends only on the initial and final concentrations of the solution at different time intervals. It is incorrect to apply simple kinetic model such as first and second order rate equations to adsorption process with solid surface, which is rarely homogeneous. Secondly, the effects of transport and chemical reaction are often experimentally inseparable.

Several kinetic models have been proposed to clarify the mechanism of solute adsorption from aqueous solution onto an adsorbent:

- Pseudo first order/Lagergren kinetic model
- First order reversible kinetic model
- Pseudo-second order kinetic model

2.5.2.1. Pseudo-first-order/Lagergren kinetic model

The Pseudo-first-order or Lagergren kinetic rate equation for the adsorption of liquid-solid system was derived based on solid adsorption capacity. It is one of the most widely used adsorption rate equations for adsorption of a solute from a liquid solution.⁷⁻¹⁰ According to the authors, the overall adsorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate $(q_e - q_t)$. Therefore, the pseudo first order kinetic equation can be expressed as:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (2.6)$$

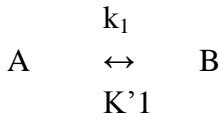
Where ‘ q_e ’ is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg g^{-1}), ‘ q_t ’ is the amount of solute adsorbed at any given time ‘ t ’ and ‘ k_1 ’ is the rate constant. By using the boundary conditions and simplifying, the equation (2.6) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.7)$$

'k₁' can be calculated from the slope of the linear plot between ln (q_e-q_t) vs. 't' for different adsorption parameters such as pH, temperature, adsorbate concentration, adsorbent dose, particle size and agitation speed.

2.5.2.2. First- order- reversible kinetic model

The adsorption process may be considered as a first order reversible reaction, [11-12] which can be expressed as



The rate equation for the reaction is expressed as

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = k_1 C_A - k'_1 C_B = C_{A0} \frac{dX_A}{dt} = k_1 (C_{A0} - C_{A0} X_A) - k'_1 (C_{B0} - C_{A0}) \quad (2.8)$$

Where 'C_A' (mg L⁻¹) and 'C_B' (mg g⁻¹) are the concentrations of the adsorbate in solution and adsorbent respectively at a given time 't'; 'C_{A0}' and 'C_{B0}' are the initial concentrations of adsorbate and adsorbent respectively, 'X_A' is the fractional conversion of the adsorbate, 'k₁' and 'k'₁' are the first order rate constants for forward and reversible adsorption respectively. At equilibrium conditions:

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} \quad (2.9)$$

And

$$X_{Ae} = \frac{K_c - (C_{B0}/C_{A0})}{K_c + 1} \quad (2.10)$$

Where 'X_{Ae}' is fractional conversion of the adsorbate at equilibrium and 'K_c' is the equilibrium constant which is defined as:

$$K_c = \frac{C_{Be}}{C_{Ae}} = \frac{C_{B0} - C_{A0} X_{Ae}}{C_{A0} - C_{A0} X_{Ae}} = \frac{k_1}{k'_1} \quad (2.11)$$

Where 'C_{Ae}' and 'C_{Be}' are the equilibrium concentrations of adsorbate in the solution and adsorbent, respectively. Applying the equilibrium conditions, equation (2.8) becomes:

$$\ln (1-U_t) = -(k_1+k_1')t \quad (2.12)$$

Where 'U_t' is the fractional attainment of equilibrium and is given by

$$U_t = \frac{C_{A0} - C_A}{C_{A0} - C_{Ae}} \quad (2.13)$$

The values of rate constant were calculated from the equilibrium conditions from the plot between $\ln (1-U_t)$ versus t .

2.5.2.3. Pseudo- second- order kinetic model

A pseudo- second- order reaction model¹³⁻¹⁴ can be applicable to kinetics of adsorption and equation for this reaction can be shown as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (2.14)$$

On integration for boundary conditions when $t=0$ to $t>0$ and $q_t=0$ to $q_t>0$ and further simplifications, equation (2.14) becomes,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t = \frac{1}{h} + \frac{1}{q_e} t \quad (2.15)$$

Where $h = k_2 q_e^2$ is known as initial adsorption rate and 'k₂' is rate constant.

The plot of t/q_t versus t at different adsorption parameters will give a linear relationship, which allows for computation of q_e , K_2 and h . Ho¹⁵ compared linear and nonlinear methods and showed the effectiveness of using nonlinear method to solve the pseudo-second-order kinetic model equation rather than using linear method which at times may lead to inaccurate results. He adopted trial and error method using solver add-in available with Microsoft's spreadsheet, Microsoft Excel. Nouri et al¹⁶ also analyzed adsorption uptake kinetics by non-linear curve fitting analysis method, using Microcal™ Origin® software, to fit the pseudo-second –order equation.

CHAPTER-3

RESULT AND DISCUSSION

3.1 Characterization of Lanthanum based hybrid material

The present study is an attempt to explore synthesis of lanthanum based hybrid material and its application for the removal of Cr (VI) from synthetic solution. A number of samples of hybrid materials were prepared by adding different molar solution of lanthanum nitrate (Table 1). The material is characterized based on the data of analysis of SEM, XRD, FTIR, CHNS and the report of the similar work.

Table- 1: Compositions of different hybrid material

| Composition numbers | Lanthanum nitrate | Ethanolamine |
|---------------------|-------------------|--------------|
| Com-1 | 0.1M | 0.2M |
| Com-2 | 1.0M | 1.2M |
| Com-3 | 1.0M | 2.0M |

The SEM micrographs of lanthanum based hybrid material are represented in Fig-1a and 1b which clearly indicate the surface structure of the material. The SEM micrograph clearly shows the surface modification, which takes place due to Cr loded in the material. The SEM micrograph of chromium loaded material shows small crystalline particle adsorbed over the surface of adsorbent.

3.1.1 SEM micrographs of lanthanum based hybrid material:

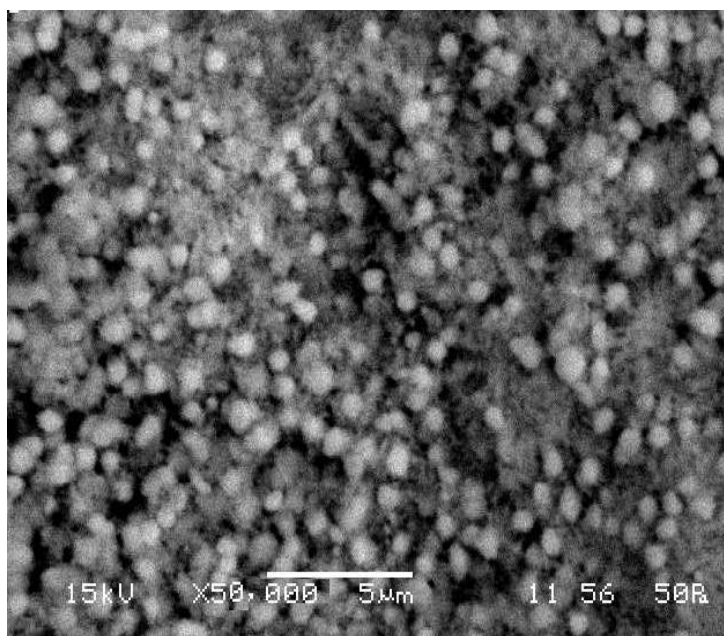


Figure1a. SEM image of Lanthanum based hybrid material (**Before Adsorption**)

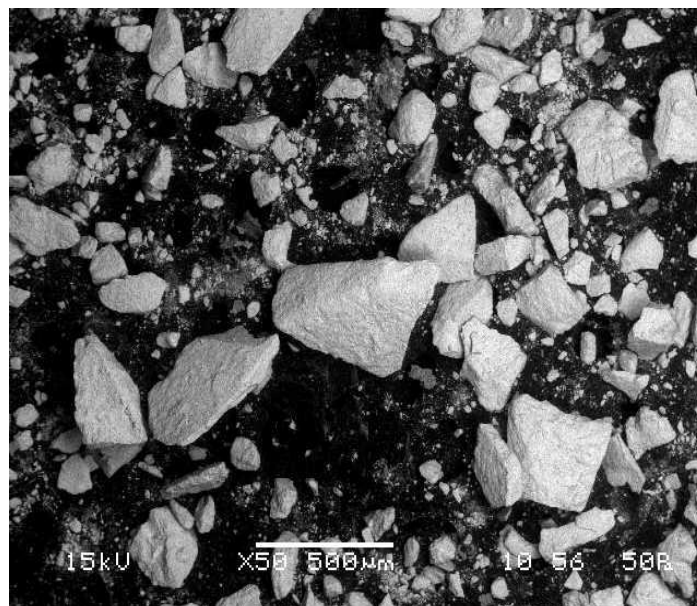


Figure 1b. SEM image of Lanthanum based hybrid material (After Adsorption)

3.1.2 BET REPORT: Surface area of untreated material samples were determined by BET method. The surface area of untreated sample was found to be 198.42 m²/g and is represented in Table-2

Table-2

| <i>Surface area data</i> | <i>Pore volume data</i> | <i>Pore size data</i> |
|-------------------------------|-----------------------------|----------------------------|
| Area | DR Method Micro pore Volume | DR Method Micro Pore Width |
| 198.42 m²/g | 1.42 E-01 cc/g | 1.152E+02 Å |

3.1.3 XRD REPORT: Powdered XRD of the material was obtained by using PHILIPS X'PERT X-Ray Diffractometer with Cu K α radiation(35 kv and 30 mA) at a scan rate of 2⁰/min and was analysed using standard software provided with the instrument. The XRD pattern of the sample is presented in Fig. 2. Broad peaks were obtained instead of sharp peaks indicating the sample was poorly crystalline. XRD was analyzed using standard software but a very low intensity peak of lanthanum nitrate was found.

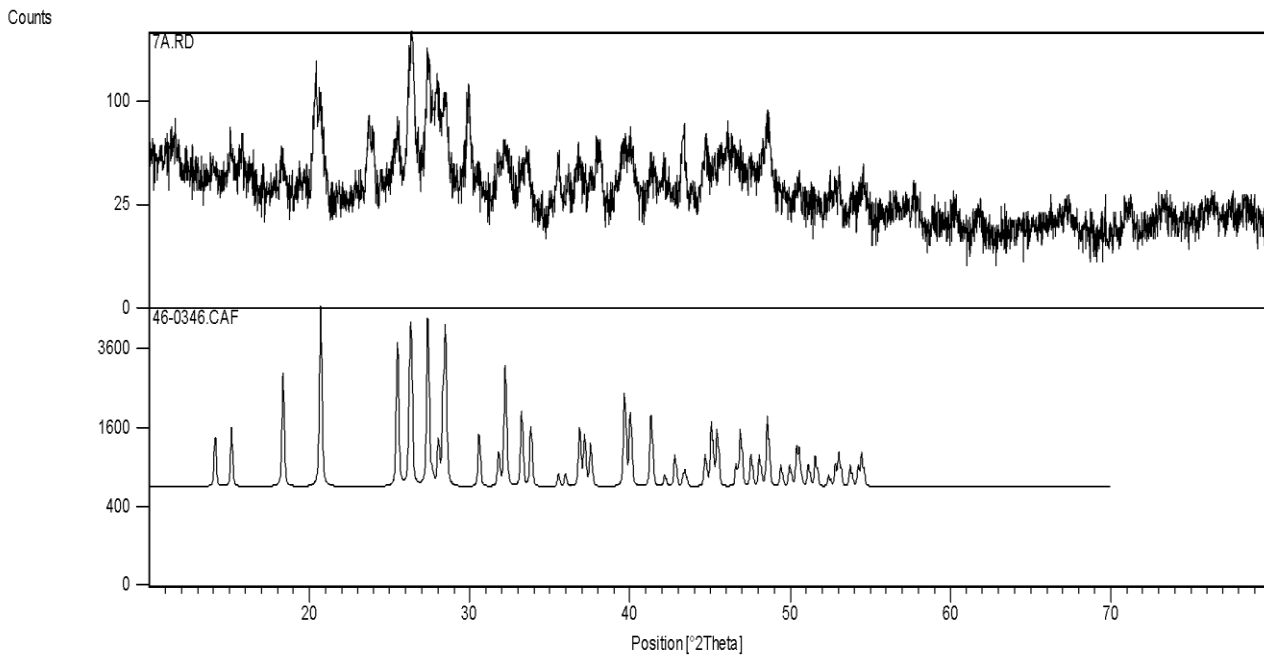


Figure 2

Crystal system: monoclinic, a (Å):21.1920, b (Å): 3.9899, c (Å):6.4048, density: 3.41, volume of cell: 494.15, $2\theta=21.711$, D-Spacing-4.814

3.1.4 IR DATA: FTIR study of the sample was carried out (Fig. 3) in order to know the presence of different groups and structures in the material. The important peaks and probable corresponding to the functional groups are represented in Table -3

Figure 3

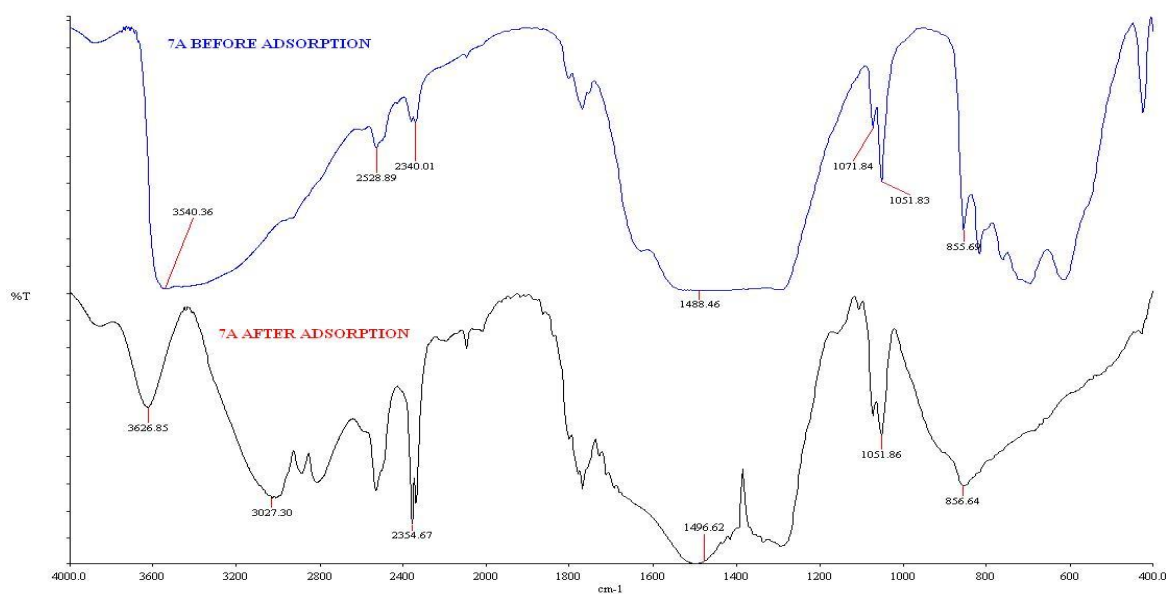


Table-3

| | | | | | | |
|-----------------|-------------|-------------|-------------|-------------|---------|------------------|
| Peak | 3540.36 | 2528.89 | 2340.01 | 1488.46 | 1051.83 | 855.69 |
| Position | 3626.85 | 3027.30 | 2354.67 | 1496.70 | 1051.86 | 856.64 |
| | N-H stretch | O-H stretch | C-N stretch | C-H stretch | CO | metal- oxygen |

The peak at 3540.36 cm⁻¹ of the sample before adsorption is broad as compared to the peak at 3626.85 cm⁻¹ of that of after adsorption. This broad peak result from the overlapping of O-H stretching with NH stretching The second peak at 2528.89 cm⁻¹ before adsorption, get splitted into a number of peaks after adsorption due to coordination of metal to nitrogen causing splitting and reduction in intensity. The peak at 2340.01 cm⁻¹ of the sample before adsorption has been shifted to 2354.67 cm⁻¹ due to blue shift indicating the coordination of nitrogen to metal ion.

3.2 Effect of different parameters on chromium (VI) removal

3.2.1 Effect of adsorbent dose

The effect of adsorbent dosage on chromium (VI) removal at fixed pH and initial chromium concentration (100 mgL⁻¹) is shown in Figure-4 .It is evident from the graph that the percentage of chromium removal increases from 97.70 to 98.70 % with the increase in the adsorbent dose from 0.1 to 0.8 gm of the hybrid material which is due to the fact that a greater amount of adsorbent provides greater number of available binding sites. After that saturation occur (at 0.8 gm.). So, 0.8 gm. /100 mL was considered as optimum dose and was used for further study.

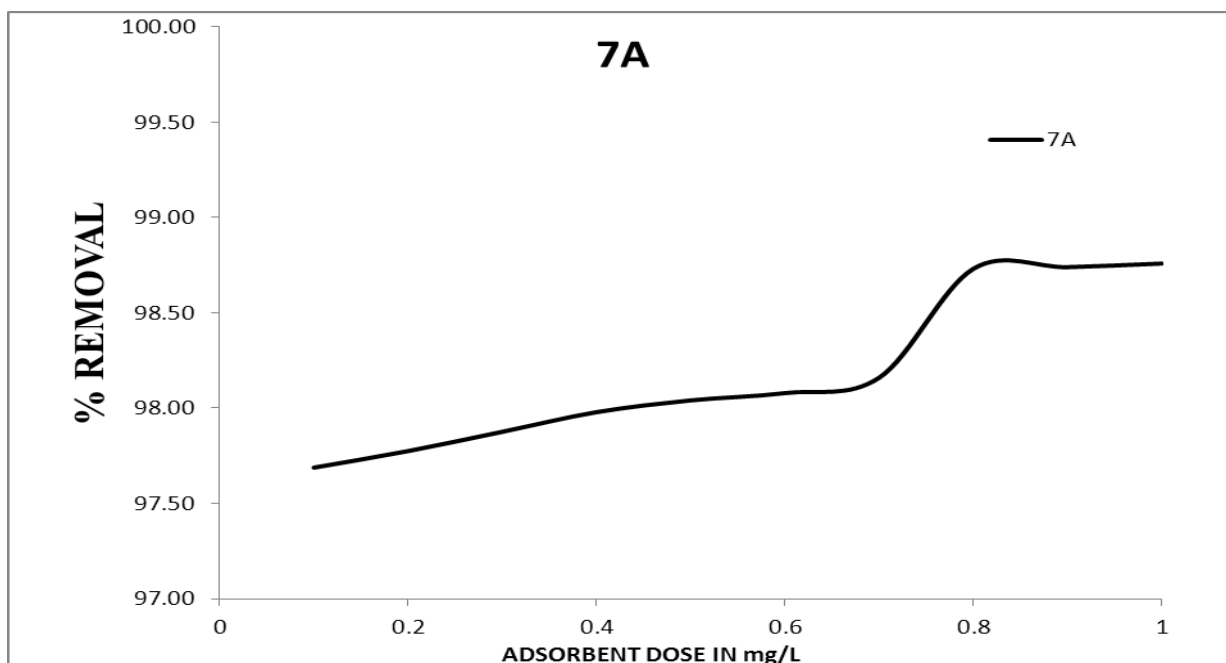


Figure 4 Effect of adsorbent dose of chromium (VI) removal. Conditions: initial Cr(VI) concentration 100 mgL^{-1} , temperature 25°C , pH 7 and contact time 1hr

3.2.2. Effect of contact times

The removal of Cr (VI) was studied at initial Cr (VI) concentration of 100 mg/L at different contact time keeping all other parameters constant. The result is shown in the figure-5. From the figure it is clear that with increase in contact time the percentage removal of Cr (VI) gradually increases and was maximum with a removal percentage of 98% at 60 minutes. This initial increase is due to ion exchange with surface hydroxyl ions of the adsorbent. Later, the rate of removal decreases significantly due to the decrease number of adsorption sites. Decreased removal rate, particularly towards the end of the experiment, indicates the possible monolayer formation of Cr (VI) ion on the outer surface. The equilibrium time for removal process is 60 min.

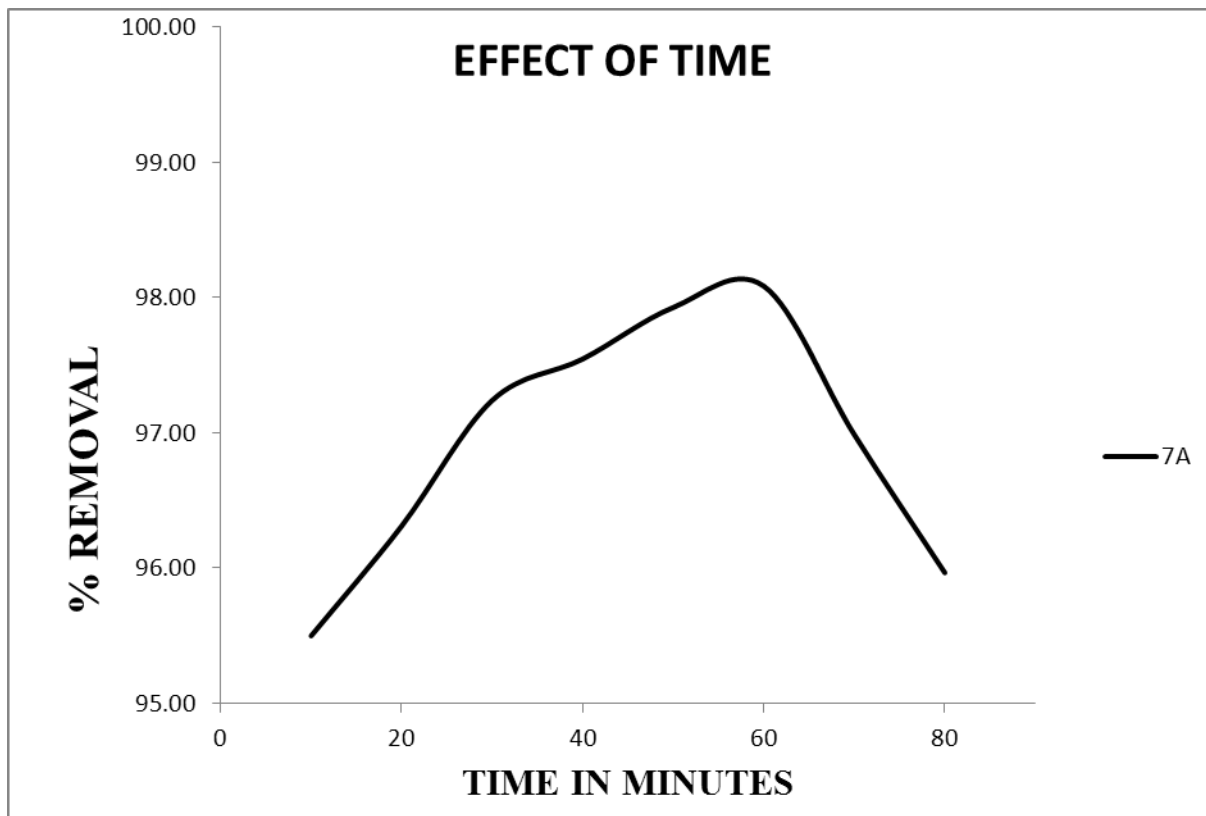


Figure 5 Effect of contact time on Cr (VI) removal. Conditions: adsorbent dose 0.8 gmL^{-1} , initial chromium concentration 100 mgL^{-1} , temperature 25°C , pH 7

3.2.3 Adsorption Kinetics

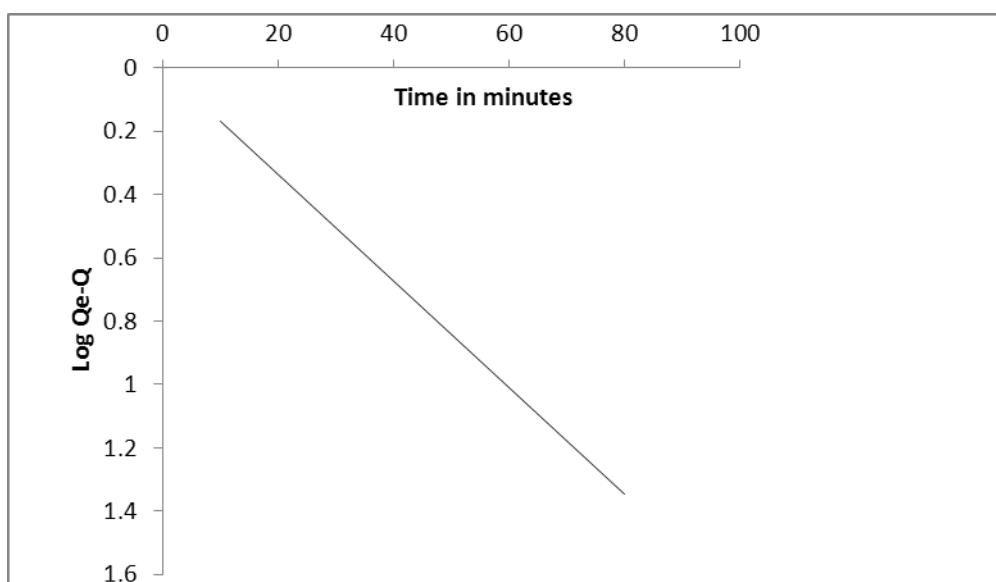


Figure 6 Adsorption kinetics, time vs. $\log (q_e - q)$ with initial fluoride concentration of 100 mg/L

Adsorption of chromium (VI) ion was rapid for the first 30 minutes and its rate slowed down as the equilibrium approached. The rate constant K_{ad} for sorption of chromium (VI) was studied by Lagergren rate equation (Das et.al.2005; sujana et al.1998) for initial concentration of 100 mg/L. These data were analysed using kinetic equations, viz. pseudo-first-order (Eq.1) and pseudo-second-order (Eq.2) given below:

$$\log(q_e - q) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_e and q_t are the amount of chromium adsorbed in mg/g at equilibrium and any time t respectively, k_1 (expressed as the inverse of time) is the rate constant of pseudo-first order adsorption reaction. k_2 is the rate constant for the pseudo-second-order adsorption reaction (given in units of g/mg/min). From the $R^2 = 0.999345$, it is indicated that the removal process follows pseudo-first order kinetics.

3.2.4. Effect of pH

The effect of pH on chromium removal was studied in the range of 1.0 to 14.0 and the results are shown in figure.-7 at a contact time of 1 h, temperature 25°C and adsorbent concentration 0.8 g/L. From the figure-7 it is found that as the pH increases from 1 to 8, the percentage removal gradually increases from 95.70 % to a maximum of 98% at then it gradually decreases with increase in pH from 8 to 14 due to ion exchange. After pH 8, the percentage removal goes on decreasing. due to high OH⁻ ion concentration, which reverse the removal process .This process occurs due to competition of OH⁻ ion with chromate ions . At higher pH, almost no removal will occur due to same reason.

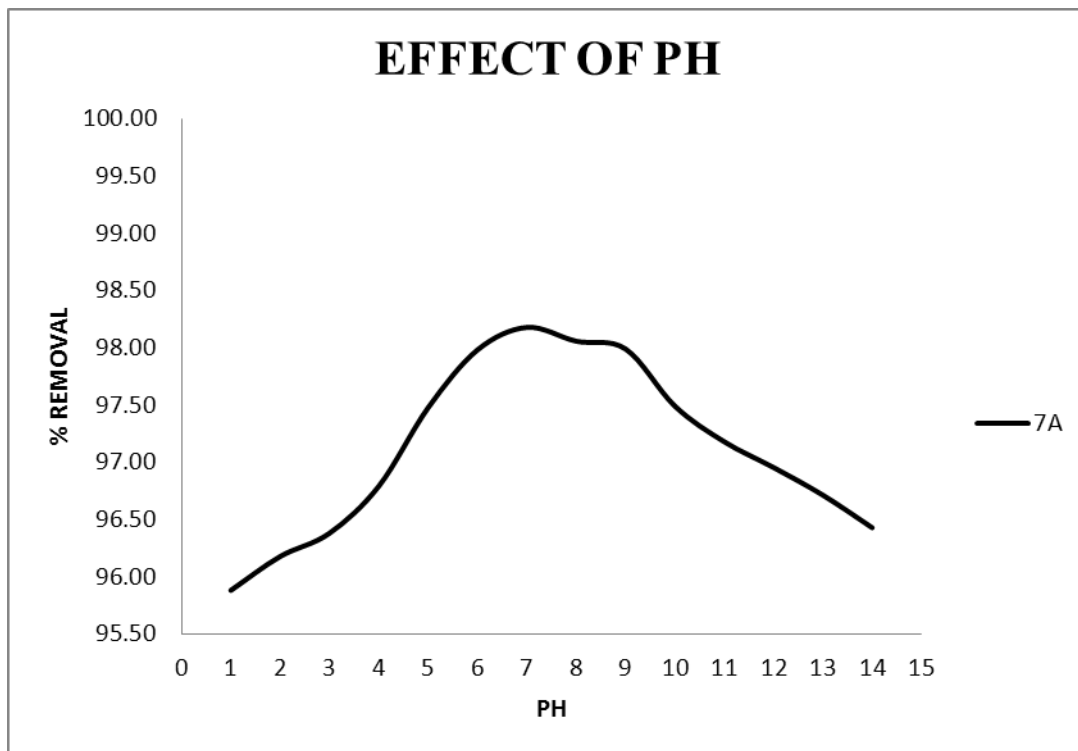


Figure 7 Effect of solution pH on chromium (VI) removal. Conditions: adsorbent dose 0.8 gmL^{-1} , initial chromium concentration 100 mgL^{-1} temperature 25°C and contact time 1hr.

3.2.5 Effect of Temperature

The effect of temperature on the adsorption of Cr (VI) with initial chromium concentration of 100 mg/L was studied using the optimum adsorbent dose (0.8 gm/100 mg/L). The result is shown in the figure-10. With the increase in temperature from 25 to 100°C the percentage removal of Cr (VI) gradually increases to a maximum of 97.50% at a temperature of 40°C and then it gradually decreases. The initial increase and then decrease shows that the process is exothermic in nature.

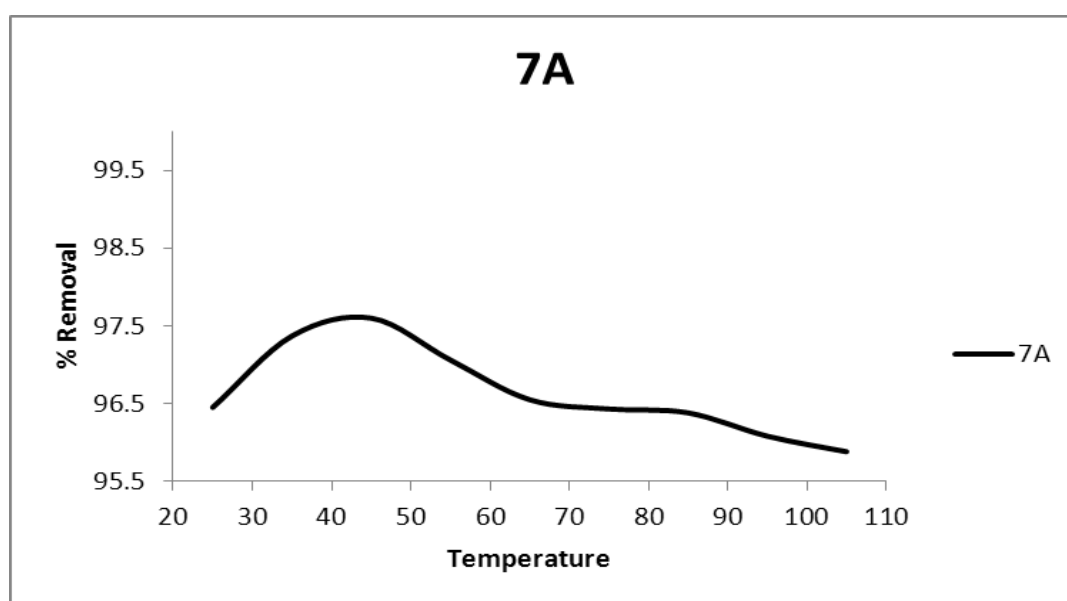


Figure 8 Effect of temperature on chromium removal. Conditions: initial Cr (VI) concentration 100 mgL^{-1} pH 7, adsorbent dose 0.8 gmL^{-1} and contact time 1hr

3.2.6 Isotherm study

To estimate adsorption capacity, the equilibrium data were fitted to the well-known Langmuir and Freundlich isotherm model. The linearized form of the Langmuir (Eq. 3) and Freundlich isotherm (Eq. 4) are given below.

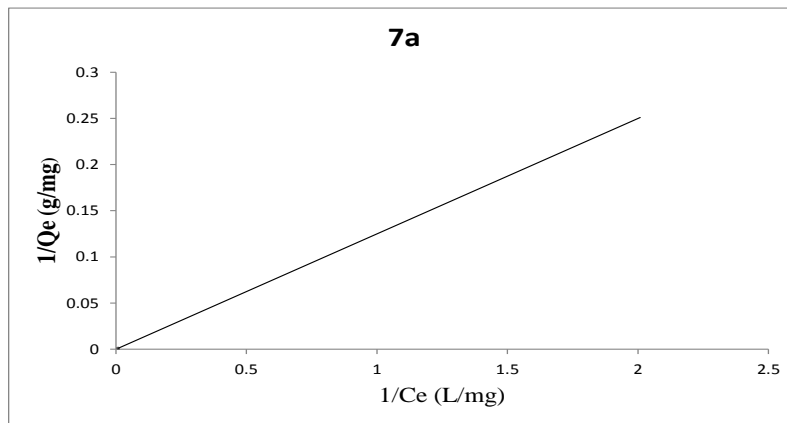
$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3)$$

Freundlich isotherm equation is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where C_e is equilibrium concentration (mgL^{-1}), q_e is the amount adsorbed at equilibrium (mgg^{-1}), Q_o is sorption capacity for Langmuir isotherms and 'b' is an energy term which varies as a function of surface coverage strictly due to variations in the heat of adsorption $1/n$ and K_F are isotherm constants for Freundlich plots. The results indicate that the chromium (VI) adsorption data fitted Langmuir isotherm well and the related correlation coefficient $R^2=0.999672$

Figure 9 Langmuir isotherm plot



| slope | constant | Qo | b | r | r ² |
|-------|----------|----------|---------|----------|----------------|
| 8 | 3.1234 | 0.320164 | 0.04002 | 0.999672 | 0.999345 |

CHAPTER- 4

CONCLUSION

4.1: Conclusion

From the work represented in the studies of chromium adsorption, few important observations are made. The material was found to be poorly crystalline as evident from the XRD data. The BET surface area of the hybrid material was found to be 198.42 m²/gm. The removal efficiency of chromium (VI) by using these materials are conducted by varying the variable parameters like contact time, pH, amount of adsorbent, and temperature to know the optimum condition. The novel material was found to have a maximum efficiency for the removal of chromium (VI) with 95 to 98 % at pH range of 6 to 8, adsorbent dose of 0.8 gm/L, time 60 minutes and temperature of 25-30°C. The exothermic nature of the process is ascertained from the thermodynamic parameters. From all the results it may be concluded that the material is suitable to act as an adsorbent for the removal of Cr- VI. However to make the material useable, further studies are required which are going on.

4.2: Future work

- ✓ *To go for the detailed characterization of the synthesized material*
- ✓ *To study the validity of different isotherm models.*
- ✓ *Practical application of the material.*
- ✓ *Formulating a working model which can be implemented in field studies incorporating all the data.*
- ✓ *To remove all the oxidation states of chromium.*
- ✓ *To study the removal of other heavy metal*
- ✓ *Calculating or estimating the cost in implementing this technique in the removal process*

5. References:

1. Rasheed M.A.Q. Jamhour, Department of Applied and Basic Science, Tafila Applied university college, Jordan New Inorganic Ion-exchange Material for the Selective Removal of Fluoride From potable Water using Ion-Selective electrode, American journal of Environmental Science1(1): 1-4, 2005, ISSN 1553-345X © Science Publications, 2005
2. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Chromium. U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1998.
3. SAIC. PM/Toxics Integration: Addressing Co-Control Benefits. Submitted to U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. 1998.
4. U.S. Environmental Protection Agency. Toxicological Review of Trivalent Chromium. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1998.
5. U.S. Environmental Protection Agency. Toxicological Review of Hexavalent Chromium. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1998.
6. World Health Organization. Chromium. Environmental Health Criteria 61. Geneva, Switzerland. 1988.
7. U.S. Department of Health and Human Services. Registry of Toxic Effects of Chemical Substances (RTECS, online database). National Toxicology Information Program, National Library of Medicine, Bethesda, MD. 1993.
8. U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Chromium VI. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1999.
9. U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Chromium III. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1999.
10. Occupational Safety and Health Administration (OSHA). Occupational Safety and Health Standards, Toxic and Hazardous Substances. Code of Federal Regulations. 29 CFR 1910.1000. 1998.
11. American Conference of Governmental Industrial Hygienists (ACGIH). 1999 TLVs and BEIs. Threshold Limit Values for Chemical Substances and Physical Agents, Biological Exposure Indices. Cincinnati, OH. 1999.

12. . WHO: *Guidelines for drinking water quality, second edition, Volume 2, Health criteria and other supporting information, Geneva, World Health Organization (1984).*
13. *National Institute for Occupational Safety and Health (NIOSH). Pocket Guide to Chemical Hazards. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention. Cincinnati, OH. 1997.*
14. *A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, English Language Book Society and Longmans Green Publishers, London (2000).*
15. *S. Verbych, M. Bryk, A. Alpatova and G. Chornokur, Ground water treatment by enhanced ultrafiltration, Desalination 179 (2005), pp. 237–244*
16. *T. Mohammadi, A. Razmi and M. Sadrzadeh, Effect of operating parameters on Pb²⁺ separation from wastewater using electrodialysis, Desalination 167 (2004), pp. 379–385.*
17. *A.K. De and P. Chakraborty, Synthetic inorganic ion exchangers XXI. Electrochromatographic separations of metal ions on lanthanum antimonite-impregnated paper, Electrophoresis 2 (5–6) (2005), pp. 330–332.*
18. *F. Pearce, Bangladesh's arsenic poisoning: who is to blame? The UNESCO Courier. (2008).*
19. *M. Islam, R.K. Patel, Evaluation of Removal efficiency of fluoride from aqueous solution using quick lime, J.Hazard. Mater. 143 (2007) 303-310.*
20. *B. Salamatinia, A.H. Kamaruddin, A.Z. Abdullah, Modeling of the continuous copper and zinc removal by sorption onto sodium hydroxide-modified oil palm frond in a fixed-bed column, Chem. Eng. J. 145 (2008) 259-266.*
21. *R. Apiratikul, P. Pavasant, Batch and column studies of biosorption of heavy metals by caulerpa lentillifera, Bioresource Technol. 99 (2008) 2766-2777.*
22. *M Ghorbani, H Esfandian, N Taghipour ,Application of polyaniline and polypyrrole composites for paper mill wastewater treatment, Desalination, (2010) – Elsevier*
23. *MR Samani, SM Borghei, A Olad ,Removal of Chromium from Aqueous Solution Using Polyaniline-Poly Ethylene Glycol Composite Journal of Hazardous ..., (2010) – Elsevier*
24. *L Shi, X Zhang Removal of Chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron Water research, (2010)- Elsevier*