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A Comparative Study of Modified and Unmodified Algae (*Pediastrum boryanum*) for Removal of Lead, Cadmium and Copper in Contaminated Water

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Additional information is available at the end of the chapter

Abstract

The presence of heavy metals in water is of concern due to the risk toxicity. Thus there is need for their removal for the safety of consumers. Methods applied for removal of heavy metals include adsorption, membrane filtration and co-precipitation. However, studies have revealed adsorption is highly effective technique. Most adsorbents are expensive or require extensive processing before use and hence need to explore for possible sources of inexpensive adsorbents. This research work investigated the use an algal biomass (*pediastrum boryanum*) as an adsorbent for removal of Lead, Cadmium and Copper in waste water in its raw and modified forms. The samples were characterized with FTIR and was confirmed a successful modification with tetramethylethlynedia-mine (TMEDA). Sorption parameters were optimized and the material was finally applied on real water samples. It was found that the sorption was best at lower pH values (4.2-6.8). Sorption kinetics was very high as more that 90% of the metals were removed from the solution within 30 minutes. The adsorption of copper fitted into the Langmuir adsorption isotherm indicating a monolayer binding mechanism. Cadmium and lead fitted best the Freundlich adsorption mechanism. Sorption of lead and cadmium was of pseudo-second order kinetics, confirming a multisite interaction whereas copper was pseudo-first order indicating a single site adsorption. The adsorption capacity did not improve upon modification but the stability of the material was improved and secondary pollution of leaching colour was alleviated. This implies that the modified material is suitable for application on the removal of metals from water.

1. Introduction

The release of wastewater into the environment poses a great problem worldwide due to enhancement and mobilization of toxic trace metals due to solubilization [1, 2]. This is enabled by the presence of functional groups capable of forming metal complexes with the metals [3–5]. Unlike organic pollutants which are susceptible to degradation, metal ions remain in the environment available to cause pollution [6]. This makes the presence of heavy metal in the environment a major concern due to their toxicity to various life forms. Even when most metals in the environment are in trace levels or masked by matrices, the presence of wastewater problem exacerbates the toxic nature of heavy metals. The net result is scarcity and insufficient supply of safe water, hence the quality of life. As such, methods for the removal of such contaminants need to be explored to mitigate the effects of metal pollution.

Conventional methods for the removal of metals such as precipitation, coagulation, evaporation and membrane filtration are expensive and not effective when the concentrations are in trace levels ranging from 1 mg l^{-1} to 20 mg l^{-1} [7, 8]. Due o such limitations, a need therefore arises for the development of cost-effective methods to remove heavy metals in waste purification processes. The presence of functional groups within the structure of sorbents from plant origin has received increasing attention for the removal and recovery of heavy metals in aqueous media [9]. However, they have been found to leach organic matter in the water during the treatment process. This has resulted in treating the sorbents first, before applying them for the water treatment activity.

A solution to this was achieved by modification of the raw biomaterial using tetramethylethylenediamine [10]. This work reports on the modification of algae and its subsequent application for the removal of some selected heavy metals through a biosorption process. The effects of modification on secondary pollution and adsorption parameters were also investigated. This was to obtain the information that will contribute to determining adsorption capacity, sorption mechanism and kinetics with a view to apply the material at a point of use. This was intended to contribute to knowledge for social-economic development, to address the availability of clean water to the rural communities who source their water from rivers, dams, boreholes and shallow wells whose water quality is not known. The adsorbent is intended to be applied for purification of water by removal of heavy metals for domestic consumption at a small scale with a view to offer a cheap solution to metal-related toxicity. This is a simple and sustainable water management approach.

Methods applied for separation and preconcentration techniques include adsorption, membrane filtration, cloud-point extraction, solvent extraction and co-precipitation [11]. Studies by Marshall [12] have revealed adsorption by the use of activated carbon to be highly effective for

the removal of heavy metals from wastewaters. Despite its extensive use in water and wastewater treatment industries, activated carbon remains an expensive material [13]. In view of this, the need for safe and economical methods for the elimination of heavy metals from polluted and contaminated water has to be explored.

This has necessitated researchers to develop methods to mitigate the effects of heavy metals in water. Low-cost agricultural waste by-products such as sugarcane, bagasse, rice husks, sawdust and coconut husk, oil palm shell, neem bark and maize tassels have been studied and applied for the removal of heavy metals from wastewater. The cost of such materials is an important parameter for comparing the sorbent materials. Such agricultural wastes are abundant, require little processing and therefore have a potential to be applied as low-cost sorbents that are environmentally friendly [14]. But these materials suffered a setback due to leaching of dissolved organic matter in water during the treating process. To overcome such cases of secondary pollution, there is need to explore sorbents for their feasibility for the removal of heavy metals from wastewater. This study investigated the use of algal biomass which is an aquatic plant for the remediation process. Algae does not normally leach colour in the water but only contribute in the water oxidation process and interaction with metals.

Due to those qualities of algae, a solution experienced while using other biosorbents was expected to be solved. The algal biomaterial was modified with tetramethylethylenediamine to form a resin material with suitable functional group to complex with metal ions and remove them from water. The resulting solid material was capable of interacting with metals in water and attracting them to its surface, hence removing them, and was found to be regeneratable and did not leach soluble organic compounds in the treated water.

2. Materials and methods

2.1. Research design

The focus of our study was to synthesize a sorbent by anchoring functional groups capable of interacting with metal ions and removing them from aqueous media. The protocol in preparation was to use non-toxic and environmentally friendly materials. The study was carried out in several parts. This comprised of sampling, synthesis, characterization of the modified material, optimization of removal parameters and then its subsequent application for the removal of fluorides from both synthetic and environmental water samples.

2.2. Chemicals and reagents

All the solutions were prepared in double-distilled water and the reagents were of analytical grade. Metal standard stock solution of 1000 mg/L was prepared by dissolving 1.00 g of the respective metal in one litre of 0.1 M sodium acetate. It was from this solution that subsequent working solutions were prepared from. Separate solutions of 0.01 M nitric acid and 0.01 M sodium hydroxide were prepared and used to adjust the pH of the working solutions to the

desired value. The above chemicals and tetramethylethylenediamine (TMEDA) were supplied by Kobian Kenya Ltd. which is Sigma-Aldrich's outlet in Kenya.

2.3. Instrumentation

The modified and unmodified algae were characterized using a Fourier transform infrared (FTIR) spectrometer (FTIR-8400, Shimadzu Tokyo, Japan) to establish the functional groups present. The concentration of metal pollutants in the water samples was determined using atomic absorption spectroscopy (AAS) (Buck, model 210 VGP) set at the optimum operating conditions and wavelength of each respective metal. All pH measurements were done using a calibrated (Jenway 3505) pH metre equipped with a standard calomel electrode (SCE). A constant shaker model CFC 3018 with a water bath was used to shake the samples at the required shaking speeds.

2.4. Sampling and pretreatment of the algae

Samples of the algae *Pediastrum boryanum* were collected in Molo, Nakuru County, Kenya. The algal material was cleaned using tap water, dried, ground into powder and then stored in clean plastic bottles. The dried powdered algae were used as a sorbent and for the modification process.

2.5. Modification of the dried algae

The algae were modified by anchoring tetramethylethylenediamine onto its chemical structure to improve its chelating property [15]. The modification procedure involved chlorination of the biomaterial first and then condensing the resultant with the amino compound. A sample of the algae (30 g) was chlorinated using thionyl chloride (SOCl$_2$) 100 ml, and the mixture heated under reflux at a temperature of 80°C for 4 h with continuous stirring. The chlorinated biomaterial was then washed with 100 ml of distilled water. The solution was filtered using Whatman No. 1 filter paper and dried in an oven set at 60°C. The dry chlorinated sample was then treated with 25.0 ml of tetramethylethylenediamine and refluxed for 3 h to anchor the tetramethylethylenediamine structure into the algal biomass.

2.6. Batch sorption experiments

Sorption studies were carried out on a mechanical reciprocating shaker (SKZ-1 NO. 1007827, India) using plastic screw cap bottles. Batch experiments were conducted to investigate the effects of pH, adsorbent dosage, adsorbate concentration and contact time on the adsorption of Pb^{2+}, Cd^{2+} and Cu^{2+} on the modified and unmodified algae. The pH of the model test solutions containing a known concentration of the metal ion was adjusted to values between 3 and 7. A known weight of the sorbent (0.03 g) was added to each of the solutions and then allowed to equilibrate giving sufficient time for sorption. The resulting mixture was filtered through Whatman No. 42 filter paper, and the metal ions in the filtrate were determined by atomic adsorption spectrophotometry (UNICAM 919).

2.7. Optimization of sorption parameters

2.7.1. Effect of pH on sorption

2.7.1.1. Calibration of the pH metre

The pH metre was calibrated using special buffer tablets for pH 3.0, 5.0, 7.0 and 9.0. Each tablet was dissolved separately in 100 ml of distilled water and then used. The electrode of the pH metre was conditioned with saturated potassium chloride overnight to wet the membrane and make it more sensitive. It was later calibrated with the buffer solutions. This procedure was undertaken before any pH measurements were made [16].

2.7.1.2. Effect of pH of adsorption

The effect of pH of the adsorbate on the adsorption of the metal ions by both modified and unmodified algae was investigated by mixing 0.2 g of the sorbent material with 50 ml of 10 ppm model solution buffered at different pH environments. The pH was brought to the desired values (3–10) by adding drops either 0.01 M nitric acid or 0.01 M sodium hydroxide. The resulting mixture was allowed to equilibrate for 120 min. The resulting mixture was then filtered through Whatman No. 1 and the concentration of the metal ions in the filtrate determined by atomic absorption spectroscopy.

2.7.2. Effect of contact time on sorption

The effect of contact time on sorption of lead (II), cadmium (II) and copper (II) by modified and unmodified algae was done by taking a sample, 0.2 g of the sorbent (modified and unmodified algae) into the plastic bottles and 50 ml of the adsorbate of concentration 10 ppm added. The mixture was buffered to the optimum pH value for each metal and agitated at predetermined time intervals of 2–150 min. The samples were then removed from the shaker and the solutions filtered, and the metal ion concentration in the filtrate was determined.

2.7.3. Effect of initial metal ion concentration on sorption

The extent to which metal ions are adsorbed as a function of the initial ion concentration was investigated by mixing 0.2 g of finely ground modified and unmodified algae separately with 50 ml of varying concentrations of the test solutions, buffered at the optimal pH value for each respective metal. The respective mixtures were allowed to equilibrate for a sufficient duration and then filtered and the concentration of the metal ions in the filtrate was determined.

2.7.4. Effect of sorbent dose on percentage metal removal

The effect of sorbent dose was investigated by agitating 50 ml (10 μg ml^{-1}) of the adsorbate solutions of lead (II), cadmium (II) and copper (II) with various dosages of the sorbents. 0.1, 0.5, 1.0, 1.5 and 2.0 g of modified and unmodified algae were used. The solutions of the adsorbate were buffered to the optimum pH of each respective metal ion under investigation.

The solutions were for 2 h with the temperature set at 25°C. The resulting mixtures were filtered and the concentration of the residual metal ions determined.

2.7.5. Determination of adsorption capacity of modified and unmodified algae

The adsorption capacity was determined by mixing 0.2 g of finely ground sorbent material with 50 ml of varying concentrations of the test metal solution (concentrations 10–250 ppm) buffered at the optimum pH for each respective metal. The mixtures were agitated for 30 min and then filtered, and the concentrations of metal ions were determined.

2.7.6. Adsorption models

The experimental data on metal sorption were also analyzed using adsorption models so as to establish the sorption kinetics and mechanism.

2.7.7. The kinetics of adsorption

To determine the necessary time, different solutions of for adsorption lead (II), cadmium (II) and copper (II) 20 ml containing 10 µg ml^{-1} of the adsorbate were introduced in different sets of plastic bottles containing 0.2 g of the adsorbent, and the pH sets an optimal value for each metal. The mixtures were then introduced in the shaker temperature of 25°C and equilibrated at different time intervals of 2, 5, 10, 20, 30, 60, 90 and 120 min. They were then filtered, and the filtrate was analyzed for adsorbate concentration. The data obtained was treated with Lagergren's [17] pseudo-first-order and Ho et al.'s [18] pseudo-second-order equations to determine molecularity of the adsorption.

The Lagergren first-order and Ho's second-order kinetic models are expressed as shown in equations 5.1 and 5.2, respectively:

$$\ln(C_o - C_t) = Kt + A \tag{1}$$

$$\frac{1}{q_e} = Kt + A \tag{2}$$

where C_o is the adsorption per unit mass of adsorbent at equilibrium, K is the adsorption rate constant, A is intercept and C_t is the concentration at time t.

2.7.8. Adsorption isotherms

The experimental data for the effect of metal ion concentration obtained was treated with the Freundlich and Langmuir isotherm models to obtain the adsorption mechanism.

2.7.8.1. Langmuir isotherm

For molecules in contact with a solid surface at a fixed temperature, the Langmuir isotherm, developed by Irving Langmuir in 1918, describes the partitioning between gas phase and adsorbed species as a function of applied pressure [19]. Langmuir adsorption isotherm is the widely used isotherm for modeling of adsorption data [20]. Langmuir considered adsorption of an ideal gas on an ideal surface. It is based on the assumption that adsorption can only occur at fixed sites and only hold on one adsorbate molecule (monolayer). All sites are equivalent with no interaction between adsorbed molecules, and the sites are independent as reported by Langmuir [19]. The Langmuir equation was derived from Gibbs approach which takes the form shown in equation 5.3 [19, 21]:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{3}$$

where C_e is the equilibrium concentration, K_L is the equilibrium constant, q_e is the metal concentration on the sorbent phase at equilibrium in mg g^{-1} and a_L is a Langmuir constant. Eq. (3) can be linearized and often referred to as linearized Langmuir equation as shown in equation 5.4:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \tag{4}$$

The experimental data was applied on the equation above, and a plot of $\frac{C_e}{q_e}$ against C_e gave a linear regression. This indicates that the adsorption prescribes to the Langmuir model, where the gradient $\left(\frac{a_L}{K_L}\right)$ is the theoretical saturation capacity (units in mg g^{-1}) and the intercept is $\frac{1}{K_L}$ [19, 22, 23].

2.7.8.2. Freundlich isotherm

Freundlich isotherm is an empirical equation based on heterogeneous surface [23]. This is a multi-site adsorption isotherm for heterogeneous surfaces and has a general form as shown in Eq. (5):

$$q_e = K_F C_e^{bF} \tag{5}$$

The equation was linearized by taking logarithms and then applied to determine if the systems are heterogeneous with highly interactive species [24]:

$$\ln q_e = \ln K_F + b_F \ln C_e \tag{6}$$

where q_e and C_e have the same meaning as in Eq. (3); the numerical value of K_F presents adsorption capacity, and b_F indicates the energetic heterogeneity of adsorption sites [24]. From the data, if a plot of **ln** q_e versus **ln** C_e gave a straight line, it indicates that the adsorption prescribes to the Freundlich model.

3. Results and discussion

3.1. Introduction

The algal material was modified with an amino compound to improve its thermal stability [9]. The resulting product obtained was a water-insoluble solid material. The raw and the modified products were characterized using FTIR to obtain the functional groups present; sorption parameters were established and then used for adsorption experiments in both synthetic solutions and real water samples.

3.2. FTIR analysis of modified and unmodified algae

The modified and unmodified materials were characterized with FTIR, and the resulting spectra are presented in **Figure 1**.
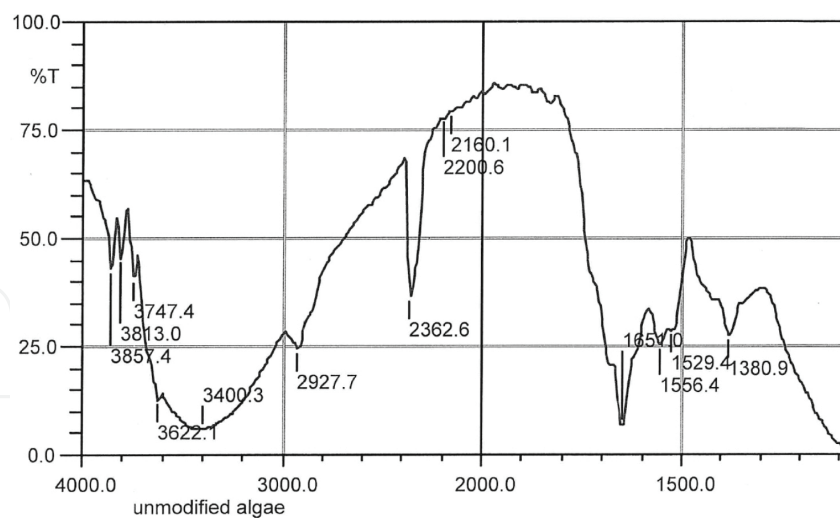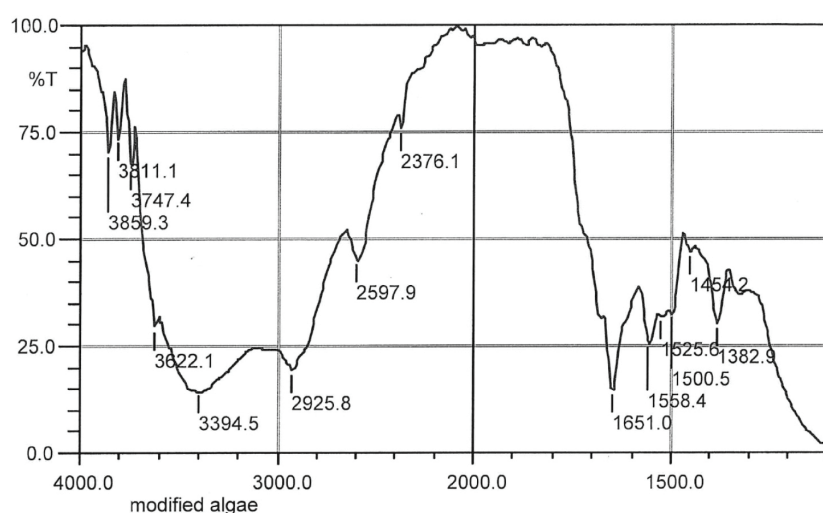

Figure 1. FTIR spectrum of unmodified algae.

The results show the presence of many functional groups capable of metal sorption. The broad and strong band at 3400.3 cm^{-1} could be attributed to either —OH or —NH group [25]. The band at 2927.72 cm^{-1} was assigned to C—H stretches, while the band at 1651.0 cm^{-1} was assigned to stretching —OH, C=O or N=C [25]. The band at 1380.9 cm^{-1} confirms the presence of an amide

group of an amide or sulphamide group [26, 27]. The material was modified with tetramethy-lethylenediamine, and results obtained are presented in **Figure 2**.

Upon modification, the band at 3400.3 cm^{-1} that was attributed to the ─NH of an amide shifts to a lower value of 3394.5 cm^{-1}. The intensity of the band also decreases. This can be attributed to suppression influenced by the carbon atoms from anchored tetramethylethylenediamine functional groups. Similar observations were reported by Schluter [28] as he studied the treatment of poly(1.1.1)propellane with lithium organic initiators and then investigated its rigidity. Mwangi and Ngila [29] also recorded the same observation when studying the removal of heavy metals from contaminated water using ethylenediamine-modified green seaweed. New bands are also seen to appear at 1454.2 cm^{-1} and 2597 cm^{-1}. The band at 1454.2 cm^{-1} can be attributed to an NO$_2$ group and that at 2597 cm^{-1} can be attributed to an additional ─OH groups from a phenolic compound. Both the parent and the modified material were applied for sorption experiments.


Figure 2. FTIR spectrum of modified algae.

3.3. Effect of pH on sorption

The adsorption of metal ions into the biosorbent is dependent on pH of the solution. pH affects the biosorbent surface charge and degree of ionization. The sorbent also has nitrogen atoms (with a lone pair of electrons) which can be influenced by the pH of the medium. The effect of pH on sorption of lead, cadmium and copper ions are represented in **Figure 3**.

The pH of the solution influences the chemistry of the metal binding sites and the behaviour of the metal itself in solution. The results show that the maximum adsorption for lead was found to occur at a pH of 3.5 by the unmodified sorbent and at a pH of 7.0 for this same metal by the modified adsorbent. There was an increase in the amount adsorbed as the pH increased from 3.5 to 7.0. Beyond this, as the pH increases, the amount adsorbed decreases. Similar results have been reported for other biosorbents [29]. Singh and co-workers (2006) also reported that

the highest percentage of lead (II) ions was adsorbed by phosphatic clay at a pH of 5.0 [30]. Similar results were reported by Matheickal et al. [26] when they studied the biosorption of lead by marine alga *Ecklonia radiata*. Benhima et al. [31] observed that there was an increase in lead (II) ion uptake by inert organic matter (IOM) as the pH increased from 2.0 to 6.0. This is in agreement with the observed results for lead (II) ions.
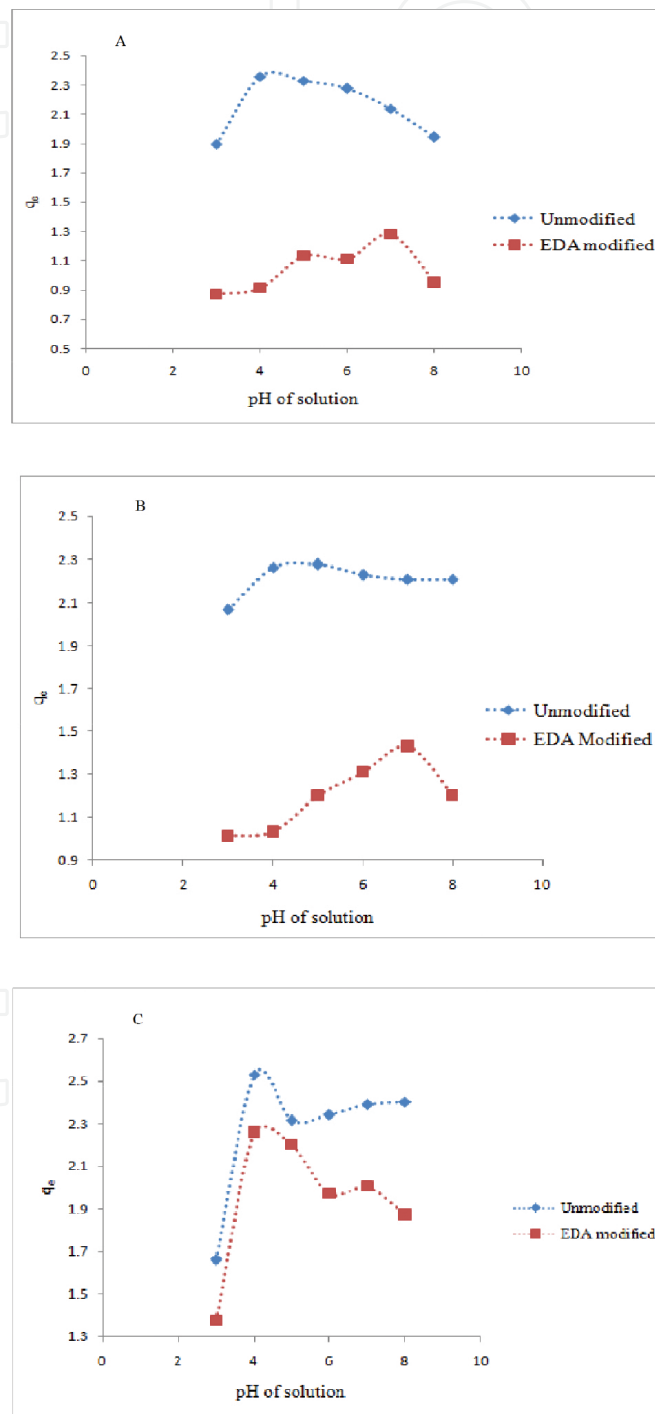
Figure 3. Effect of pH on adsorption of lead, cadmium and copper ions—A, B and C, respectively.

At low pH, the biomass surface would be completely covered with hydrogen ions. H^+ lead (II) ions cannot compete effectively for the adsorption sites. This can be attributed to the fact that protons are strongly competing due to their high concentration. Godhane et al. [32] reported that the minimal sorption obtained at low pH may be due to high mobility of protons and partly due to the fact that the solution pH influences the sorbent surface charge.

The unmodified biosorbent has a maximum adsorption for cadmium at a pH of 5.2, while the modified form was at a pH of 6.7. Similar results were obtained by Singh and co-workers [30] when they investigated the adsorption of cadmium using phosphatic clay. They observed maximum adsorption at a pH of 5.4.

Copper unlike the other metals has a maximum adsorption at a pH of 4.2 for both the modified and unmodified sorbents. This can be explained by the small size of copper giving it a high polarizing power on electrons of the adsorbent [33].

The sorbent has nitrogen atoms (with alone pair of electrons) as well as other functional groups, all of which may be influenced by pH. At low pH, the adsorbent is positively charged because the pH is lower than the isoelectric point or point of zero charge (PZC), i.e. pH < PZC. At such low pH range, adsorption is poor due to the charge on the adsorbent [34]. At high pH (pH > PZC), the adsorbent is negatively charged contributing to the high adsorption [26]. This arises from the fact that when the metal is in solution, it is positively charged and will be attracted to the surface of the negatively charged adsorbent at pH > PZC favouring adsorption. At pH > 7, there is metal hydrolysis leading to precipitation due to formation of hydroxyl metal ions [35].

3.4. Effect of contact time on sorption

The dependence of the adsorption process on the residence time of the adsorbate at the solid solution interphase was studied using batch sorption experiments for both the modified and unmodified algae. The solutions were set at optimal pH values of each metal, and the results of time-dependent adsorption obtained are shown in **Figure 4**.

It was observed that the general uptake rate was fast as over 90% of the adsorption which took place within the first 30 min for all the three metals after which a steady adsorption rate was realized (**Figure 3**). Keskinkan et al. [36] reported similar findings while studying the biosorption of lead (II) ions using aquatic *Ceratophyllum demersum*. Also, Yang and Volesky [37] made similar observations while studying the biosorption of cadmium (II) ions using dead brown *Sargassum fluitans*. The initial rapid uptake may be due to the physical adsorption or ion exchange at the cell surface and the subsequent slower phase due to the other mechanisms such as complexation, micro-precipitation or saturation at the binding sites [38]. Generally, there was a decrease in adsorption for the modified sorbent with the decrease more pronounced for cadmium (II) ions. Different functional groups with different affinities for the metal ions are usually present on the biomass surface; these are significantly altered by modification. New groups are also introduced which affect the binding ability of the sorbent.

An example of a functional group that was affected is the –NH group which appeared at 3400.3 cm⁻¹ and after modification shifted to a lower value of 3394.5 cm⁻¹.
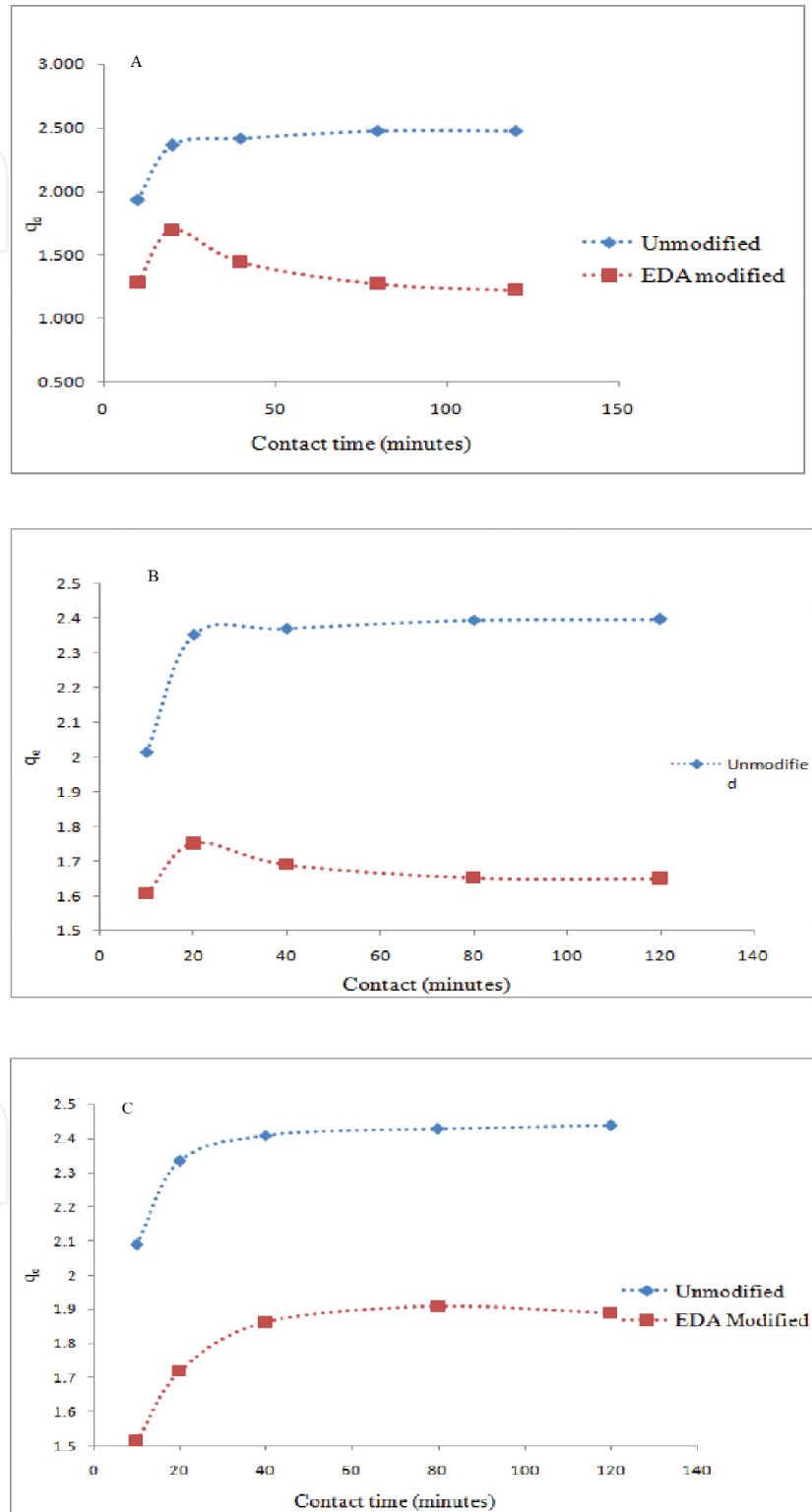

Figure 4. Effect of contact time on sorption of lead, cadmium and copper—A, B and C, respectively.

3.5. Effect of sorbent dosage on sorption

Results presented in **Figure 5** show the effect of varying the mass of the sorbent on the adsorption of the metal ions. The experiment was performed while the solutions were buffered at optimal pH value of each respective metal ion.
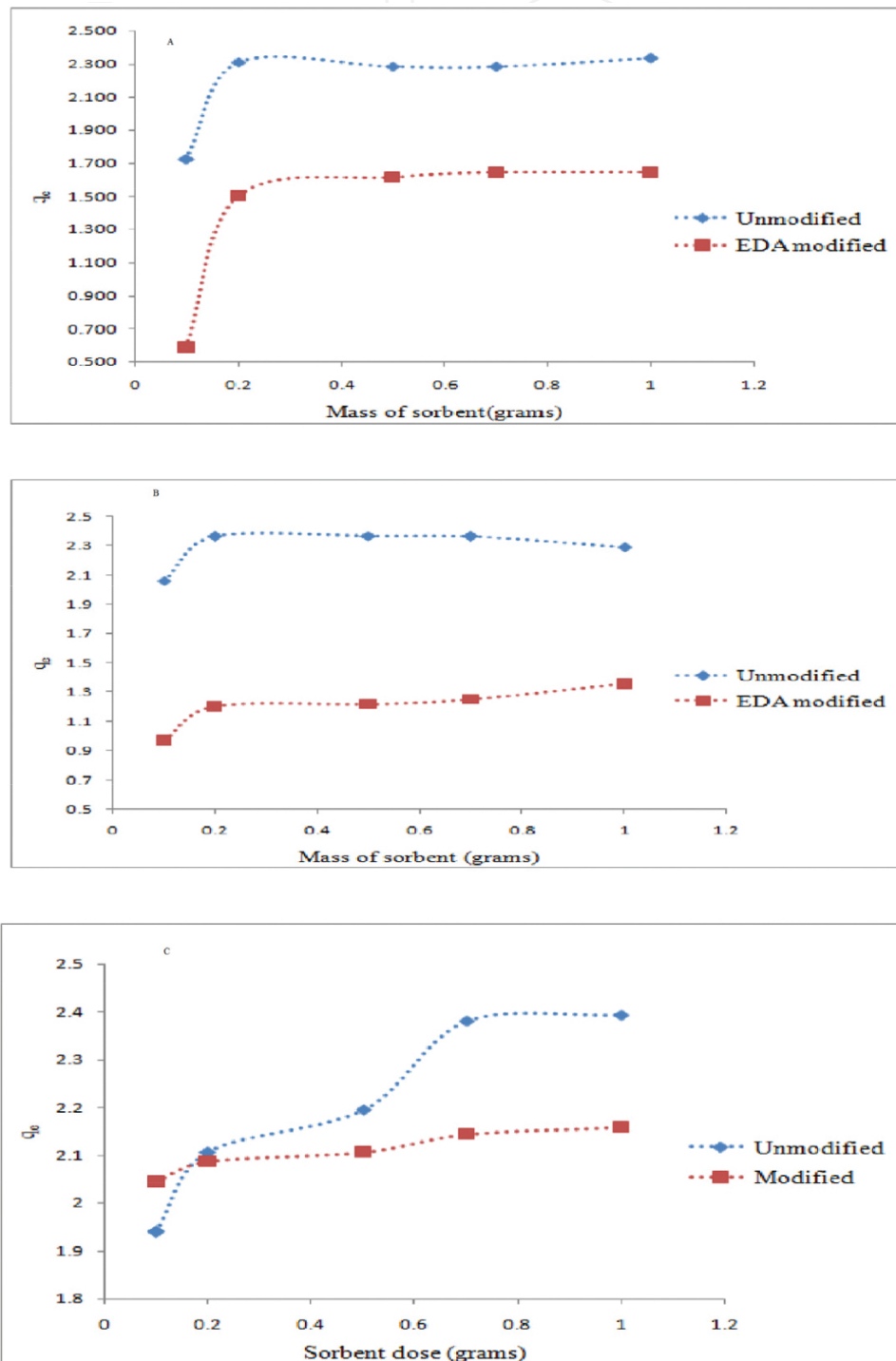
Figure 5. Effect of sorbent dose on sorption of lead, cadmium and copper—A, B and C, respectively.

The general observation is that the amount adsorbed metal ions increased with increase in sorbate dose. This can be attributed to the fact that as the concentration of the adsorbent increases, more adsorption sites are available due to increased surface area. More metal ions can therefore occupy those available active sites [39]. It was also noted that for both the unmodified adsorbates, copper was adsorbed more than both lead and cadmium. This could be attributed to the fact that the affinity to the binding sites is related to the ionic sizes of the respective metals, hence the polarizing power of copper being responsible for the observation. Maximum adsorption by the unmodified sorbate occurred at a mass of about 0.2 g for both lead and cadmium. Mwangi and Ngila [29] reported a similar observation while studying the biosorption of lead and cadmium using green seaweed, *Caulerpa serrulata*. Higher metal ion uptake at low sorbate mass concentrations has been attributed to an increased metal to biosorbent ratio which decreases upon an increase in sorbate mass concentration [40]. The modified sorbate showed maximum adsorption at a mass of 0.7 g for these two metals. For copper, maximum adsorption occurred at a sorbate mass of about 0.7 g for both modified and unmodified algae *Pediastrum boryanum*. A plateau is reached after a certain mass for all the metal ions. The unmodified sorbent material removed more metal ions than the modified material. This decrease in the adsorption capacity could be attributed by the fact that the functional groups in the parent material responsible for binding the metals had higher complexation ability than the anchored group [41]. A similar observation was reported by Drake and co-workers as they studied the sorption of chromium by *Datura inoxia* biomaterial [42].

3.6. Effect of initial ion concentration for determination of adsorption capacity

In order to investigate the adsorption capacity of both modified and unmodified algae, 50 ml solutions of concentrations ranging from 10 µg l^{-1} to 100 µg l^{-1} were added to 0.2 g of the biosorbent. **Figure 5** shows the results that were obtained.

A linear pattern of metal uptake was observed followed by some plateau for all metals. This may be attributed to the saturation of the binding sites as the concentration of the ion increases resulting to a steady state. The saturation is more pronounced at very high concentrations [31]. This is attributed to the fact that concentration is the driving force for metal ions to occupy the available binding sites [38]. It was observed that there was no significant difference in the sorption of copper and cadmium by the parent and modified material (see **Figure 6**).

The experimental data above was fitted into the Langmuir and Freundlich adsorption isotherm represented by equations (3) and (4) in Chapter 3 to determine the adsorption capacity for the metal ions using both modified and unmodified algal materials. **Table 1** is a summary of the results that were obtained.

Table 1 shows that the adsorption for both cadmium and lead fitted well with the Freundlich model, while copper fitted well with the Langmuir model. Similar results were obtained by Ng and co-workers [22] as they studied the adsorption of metals on cross-linked seaweed. This indicates that the adsorption process for lead and cadmium is a multi-site or physical sorption as a result of weak Van der Waals forces.
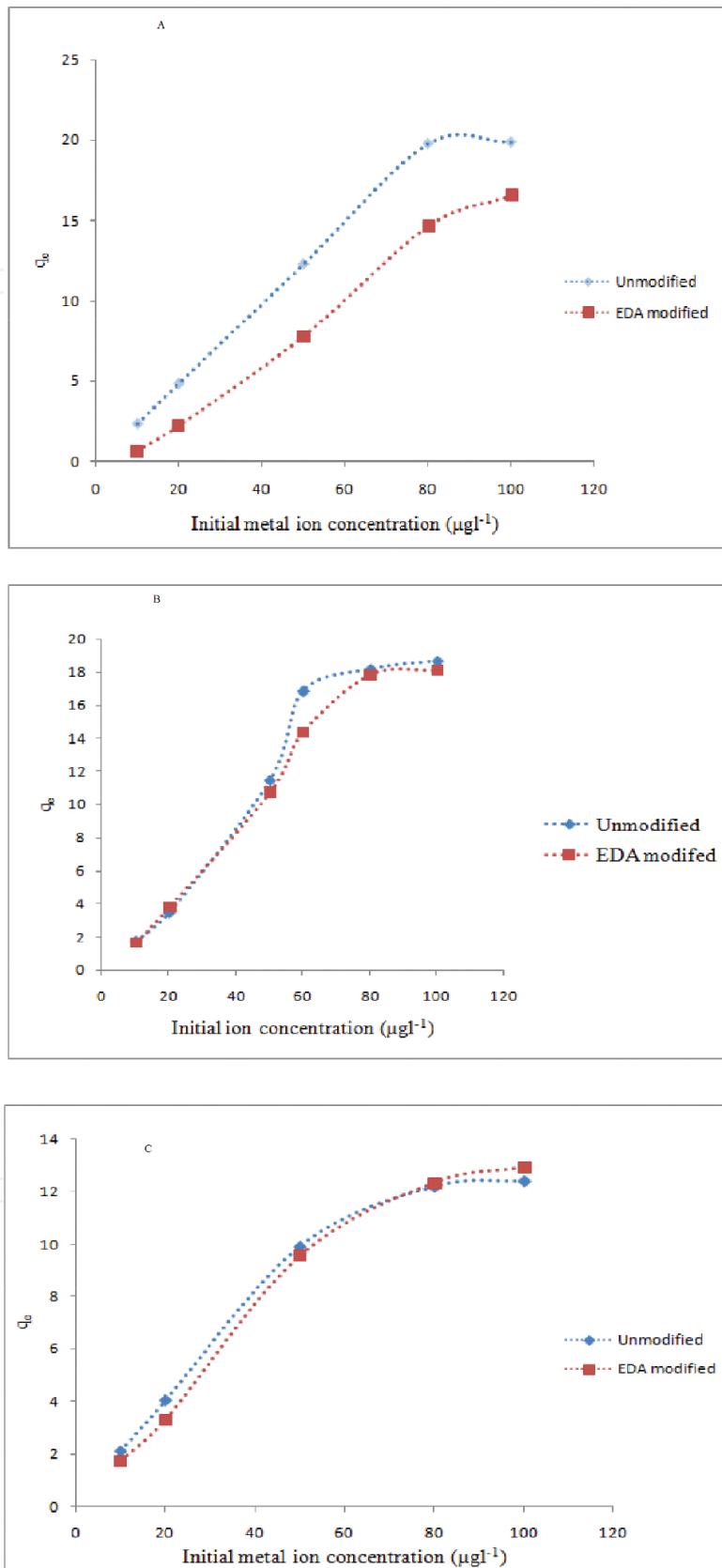
Figure 6. Effect of initial ion concentration on sorption of lead, cadmium and copper ions—A, B and C, respectively.

Metal	Langmuir			Freundlich		Comment
	R^2	Adsorption capacity		R^2	K_F/mg g^{-1}	
Copper						
Unmodified	0.974	0.059		0.605	0.948	Langmuir
Modified	0.512	0.001		0.502	–	Langmuir
Cadmium						
Unmodified	0.043	0.060		0.251	1.137	Freundlich
Modified	0.941	0.276		0.993	2.843	Freundlich
Lead						
Unmodified	0.570	0.021		0.929	0.791	Freundlich
Modified	0.560	0.112		0.906	1.695	Freundlich

Table 1. Results for Langmuir and Freundlich models.

Copper on the other hand fitted well with the Langmuir model with R^2 values of 0.974 for the unmodified and 0.512 for the modified algal material. These values show that the data has a strong correlation and therefore the sorption mechanism can be prescribed to the Langmuir model. The adsorption capacities were found to be 0.059 and 0.001 mg g^{-1} for copper, by the unmodified and modified materials, respectively. Sorption of cadmium and lead prescribed to the Freundlich model with a sorption of 1.137 and 2.843 and 0.791 and 1.695, respectively, by the unmodified and modified adsorbent materials in the same order.

3.7. Kinetics of adsorption of the metal ions

Lagergren's first-order and Ho's second-order kinetics were applied to the data that was obtained [17, 18]. This was used to determine the molecularity of the adsorption and the rate controlling step. A summary of the results that were obtained for all the three metals is shown in **Table 2**.

Metal	Lagergren	Ho	Comment
	R^2	R^2	
Lead			
Modified	0.936	0.954	Pseudo-second order
Unmodified	0.846	0.849	Pseudo-second order
Cadmium			
Modified	0.574	0.584	Pseudo-second order
Unmodified	0.765	0.770	Pseudo-second order
Copper			
Modified	0.512	0.502	Pseudo-first order
Unmodified	0.583	0.573	Pseudo-first order

Table 2. The Lagergren first-order and Ho et al. second-order data.

For all metals the adsorption rates are very fast initially and become almost constant as time increases showing that an equilibrium has been reached.

For cadmium and copper, the adsorption followed pseudo-first-order kinetics showing that only one molecule was involved in the rate determining step [43]. The adsorption of lead followed pseudo-second-order kinetics for both the ethylenediamine modified and the unmodified algal material. Similar results were obtained by Mwangi and Ngila [29] when studying the removal of heavy metals from wastewater using ethylenediamine-modified seaweed.

3.8. Analysis of wastewater samples

Fifty millilitre samples of water from Turi River were placed into plastic bottles and spiked with known concentrations of lead, cadmium and copper. The solution was agitated in a shaker for 30 min and then filtered, and the filtrate was analyzed for lead, cadmium and copper samples using AAS. The percentage of the metal recovered from the water samples was then recorded. Results from this analysis are shown in **Table 3**.

Metal	Concentration added/μgl^{-1}	Concentration recovered/μgl^{-1}	% Recovery
Copper			
Unmodified	00.00	2.050	
	10.00	10.363	86.0
	20.00	18.191	82.5
	30.00	19.871	62
Modified	00.00	2.010	
	10.00	8.191	68.2
	20.00	6.163	28.0
	30.00	7.682	24.0
Cadmium			
Unmodified	00.00	1.137	
	10.00	8.019	72.0
	20.00	14.627	69.2
	30.00	18.370	59.0
Modified	00.00	1.145	
	10.00	8.916	80.0
	20.00	16.070	76.0
	30.00	22.892	73.5
Lead			
Unmodified	00.00	2.185	
	10.00	9.870	81.0
	20.00	17.659	79.6
	30.00	19.633	61.0
Modified	00.00	2.070	
	10.00	9.885	81.9
	20.00	16.729	75.8
	30.00	22.449	70.0

Table 3. The percentage recovery of metals from real water samples.

From the results, the percentage recovery is high at low concentrations but decreased as the concentration of the metal in the water sample increased. The adsorption of copper by the unmodified sample was found to be the best and cadmium the least. For the modified sample, the adsorption of lead was the most and cadmium was the least. This can be explained by the fact that copper ions unlike lead and cadmium have relatively high affinity for ligands containing the nitrogen atom [44]. Such ligands which are smaller than the adsorbent have high affinity for the metal ion due to their high basicity [45]. These results show that the algal biomass has shown good potential to be used in water resource management.

4. Conclusions

The study successfully functionalized the algal material with tetramethylethylenediamine, and the FTIR spectrum provided evidence of its functional groups capable of binding metal ions. Adsorption of the three metals was best at lower pH values (4.2–6.8). Beyond these values, the adsorption decreased considerably. The rate of adsorption was very fast as more that 90% of the metals were removed from the solution within 30 min. The adsorption of copper fitted into the Langmuir adsorption isotherm with R^2 values of 0.974 and 0.512 for the unmodified and modified sorbents, respectively, indicating a monolayer-binding mechanism. Cadmium and lead fitted into the Freundlich adsorption mechanism (R^2 values were Cd modified = 0.993, unmodified = 0.251, Pb modified = 0.906, unmodified = 0.929). The adsorption of lead and cadmium was by Ho's pseudo-second-order kinetics confirming a multi-site interaction, whereas copper followed the pseudo-first-order kinetics, evidence of single-site adsorption. The adsorption by the algal material did not improve upon modification since natural ligands were replaced with ethylenediamine which has a lower stability constant for the metal analytes but minimized leaching of dissolved organic matter. In general the study has shown that the algal material can be used for as an effective sorbent for removal of lead, cadmium and copper from contaminated wastewater at low pH values.

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