Combined Clay Adsorption-Coagulation Process for the Removal of Some Heavy Metals from Water and Wastewater

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Abstract Heavy metals pollutions from wastewater discharges present an increasing concern for health, eco-system and the environment due to their persistence and bio accumulation via the food chain. Heavy metals in excess concentration cause problems of toxicity and growth inhibition to living things. While the cation exchange capacity of clay with respect to heavy metal removal is well documented, a two-step clay-coagulation combined process is studied in this research in which an excess clay addition in powder form to wastewater is followed by coagulation with aluminum sulphate to further remove heavy metal by synergy with the clay adsorption and to settle the clay adsorbent through flocculation and settlement. High percentage removal of heavy metals ranging from 96-99% has been observed. The saturated adsorption is adequately modelled by Freundlich as well as Langmuir isotherm models for the excess clay range studied. The clay-coagulation combined treatment technology can also be adapted to heavy metal removal in water treatment applications in which coagulation is often used for the removal of the colloidal portion of suspended solids.

Keywords Heavy metal removal, Clay adsorption, Wastewater treatment, Pollution, Coagulation, Freundlich isotherm, Environmental protection

1. Introduction

The presence of heavy metals in the natural environment including air, water, soil and plants is becoming an increasing health and environmental concern owing to the wide range of anthropogenic sources of heavy metals polluting the environment with growing industrialization and extensive use of chemicals (Srinivasan, 2011; Kinder, 1997, Yakun *et al*., 2014). Wastewater effluent streams from many industries display wide range of heavy metals in varying concentrations (Missana and Garcı, 2007). Heavy metals can directly enter the human body through the food chain causing serious health danger if present in excess concentration beyond permissible limits (Lin *et al*., 2000). Heavy metals are persistent and can bio accumulate in organisms disrupting the metabolic functions and vital organs in humans and animals (Tchounwou *et al*., 2012). They can cause wide range of illnesses including renal and organ damage, neurological dysfunction, heart disease,

allergy, asthma, respiratory problems, cancer as well as cardio vascular effects (Barbooti, 2015).

Heavy metals are present in water either in the form of free ions or as complexes with organic and inorganic ligands (Alleoni *et al*., 2003). Various types of treatment technologies have been adopted in the past for heavy metal pollutant removal. These include liquid membrane (Gürel *et al*., 2005), bagasse (Gupta *et al*., 1998), clay (Al-Jlil and Alsewailem, 2009), ion exchange (Rengaraj *et al*., 2003; Roque-Malherbe *et al*., 2007), precipitation (Esmaeili *et al*., 2005) and biosurfacant (Kim and Vipulanandan, 1997).

Adsorption is a surface phenomenon, a physico-chemical separation process whereby the adsorbate material is transferred from the bulk liquid phase to the adsorbent solid surface. Removal of heavy metals through adsorption is well studied and is claimed to have several advantages over other methods of removal such as precipitation, ion exchange or membrane based processes. Such advantages include low cost and easy availability especially with natural clay being abundantly available worldwide. Such adsorbents provide cost effective alternatives to conventional treatment technologies (Srinivasan, 2011; Sanchez *et al*., 2002). Other advantages include simplicity of operation and high removal efficiency (Oswald *et al*., 2008).

Compared with several other adsorbents available for heavy metal removal, adsorbents of natural clay material

offer better adsorption capacity while being low cost and easily available (Srinivasan, 2011). Adsorbents such as activated carbon are reportedly 20 times more expensive than clay (Babel and Kurniawan, 2003; Virta, 1996).

Clay minerals are alumino sillicates groups with sizes falling in the colloid fraction of soils with particle sizes smaller than 0.002 mm (Pinnavaia, 1983; Oloafe *et al.*, 2015). They are classified into: montmorillonite, smectite, kaolinite, illite, and chlorite. Montmorillonite, kaolinite, and illite are commonly used adsorbents owing to their greater surface area and structural rigidity (The Clay Mineral Group, 2011; Lin and Juang, 2002; Krishna *et al.*, 2000; Bailey, 1999). Clay soils are known for their high cation exchange capacity that makes them preferred adsorbent materials (Cadena *et al.*, 1990). The net negative charge present on the clay structure is because of substitution of silicon ion (Si^{4+}) by aluminum ion (Al^{3+}) that gives rise to Bronsted acidity formed on the surface by dissociation of water molecules. This acidity enhances the adsorption capacity (Tanabe, 1981). Lewis acidity in turn arises because of exposed trivalent Al^{3+} ions following structural rupture of the Si-O-Al bonds by dehydroxylation of some Bronsted acid sites (van Olphen, 1977).

Clay adsorbents have demonstrated excellent removal of heavy metals or metalloids including As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn from water. Montimorrlinite have high adsorption capacity compared with kaolinite and illite (Bhattacharyya and Gupta, 2008). Lead was removed almost 100% and chromium 86% according to Barbooti (2015) indicating lead is removed better than chromium. High percentage removal of heavy metal is aided by excess clay addition as much 12.5 g/L of wastewater using montmorillonite clay (Barbooti, 2015). Arsenic removal has been studied with membranes formed from montmorillonite, kaolinite, and illite operated through pumping (Fang *et al.*, 2006). Removal by rejection as high as 90% of arsenic in the feed stream has been reported.

Nanostructured polymer-clay composites, in which small amount of nano-clay particles are added to enhance mechanical, thermal, dimensional and barrier performance properties, have been used as sorbents for wide range of pollutants in ionic form, organic pollutants, herbicides, atrazines and others (Churchman, 2002; Breen, 1999; Radian and Mishael, 2008; Zadaka *et al.*, 2008).

Adsorption parameters such as pH, adsorbent dosage, adsorption kinetics, mixing time, ionic strength of the wastewater and temperature are important parameters as they exert influence on the adsorption process. Higher pH favours greater removal of heavy metals with increasing acidity facilitating desorption process because of increased competition from excess hydrogen ions present at low pH. When the pH increases from the acid to neutral range, the extent of adsorption increases. On the other hand, as the pH increases further to the basic range the mode of removal shifts from adsorption to removal by precipitation (Heba and Mikhail, 2014). Beyond pH 8, the dominant removal mechanism of heavy metals is precipitation, electrostatic

attraction and surface complexation (Bellir *et al.*, 2013). In a batch equilibrium study made by Sajidu *et al.* (2006), complete removal of chromium was obtained from pH 3 to 5. Zinc was removed completely above pH 7, copper above pH 4, cadmium between pH 6 and 9 and lead above pH 7.7. However, no effective removal of $AsO4^{3-}$ anion was observed.

Adsorbent dosage directly influences the adsorption efficiency since with greater amount of adsorbent used the number of active sites available for adsorption increases thereby increasing the adsorption efficiency. According to Bellir *et al* (2013), adsorbent dosage of 0.5 g/l was associated with 85% removal of heavy metals. Increasing the dosage to 0.8 g/l increased the percentage removal to 92%.

The kinetics of removal appears to be second order overall (Barbooti, 2015). This has also been confirmed by Bellir *et al* (2013) in their research on adsorption of cadmium and zinc on clay bentonite. The pseudo first order model gave poor data fit with poor correlation coefficient whereas the pseudo second order kinetics gave the best fit with very high correlation coefficient value.

Mixing time required for adsorption is influenced by the different phases of adsorption processes involving bulk diffusion, film diffusion, intra particle diffusion and adsorption onto the interior active sites. A mixing (shaking) time between 30 and 60 minutes will ensure maximum adsorption reaching equilibrium concentrations after overcoming the different resistances (Bellir *et al.*, 2013).

The ionic strength of the wastewater influences the extent of adsorption of heavy metals on to clay since solutions with higher ionic strength create competition of these ions with heavy metals for adsorption. Therefore, the higher the ionic strength of the wastewater, the lesser will be the extent of heavy metal adsorption (Ihaddadene, *et al.*, 2016).

Temperature directly influences the adsorption process, as adsorption is often endothermic reaction whereby the rate of adsorption increases with increase in temperature. According to the experiments of heavy metal adsorption on bentonite clay by Aljlil and Fares (2014), increasing the temperature of reaction resulted in positive enthalpy change confirming that the adsorption is an endothermic process. In addition, the Gibbs free energy change decreased with increasing temperature demonstrating further that adsorption is favoured at higher temperature.

The concept of combined-clay coagulation for the removal of heavy metals adopted in this research is thought to derive maximum benefit from the synergy of clay adsorption capacity with the coagulation potential of coagulants while achieving easier removal of adsorbent through flocculation. The synergy between the clay and the coagulant may be attained further through increased mobility of heavy metals from the diffuse layer to the clay during the flocculation process because of the decrease of the zeta potential. According to Almeida *et al.* (2012), the formation of electrical double layer with the fixed and diffuse layers decreases the adsorptive capacity of the clay adsorbent because of the existence of metals in the diffuse layer that

moves eventually with the liquid during the separation process. Tushar *et al.* (2002) also reasoned that leakage of heavy metals occurs because of transport of colloidal size particles with the flow especially where the solid-liquid separation process is not efficient. Furthermore, the use of coagulation alone for heavy metals removal requires higher coagulant dosage in order to remove the metal by co-precipitation (Akbal, and Camci, 2010). In the proposed combined clay-coagulation setup used in this research, less coagulant dosage would be needed, as adsorption by the clay adsorbent would be the dominant mode of heavy metal removal.

2. Materials and Methods

The method employed for heavy metal removal process in this research is based on a combination of clay addition into wastewater in a powder form followed by the process of coagulation for enhancing the removal of heavy metal through synergy with the clay adsorbent and for the removal of the clay adsorbent by flocculation and settlement. The addition of excess clay ensures a good percentage removal of heavy metal whereas the coagulation process makes it easier to separate the clay adsorbent from the wastewater in addition to decreasing the zeta potential and thereby enabling further adsorption of metals from the diffuse layer onto the clay adsorbent. Coagulation further removes the heavy metals by co-precipitation during the flocculation-precipitation stage. The addition of clay in powder form eliminates the pore resistance to adsorption as well as frictional resistance to flow that are normally present in packed adsorbent columns. Besides, coagulation removal of clay adsorbent is handier and efficient than removing clay through filtration process.

Wastewater leachate samples were collected from the Mpolonjeni solid waste landfill site that is located in Mbabane City. Because of the limited heavy metal content of the leachate samples present during the time of collection, the method of standard addition was used in order to increase the heavy metal contents of the wastewater. The experimental procedure consisted of adding known concentrations of heavy metals to measured volumes of wastewater samples followed by addition of clay adsorbent in powder form. The final step was coagulation with aluminum sulphate for the removal of the clay adsorbent followed by flocculation and settlement. The detail procedure followed during the experiments is specified below.

2.1. Preparation of Heavy Metals for Addition into Samples

Heavy metal standards to be added to the wastewater samples were prepared for each of the heavy metals of copper, iron and lead. Stock solutions of each heavy metal with concentration measuring 1000 mg/L were used which were analytical reagent grade metal standards with 1% nitric acid added into the stock solutions. The volumes of heavy metals added from the stock solution for each of the heavy metals to give different heavy metal concentrations are summarized in Table 1.

Table 1. Preparation of heavy metals for standard addition to samples of wastewater

Waste water sample	S0	S1	S2	S3	S4	S5
Heavy metal concentration (mg/L)	0	5	10	20	50	100
Sample volume (mL)	200	200	200	200	200	200
Heavy metal weight needed in mg per 200 mL	0	1	2	4	10	20
Concentration of Heavy metal stock solution (S_0)	1 mg/mL	1 mg/mL	1 mg/mL	1 mg/mL	1 mg/mL	1 mg/mL
ml added from stock	0	1	2	4	10	20

Table 2. Preparation of heavy metal standards for Atomic absorption spectrometer calibration

Heavy metal Standard	Blank	St1	St2	St3	St4	St5	St6
Concentration (mg/L)	0	0.1	0.2	0.5	1	2	5
Volume of standard solution (mL)	100	100	100	100	100	100	100
mL of heavy metal to be added to standards	0	0.01	0.02	0.05	0.1	0.2	0.5
Concentration of standard solution (S2) (mg/L)	0.01 mg/mL	0.01 mg/mL	0.01 mg/mL	0.01 mg/mL	0.01 mg/mL	0.01 mg/mL	0.01 mg/mL
mL to be added from standard solution (S2)	0	1	2	5	10	20	50

Table 3. Preparation of samples for optimum coagulant dosage experiment

Sample	S0	S1	S2	S3	S4	S5	S6
Volume of wastewater sample (mL)	200	200	200	200	200	200	200
Weight of red clay added (g)	20	20	20	20	20	20	20
Coagulant dosage (mg/l)	0	20	50	100	150	300	400
Weight of coagulant to be added to 200 mL sample	0	4	10	20	30	60	80
Stock aluminum sulphate solution strength (mg/mL)	1 mg/mL (1000 mg/L)	1 mg/mL	1 mg/mL	1 mg/mL	1 mg/mL	1 mg/mL	1 mg/mL
mL of coagulant added from stock solution	0	4	10	20	30	60	80

2.2. Preparation of Heavy Metal Standard Calibration Solutions for Atomic Absorption Spectrometer Measurement

Standards ranging between 0 and 5 mg/l were prepared since in this low range linearity of the standard calibration for the studied heavy metals is ensured by the atomic absorption spectrometer instrument. From the stock solution of heavy metals measuring 1000 mg/L, subsequent standard solutions (S_1 and S_2) were prepared to give concentrations respectively of 100 mg/L for S_1 and 10 mg/L for S_2 standards. Distilled-deionized water was used for the dilution water needed for preparing these standards. Suitable mL volumes were added from standard solution S_2 to give the desired standard ranging between 0 (blank) and 5 mg/L. This procedure is summarized in Table 2.

2.3. Adsorbent Clay Material

Red clay soil (Utisol) samples needed for experiment were collected from suitable locations in Mbabane City. These clay soils are abundantly available in Swaziland, their common use being for traditional pottery, ceramics and as building materials such as bricks. Utisols have varieties of clay minerals but the dominant one is kaolinite. It has been demonstrated (Talaat, 2011) that raw kaolin, rather than kaolin treated with acid washing, gives better performance in terms of heavy metal removal by adsorption. Untreated raw red clay samples have been demonstrated to have had higher cation exchange capacities due to the presence of organic material and iron oxides (Pare *et al.*, 2012). In this experiment, therefore, no acid treatment has been applied to the red clay used for adsorption.

The clay samples were ground and sieved to mesh size #100 and then dried at 120°C for 3 hours. The clay samples were weighed for addition into samples of wastewater in which heavy metals were present. Since the experiments were based on excess clay addition in order to test the feasibility of the combined clay-coagulation process, 20 g. of clay were added to each of the 200 mL of water samples with differing heavy metal concentrations.

2.4. Determination of Optimum Coagulant Dosage

The optimum amount of aluminum sulphate coagulant needed to settle the clay adsorbent was determined through jar test. First a stock solution of aluminum sulphate was prepared to give a concentration measuring 1000 mg/L. From this stock solution, different coagulant dosage volumes were added to each of the six beakers each of which contain the excess 20 g. red clay adsorbent in 200 mL of water. The coagulant addition was immediately followed by rapid mixing for one minute and subsequent flocculation through slow stirring for 15 minutes. The flocs formed after flocculation were then allowed to settle for 30 minutes. The turbidity of the settled supernatant was measured afterwards.

Table 3 shows the procedure employed for coagulant addition in preparation for the jar test experiment.

2.5. Combined Clay-Coagulation Experiment

The combined clay-coagulation experiment was conducted using the optimum coagulant dosage that was determined through the Jar test for a given weight of excess clay adsorbent used in the experiments. First 200 mL of the wastewater samples were added to each of the beakers used for the experiment. This was followed by the addition of heavy metals into the sample beakers to give concentrations ranging between 0 and 100 mg/L. Then after the excess clay adsorbent was added to each of the wastewater samples and the mixture was thoroughly mixed allowing at the same time sufficient time for adsorption to occur. Procedures such as centrifuging and filtration used to separate the heavy metal from the clay adsorbent were not necessary in this experimental setup as the coagulant readily removes the clay adsorbent in simpler coagulation process. Finally, the optimum aluminum sulphate coagulant dose determined from the jar test was added to each of the samples, which was accompanied by rapid mixing, flocculation ad settlement. The settled supernatant samples were decanted and taken for heavy metals determination using atomic absorption spectrometer.

The heavy metal concentrations remaining in the supernatant following the combined adsorption-coagulation were determined using flame atomic absorption spectrometer, FAAS (AA-250 Varian). Air and acetylene were used for creating the gas flame. The instrument was calibrated in the linear range using standard series in the range between 0 and 5 mg/|L prepared for each of the heavy

metals. This calibration was done for each of the heavy metals determination before measurements were taken. Where dilutions were needed for sample measurements that were out of the linear range, the needed dilutions were made and measurements recorded.

The amount of heavy metal adsorbed (X) per unit mass of clay adsorbent used (M) was calculated using the following formula

$$\frac{X}{M} = \frac{(C_o - C) * V}{M} \quad (1)$$

Where:

X = The amount of heavy metal adsorbed onto the clay adsorbent (mg)

M = The mass of clay adsorbent used in the experiment (mg)

C_0 = The initial heavy metal concentration present in the sample (mg/L)

C = The final heavy metal concentration present in the sample after separation from the adsorbent (mg/L).

V = The volume of wastewater sample used in the experiment (liters)

The percentage removal of heavy metal following adsorption was calculated using the formula:

$$\% \ Removal = \left(\frac{(C_o - C)}{C_o} \right) * 100 \quad (2)$$

Where C_o and C are the initial and final heavy metal concentration present in the wastewater sample.

2.6. Adsorption Modeling

Modeling of the adsorption process of heavy metals using clay adsorbents are often based on either Freundlich or Langmuir isotherm models. The Langmuir isotherm assumes uniform adsorption resulting in a saturated monolayer of adsorbate materials occupying the adsorption surface. It also assumes that there is no further interaction among the adsorbate materials (Kim et al., 2013; Foo and Hameed, 2010). The Freundlich isotherm by contrast is an empirical model whereby the adsorption is composed of heterogeneous processes with the stronger binding sites occupied first and with decreasing energy of adsorption as the adsorption progresses towards the weaker processes (Al-Shahrani, 2014).

In many cases, the Freundlich isotherm gives best fit to the adsorption data (Burham and Sayed, 2016) rather than the Langmuir adsorption isotherm. Several researches carried out reported Freundlich isotherm model giving the best data fit confirming that the clay adsorption of heavy metals is a multi-layer sorption process (Glatstein and Francisca, 2015; Eren et al., 2010). In this research, both the Freundlich and Langmuir isotherms were fitted to the adsorption data to test their appropriateness to the combined clay-coagulation adsorption process. The Freundlich isotherm model is based on the equation:

$$\left(\frac{X}{M} \right) = A . C^{1/N} \quad (3)$$

Where:

X = The mass of heavy metal adsorbed on the clay (mg)

M = The mass of clay adsorbent used in the batch experiment

C = The saturated heavy metal concentration remaining in the water after equilibrium has been reached.

A, N = Constants

The constants A and N were evaluated using linear regression after the Freundlich equation was converted into linear form by taking the logarithm of the ratio of the mass of adsorbate per unit mass of adsorbent (X/M) as well as the saturated concentration of heavy metals remaining in water after equilibrium is reached (C).

The Langmuir isotherm model is based on the equation:

$$\frac{X}{M} = \frac{abC}{1+aC} \quad (4)$$

Taking the reciprocals of both the left and right terms of equation (4) enables the Langmuir model to be expressed in linear form as follows:

$$\frac{1}{\left(\frac{X}{M} \right)} = \frac{1}{b} + \frac{1}{ab} \left(\frac{1}{C} \right) \quad (5)$$

A plot of the adsorption data in equation (5) using (1/(X/M) as the y variable and (1/C) as the x variable yields a linear plot from which the intercept (1/b) and the slope (1/ab) can be determined eventually yielding the constants a and b needed for the Langmuir model.

In both the Freundlich and Langmuir model tested, the goodness of fit was evaluated through the computation of the coefficient of determination (R^2) of the linear regression model.

2.7. Initial Wastewater Quality Assessment of the Leachate Sample

The initial wastewater quality of the leachate sample on which heavy metal standard addition was made were determined for a number of parameters that may influence the adsorption process. The parameters determined include conductivity, total dissolved solids, pH, suspended solids, COD, BOD, ammonia, colour, chloride, dissolved oxygen, turbidity and sodium. The standard operation procedures specified in the Standard Methods for the examination of water and wastewater were used for the determination of these water quality parameters.

3. Results and Discussion

The initial wastewater quality analysis of the leachate sample was carried out in order to determine the environmental variables under which the clay adsorption-coagulation takes place. It was mentioned in the introduction section of this paper that parameters such as ionic strength and pH affect the adsorption process. This paper is not aimed at varying these variables as the factors are well studied. For example higher pH is known to favour adsorption and precipitation of heavy metals. Greater ionic strength of the wastewater solution also affects heavy metal

removal because of competitive adsorption by other cations present in the wastewater. Table 4 presents the result of the wastewater quality analysis of the leachate sample. It is clear that the leachate pH is high (8.9) which favours the heavy metal adsorption. On the other hand, the total dissolved solids of the wastewater is also high (958 mg/L) which to a certain extent reduces the extent of heavy metals removal because of competitive adsorption. Other parameters such as COD, BOD and ammonia are also included in the result shown in Table 4.

The optimum coagulant dosage that indicated low values of settled waste water turbidity for the samples analyzed was determined to be 100 mg/L for the excess 20 g. clay adsorbent used. This dosage is small compared to the weight of clay used in the experiment, which is an indication of the ease with which clay can be removed through coagulation and settlement.

Following the combined clay-coagulation experiments, the residual supernatant heavy metal concentrations were measured using atomic absorption spectrometer. Table 5 shows summary of the residual concentrations and percentage removal of heavy metals for each of the three heavy metals studies and for each of the initial heavy metal concentrations present in the experiment.

The tabular values indicate high percentage removal of all the heavy metals with low residual concentrations. The heavy metal removal process in this experiment is assisted by the reduction of pore and film resistance to adsorption through the use of powdered clay adsorbent. It is also clear from the graphical plots (Figures 1, 2 and 3) that the relationships between heavy metal residuals in the supernatant wastewater and initial heavy metals present are not linear.

The curves tend to be steeper at lower initial metal concentrations and tend to get flatter at higher heavy metals concentrations. It is apparent that the extent of adsorption per unit mass of adsorbent decreases when the heavy metal concentration increases. This behavior is expected because, for a fixed mass of adsorbent, the extent of adsorption decreases because of increased competition for adsorption sites by the heavy metals whenever the concentration of heavy metals increases (Heba and Mikhail, 2014). This nature of removal might also suggest that for higher heavy metal concentrations present in wastewater, the clay adsorbent can be added in sequential batches so that the later batches of clay adsorption operate to remove small heavy metal concentrations with higher efficiency.
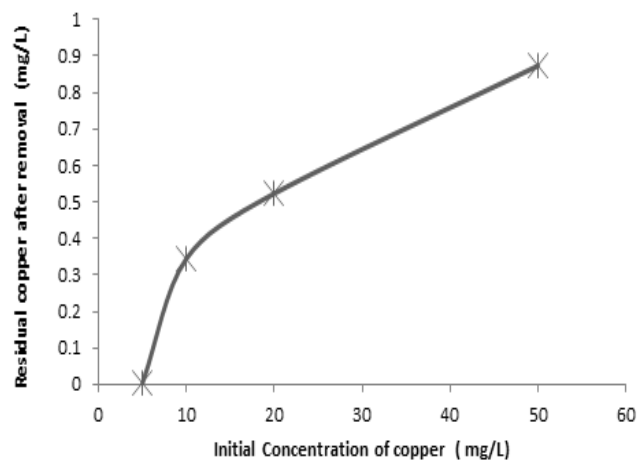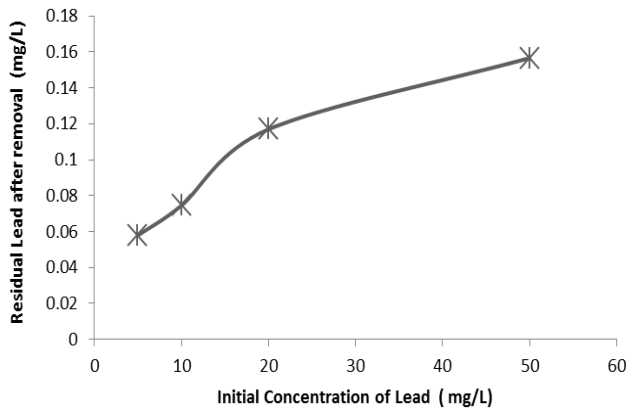

Figure 1. Variation of residual concentration of heavy metals with initial heavy metal present for copper

**Table 4.**   Initial wastewater quality data of the leachate sample

Parameter	Value	Parameter	Value
Conductivity (µS/cm at 25°C)	1914	Ammonia (mg/L)	43.6
Total dissolved solids (mg/L)	958	Colour (Pt-Co units)	71
pH at 25°C	8.9	Chloride (mg/L)	319
Total suspended solids (mg/L)	44	Dissolved oxygen (% saturation)	19.0
Chemical oxygen demand (mg/L)	227	Turbidity (NTU)	23.4
Biolgical oxygen demand (mg/L)	60	Sodium (mg/L)	228.4

Table 5.   Results of clay-coagulation removal of heavy metals

Removal of copper			Removal of lead			Removal of iron		
Initial Conc.	Final Conc.	(%) Removal	Initial Conc.	Final Conc.	(%) Removal	Initial Conc.	Final Conc.	(%) Removal
mg/l	mg/l		mg/l	mg/l		mg/l	mg/l	
5	0.0043	99.91%	5	0.0579	98.84%	5	0.0097	99.81%
10	0.3449	96.55%	10	0.0745	99.26%	10	0.0391	99.61%
20	0.5233	97.38%	20	0.1169	99.42%	20	0.0867	99.57%
50	0.8733	98.25%	50	0.1566	99.69%	50	0.1763	99.65%

Figure 2. Variation of residual concentration of heavy metals with initial heavy metal present for lead
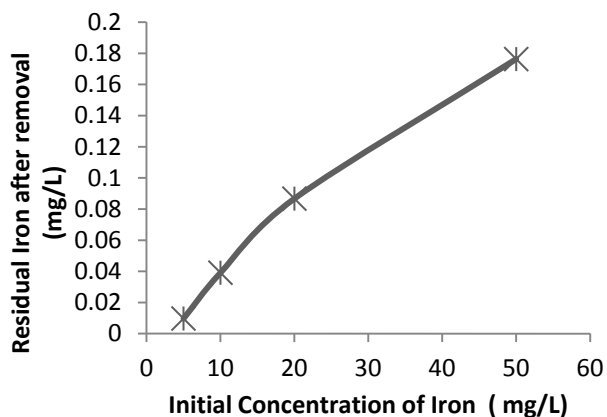
Figure 3. Variation of residual concentration of heavy metals with initial heavy metal present for iron

Comparison of the percentage removal as well as residual heavy metal concentrations among the three heavy metals shows somewhat mixed picture. At concentrations between 10 and 20 mg/L iron is removed the most followed by lead and copper in that sequence. At 50 mg/L initial heavy metal concentration, lead has the smallest residual followed by iron and copper in that sequence. Earlier studies also suggested that lead has the strongest affinity to clays as well as iron oxides (Sauve et al., 2000). At low concentration of 5 mg/L, copper is removed the most, followed by iron and lead in that sequence. The higher affinity of copper to the red clay sample used may be expected as copper (II) is known to strongly adsorb on organic matter and iron oxides than on the clay minerals (Bradl, 2004). Further removal of copper is favoured at higher pH values due to precipitation. Comparison of ionic radii among the three heavy metals shows that iron has the smallest radius (0.645 A°) followed by copper (0.73 A°) and lead (1.19 A°). According to the ionic sizes hierarchy, iron is expected to be adsorbed most followed by copper and lead in that order. This is because the smaller the ionic size the greater the facile adsorption onto active sites (Burham and Sayed, 2016). On the other hand, research work by Kamel et al. (2004) showed that the affinity of heavy metals for kaolinite clay was in the order Cu > Fe > Pb. However, according to the experimental results obtained, the hierarchy of removal efficiency is quite mixed and is not necessarily correlated only with the ionic radii of the heavy metals or according to the earlier findings cited above.

Figures 4, 5 and 6 show the Freundlich isotherm modeling of the clay-coagulation process for the three heavy metals studied. The graphs show good regression fit for all the three metals. However, this model is valid for the lower metal residuals present, which is a characteristic of excess clay addition. Table 6 shows the Freundlich model fit parameters for the three metals. The coefficients (A and N) of the Freundlich model show copper is removed at low residual concentrations corresponding to low initial metal present (low A values) whereas iron is removed most efficiently at higher residual metal concentrations corresponding to high initial metal present (higher N value). The N value in the Freundlich isotherm equation indicates the nature of adsorption (Eren et al., 2010) and whether the adsorption process reaches saturation at higher heavy metal concentrations for a given mass of adsorbent used. When the value of N is greater than one, it is an indication of increasing saturation resulting in competition among heavy metals for adsorption sites. When the value of N is less than one the adsorption increases exponentially. The experimental results indicate that for the excess clay adsorption used in this experiment the values of N for all the three heavy metals are less than one indicating increasing adsorption rate per increase in the heavy metal concentration present.

Figure 7, 8 and 9 show the Langmuir isotherm modeling of the clay-coagulation process. Similar to the Freundlich model, the Langmuir model also show good regression fit for all the three metals. Table 7 shows the Langmuir model parameters as obtained from the linear regression model after the Langmuir equation was linearized by taking the reciprocals as given in equation 5. Comparison of the regression coefficient (R^2) show that both the Freundlich and Langmuir equations adequately model the clay-coagulation combined process with regression coefficient ranging from 0.95-0.99. Comparison of the Langmuir parameters (ab) show that iron is adsorbed the most followed by lead and lastly copper which is similar to the order of removal obtained from the Freundlich model stated above.

The experimental results offer promising direction for heavy metal removal using clay adsorbent while coagulation is used further to enhance the heavy metal removal as well as for easier removal of adsorbent. Conventional treatment setups are often criticized for lacking the ability to remove heavy metals (Srinivasan, 2011). The use of coagulation alone for heavy metal removal by co precipitation often requires higher dosage of coagulants to achieve the same percentage removal obtained by this research. For example, Akbal, and Camci (2010) reported that coagulant dosages in the range of 500 – 2000 mg/L were need for over 99% removal of the metals copper, chromium and nickel. This experiment shows that by combining clay adsorption with conventional treatment techniques such as coagulation it is possible to remove heavy metals with reduced coagulant

dosage and with greater efficiency. The application can be extended not only to wastewater treatment polluted with heavy metals but also to water treatment applications.
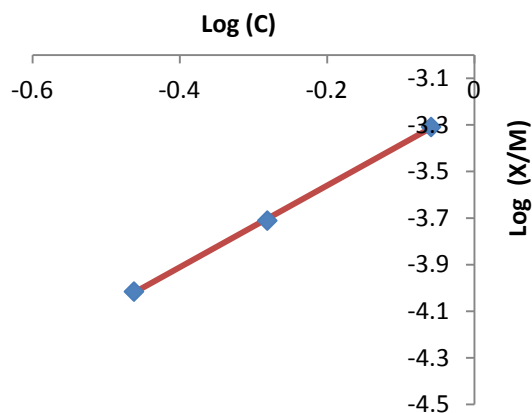

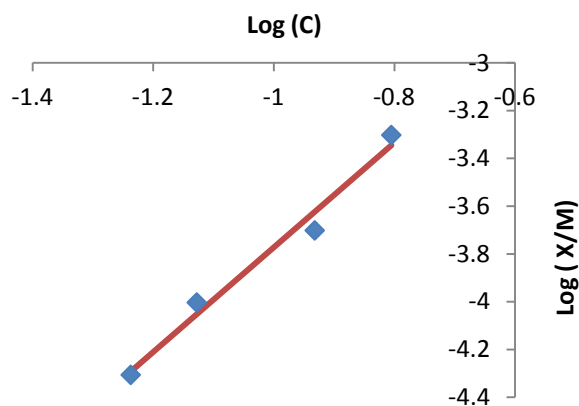**Figure 4.** Freundlich isotherm fit for the removal of copper

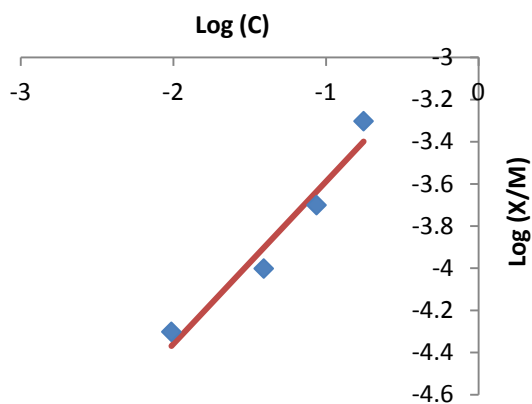**Figure 5.** Freundlich isotherm fit for the removal of Lead

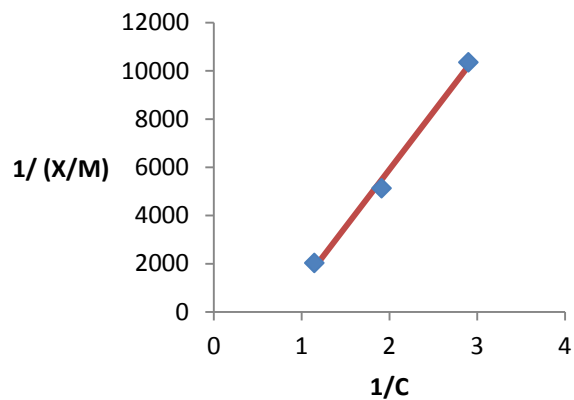**Figure 6.** Freundlich isotherm fit for the removal of iron

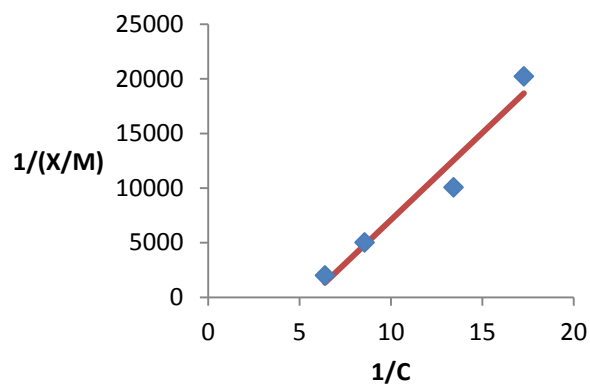**Figure 7.** Langmuir isotherm for the removal of copper

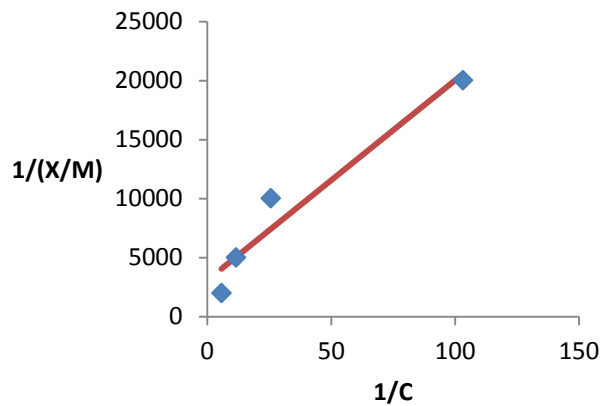**Figure 8.** Langmuir isotherm for the removal of lead

Figure 9. Langmuir isotherm for the removal of iron

Table 6. Summary of Freundlich isotherm model constants for copper, lead and iron

	Copper	Lead	Iron
Isotherm model	Freundlich	Freundlich	Freundlich
Model equation	$\left(\dfrac{X}{M}\right) = A.C^{1/N}$	$\left(\dfrac{X}{M}\right) = A.C^{1/N}$	$\left(\dfrac{X}{M}\right) = A.C^{1/N}$
Model constants	A = 0.000618 N = 0.570357	A = 0.026308 N = 0.456	A = 0.00152 N = 1.298
Regression parameters $(R^2)^*$	$R^2 = 0.99$	$R^2 = 0.98$	$R^2 = 0.95$

* R^2 denotes the coefficient of determination for the regression models.

Table 7. Summary of Langmuir isotherm model constants for copper, lead and iron

	Copper	Lead	Iron
Isotherm model	Langmuir	Langmuir	Langmuir
Model equation	$\dfrac{X}{M} = \dfrac{abC}{1+abC}$	$\dfrac{X}{M} = \dfrac{abC}{1+abC}$	$\dfrac{X}{M} = \dfrac{abC}{1+abC}$
Model constants	a = -0.76011 b = -0.00028 ab = 0.000213	a = -5.55317 b = -0.00011 ab = 0.00061	a = 18.25827 b = 0.000323 ab = 0.0059
Regression parameters $(R^2)^*$	$R^2 = 0.99$	$R^2 = 0.97$	$R^2 = 0.97$

* R^2 denotes the coefficient of determination for the regression models.

4. Conclusions

From the experimental results obtained, it is apparent that the combined excess clay-coagulation process gives high percentage removal for all the three heavy metals studied. The percentage removals range between 96% and 99%. The efficiency of removal for the red clay used in the experiment favors iron and to a certain extent lead at higher initial metal concentrations whereas at low concentrations removal of copper is favored. The clay-coagulation process significantly reduces the pore and film diffusion resistances that are normally present on adsorbent columns since the clay is applied in powder form and is eventually removed through coagulation. In addition, the coagulation step provides synergy with the clay adsorption by decreasing the zeta potential and allowing more heavy metals to be adsorbed from the diffuse layer. Removal by co precipitation occurs further following coagulation. The coagulation step, apart from enhancing the heavy metal removal by synergy with the clay adsorption, represents a simpler method for separating the adsorbent from the supernatant compared with other methods such as centrifuging and filtration where powder form is used for adsorption. Another bottleneck with the traditional clay adsorption is the low permeability of the clay adsorbent which is absent in this technological setup. The clay adsorbent is completely removed through the addition of optimum dose of the coagulant, which is used for the purpose of flocculating the clay adsorbent and separating it from the treated water by sedimentation or filtration. In addition, the combined clay-coagulation process may offer additional benefits through removal of other pollutants such as organic matter making it potentially useful for wide range of wastewater pollutants. The research setup can be used not only in wastewater treatment applications but also in conventional water treatment processes where coagulation is used. The simple modification of adding the clay adsorbent to such conventional treatment processes as combined treatment makes them capable of removing heavy metals that are otherwise difficult to remove through, conventional water treatment setups.

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