

THE EFFICACY OF RAW MALANGALI KAOLIN CLAY IN THE ADSORPTIVE REMOVAL OF CADMIUM AND COBALT IONS FROM WATER

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ABSTRACT

The suitability of raw Malangali kaolin (RMK) clay for the removal of cadmium and cobalt ions from water was investigated using a batch technique whereas the characterization of adsorbent material was performed by XRD, XRF, ATR-FTIR and N₂ physisorption techniques. Various experimental parameters were tested for the effectiveness of RMK in removing heavy metals whereby quantitative determination of both Cd²⁺ and Co²⁺ ions has shown that, the factors such as adsorbent particle size, solution pH, contact time, adsorbent dose as well as initial metal ion concentration had significant effects on the adsorption processes. The equilibrium data described by Langmuir and Freundlich isotherms were used in this study. It was shown that Langmuir isotherm displayed a better fitting model than that of Freundlich because of its higher correlation coefficient, thus, demonstrating the occurrence of monolayer coverage of Cd²⁺ and Co²⁺ ions on the surface of RMK clay. The results obtained in this study, therefore, suggest that locally available RMK clay can be used as potential and effective adsorbent for removal of heavy metal ions from aqueous solutions.

Keywords: Clays, Malangali kaolin, Adsorption, Heavy metals

INTRODUCTION

Heavy metals cause great environmental concerns because they pose a serious threat to the environment by damaging human health and life in general (Tchounwou et al. 2012). These metals are usually toxic even at low concentrations, non-biodegradable (Imamoglu and Tekir 2008), capable of accumulating in the soft tissues of living organisms and ultimately are capable of entering the food chain (Salam et al. 2011). In addition, the quality of domestic water is increasingly affected by heavy metal ions which are being added to water streams at a much higher concentration than the prescribed limits, thus leading to health hazards (WHO 2011, Zwain et al. 2014). Therefore, elimination of these metals from domestic water and wastewaters before they

are released into the environment is crucial to the protection and maintenance of public health.

The removal of heavy metals from aqueous solution employs various physical and chemical techniques such as chemical precipitation (Hui et al. 2005), ion exchange (Ijagbemi et al. 2009), adsorption (Zain et al. 2010), membrane separation (Qdaisa and Moussab 2004), and solid phase extraction (Xue et al. 2009, Dalida et al. 2011) among several others. However, it was noted that most of these processes are expensive, complicated and/or even ineffective at low metal ion concentrations rendering them unsuitable for this purpose (Kurniawan et al. 2006). Previous studies have revealed that the most preferred and effective method for

the removal of heavy metal ions from aqueous solution is adsorption due to its simplicity and high effectiveness (Liang et al. 2010). This method has unique advantages over the others in that it can be regenerated and reused, applied at very low metal ion concentrations, suitable for both batch and continuous processes, easy to operate, and also it generates small amount of sludge (Mohanty et al. 2006). In view of these unique characteristics, adsorption has been a method of choice and thus many researchers have reported the use of different adsorbent materials such as biomass materials (Annadurai et al. 2003, Vasquez et al. 2012), fertilizer waste (Gupta et al. 2010), tea waste (Mondal 2010), microorganisms (Gulper and Sarioglu 2013), charcoal (Yadav et al. 2014), yeast (Li et al. 2013), sludge ash (Weng 2002), date pits (Banat et al. 2002), lateritic minerals (Ahmad et al. 2002), red mud (Gupta et al. 2001) and clay (Naseem and Tahir 2001, Hamidpour et al. 2010), in an attempt to improve the removal of these noxious metals from the environment through the adsorption process.

It should be noted that among several adsorbents used so far, the use of clays is considered to be mostly attractive because they are cheap, readily available and environmentally benign. In addition, their chemical and physical characteristics such as high specific surface area, chemical and mechanical stability, a variety of surface and structural properties make them suitable for this purpose (Krishna et al. 2000, Lin and Juang 2002, Bhattacharyya and Sen-Gupta 2008). Raw kaolin clay has been studied and reported as an adsorbent for the removal of various toxic and hazardous pollutants of major concern to the environment (Veli and Alyuz 2007, Bhattacharyya and Sen-Gupta 2008, Talaat et al. 2011). However, the performance of Malangali Kaolin Clay in removing heavy metals from water has never been reported. Based on this

information and the abundance of kaolin clays in different parts of Tanzania, it was deemed necessary to investigate the effectiveness of raw Malangali kaolin clay in removing cobalt and cadmium ions from water through a batch process.

MATERIALS AND METHODS

Preparation of Adsorbate

Standard solutions of Cd^{2+} and Co^{2+} ions (1000 mg/L) were prepared by dissolving appropriate amounts of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (assay 98%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (assay 99%) respectively, in distilled water. The working solutions were prepared by dilution of the stock solutions with distilled water to obtain solutions of concentrations ranging 5-25 mg/L. The pH of each solution was adjusted to the required value by dropwise addition of 0.1 M NaOH or 0.1 M HCl before the adsorbent was added.

Preparation of Adsorbent

The raw Malangali kaolin (RMK) clay sample was crushed and washed thoroughly with distilled water with occasional stirring to remove the soluble inorganic salts, suspended insoluble impurities and other adhering materials attached to its surface (Omar and Al-Itawi 2007). The clay sample was then dried in an oven at 100 °C overnight, pulverized, sieved through 150 μm mesh sieve and stored in desiccator for further studies.

Physicochemical Analysis

The mineralogical composition analysis was performed using an X-ray diffractometer (Model InXITU-BTX-231, USA) operating at 30.5 kV and 0.270 mA. The FTIR spectra of the adsorbent was recorded by Fourier Transform Infra-Red (FTIR) spectrometer (Model: Bruker Optic GmbH 2011, USA), while the pore properties and Brunauer-Emmett-Teller (BET) surface area of RMK were assessed via nitrogen adsorption-desorption technique using a porosimeter (NOVA 1200e, Version 11.03,

Quantachrome Corporation, Japan). The chemical composition of the clay was determined using an X-Ray Fluorescence (XRF) model S8 TIGER-BRUKER of 200 KN, whereas the concentrations of the heavy metals in the adsorbent were determined using Atomic Absorption Spectrometer (AAS; Model: Varian AA240, Australia).

The porosity characteristics of RMK clay samples were investigated by nitrogen adsorption-desorption technique. The surface area of the sample under study was evaluated based on BET theory at a relative pressure range (P/P_0) of 0.05-0.35. The pore diameter and pore volume were determined by employing (Barrett-Joyner-Halenda (BHT) method.

Adsorption Procedure

Adsorption experiments for the removal of Cd^{2+} and Co^{2+} ions from contaminated water solution using RMK clay were studied by batch method. The optimum weight (dose) of RMK clays that gave high adsorption efficiency was contacted separately with 25 mL of the metal solution of known concentration in a conical flask while agitating at 400 rpm for 3 hours for equilibrium isotherm studies. A portion of the solution was removed and filtered for subsequent determination of the concentrations of Cd^{2+} and Co^{2+} ions using AAS.

Determination of Optimum Doses

The influence of different doses of RMK clay sample on the adsorption of Cd^{2+} and Co^{2+} ions from water was studied by varying the adsorbent dose from 0.2 to 1 g. The dose which gave the maximum heavy metal removal was used to test other parameters. The adsorption capacity and percentage adsorption were calculated by using equations (1) and (2), respectively.

$$q_e = \left(\frac{C_0 - C_e}{M} \right) \times V \quad (1)$$

$$\% \text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where, q_e is the amount of heavy metal ions adsorbed on RMK clay (mg/g), C_0 is the initial concentration of heavy metals in mg/L, C_e is the equilibrium concentration of the heavy metals in mg/L, V is the volume of aqueous solution (L), and M is the mass of RMK clay sample (g).

Determination of the Contact Time

The effect of contact time was studied by agitating 25 mL of aqueous solution containing 5 mg/L of Cd^{2+}/Co^{2+} ions with 0.8 g of RMK having 150 μm particle size at time intervals between 60 and 300 minutes. The data obtained were used to calculate the adsorption capacity and percentage adsorption by using equations (1) and (2), respectively.

Determination of the Initial Concentration

The effects of initial metal ion concentrations on Cd^{2+} and Co^{2+} ions removal were studied by batch adsorption experiments using different concentrations (5, 10, 15, 20, and 25 mg/L), pH 6 and 0.8 g of adsorbent material having 150 μm particle size for 180 minutes. The data obtained were used to calculate the adsorption capacity and percentage adsorption by substituting variables in equations (1) and (2), respectively.

Determination of the Solution pH

The effects of pH on the adsorptive removal of Cd^{2+} and Co^{2+} ions from aqueous solution was investigated by varying the solution pH from 2 to 10, while the other experimental conditions, namely initial metal ion concentration (5 mg/L), adsorbent dose (0.8 g), contact time (180 min), particle size (150 μm) and batch volume (25 mL) were maintained. The pH of the solution was

adjusted by dropwise addition of either 0.1 M NaOH or 0.1 M HCl until the equilibrium was attained. The data obtained were substituted in equations (1) and (2) to calculate the adsorption capacity and percentage adsorption, respectively.

Determination of the Adsorbent Particle Sizes

RMK clay samples (0.8 g each) with different sizes ranging from 75 to 250 μm were contacted separately each with 25 mL of aqueous solution of $\text{Cd}^{2+}/\text{Co}^{2+}$ ions containing 5 mg/L at pH 5 for 3 hrs. The adsorbent particle size that gave out maximum removal of the heavy metal ions was used for subsequent experiments. The raw data obtained were used to calculate the adsorption capacity and percentage adsorption using equations (1) and (2), respectively.

RESULTS AND DISCUSSION

Characterization of RMK

The results for mineralogical composition of RMK clay sample presented in Figure 1 revealed the presence of prominent peaks of kaolinite ($\text{Al}_2\text{Si}_2\text{SO}_5(\text{OH})_4$) at $d = 7.4188, 4.5951, 3.7768, \text{ and } 3.6091 \text{ \AA}$ at approximately $2\theta = 14^\circ, 23^\circ, 27^\circ \text{ and } 29^\circ$, respectively and albite ($\text{NaAlSi}_3\text{O}_8$) at $d = 4.1491, 3.2902, 3.0164 \text{ and } 2.6311 \text{ \AA}$ at $2\theta = 24^\circ, 32^\circ, 34 \text{ and } 39^\circ$, respectively, as the major constituent minerals of the clay. Kimambo et al. (2014), also reported similar observations.

The chemical composition results presented in Table 1 show that RMK clay sample consists of mainly kaolinite, which is manifested by the presence of large quantities of alumina and silica followed by Fe_2O_3 and Na_2O whereas other oxides,

$\text{MgO}, \text{CaO}, \text{K}_2\text{O}, \text{ZrO}_2, \text{P}_2\text{O}_5$ and TiO_2 , were present only in trace amounts.

The ATR-FTIR spectrum of RMK shown in Figure 2 revealed the presence of $-\text{OH}$ stretching absorption bands at 3690 cm^{-1} and 3620 cm^{-1} which correspond to Al-OH bonding that are characteristic of kaolinite (Panda et al. 2010). Other stretching bands, $1000\text{-}1120 \text{ cm}^{-1}$ region are due to Si-O bonds. Bending absorption peaks at 911, 787, 745, 529 and 463 cm^{-1} were assigned to the Al-Al-OH, Al-Mg-OH, Si-O-Al, Al-O-Si and Si-O-Si vibrations, respectively (Vempati et al. 1996, Njoya et al. 2006). The functional groups observed in RMK are similar to those obtained from previous studies (Panda et al. 2010) suggesting that the clay is kaolinite and could be responsible for binding heavy metal cations.

The results from the nitrogen adsorption-desorption experiments are presented in Figure 3 where a linear BET plot was displayed revealing that the studied RMK was meso-porous having an average pore diameter, pore volume and BET surface area of 2.991 nm, 0.454 cc/g, 78.691 m^2/g , respectively. In addition, the shape of the isotherm and hysteresis loop for RMK in Figure 4 confirmed that this clay displayed type IV isotherms, which are typical for mesoporous materials.

An estimate of the pore size distributions (PSD) of RMK sample using liquid nitrogen as an adsorbate at 77 K is depicted in Figure 5. It was shown that most pores lie in the mesopore region ($2 \text{ nm} < d < 50 \text{ nm}$), suggesting that the prepared adsorbent was rather effective in adsorption of heavy metals from contaminated water (El-Geundi et al. 2014).

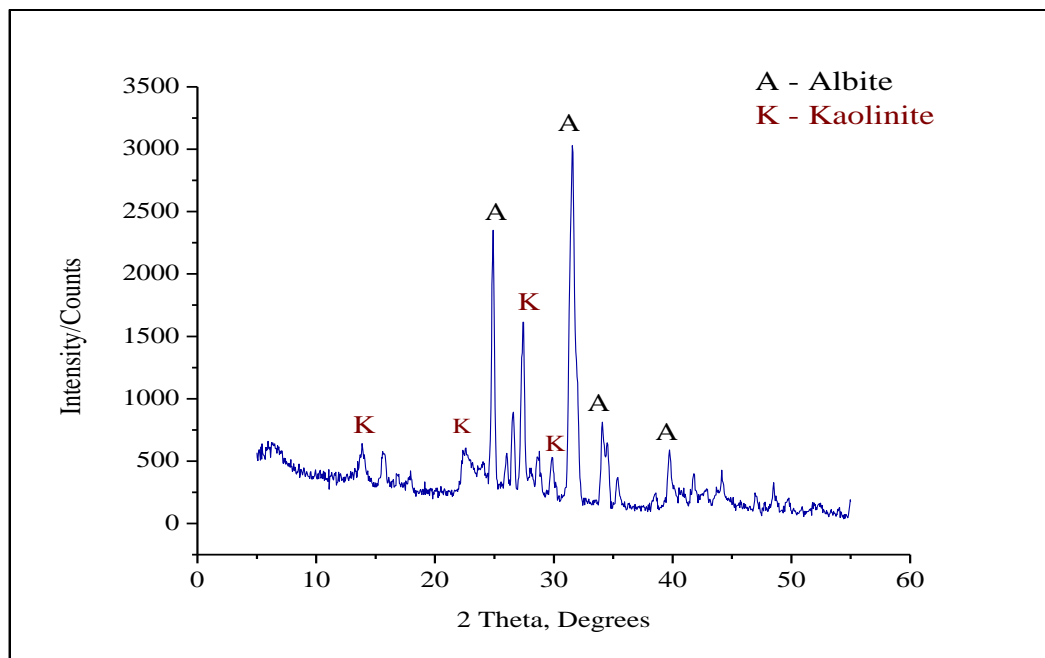


Figure 1: The Diffractogram of RMK

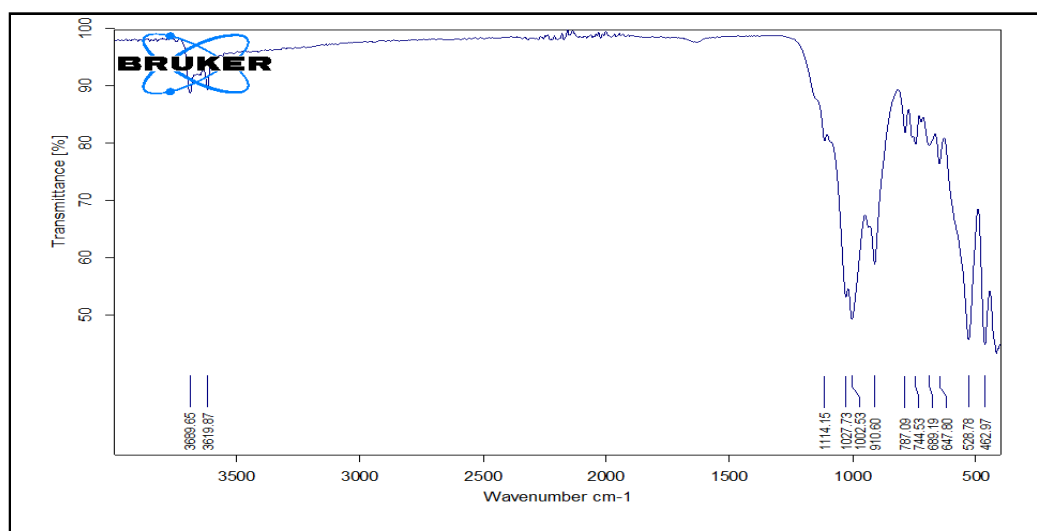


Figure 2: ATR-FTIR Spectrum for RMK

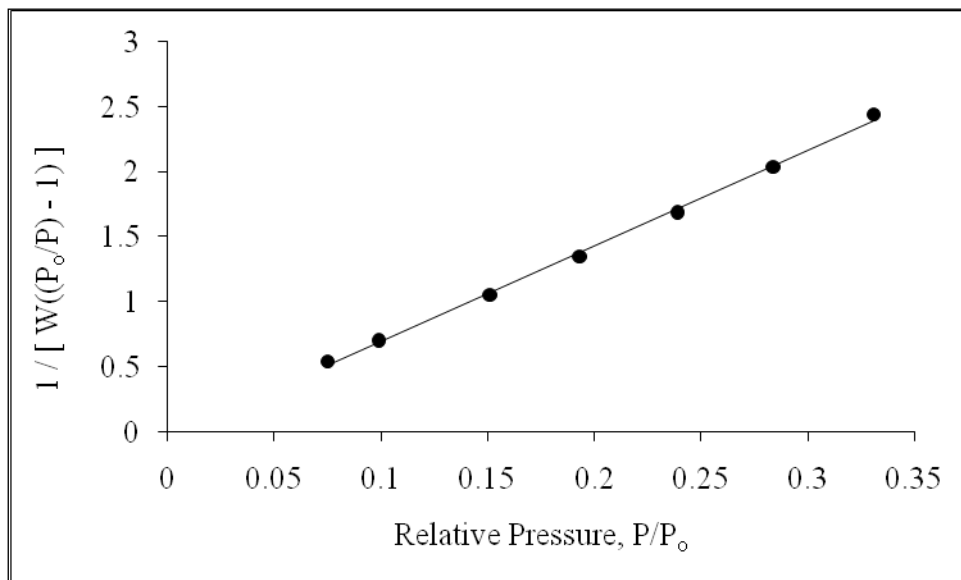


Figure 3: The BET Surface Area Plot for RMK

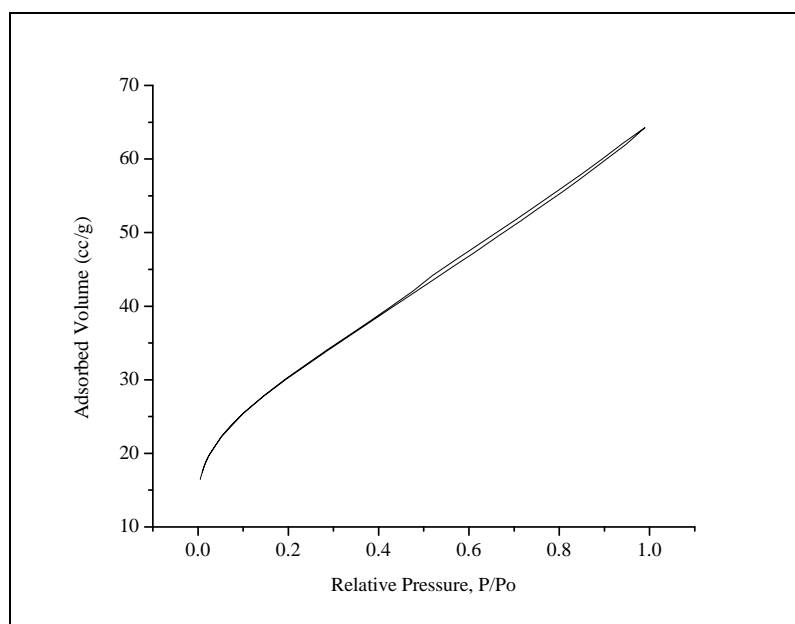


Figure 4: The Nitrogen Adsorption-Desorption Isotherm for RMK

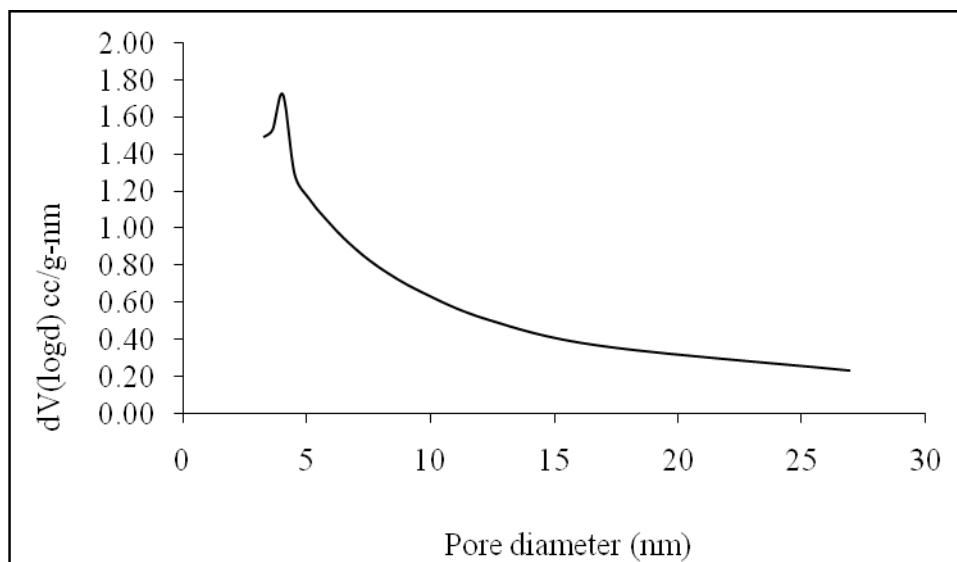


Figure 5: The Pore Size Distribution Curve for RMK

Table 1: Chemical Composition (%) of RMK Clay

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	SO ₃	TiO ₂	Loss on Ignition (LOI)
Composition (%)	49.13	33.97	1.92	0.25	1.07	0.50	
Component	MgO	Cl	CaO	P ₂ O ₅	Na ₂ O	ZrO ₂	
Composition (%)	0.59	0.06	0.53	0.08	1.40	0.06	

The Effects of Adsorbent Doses

Figure 6 shows the results obtained from adsorption experiments using initial metal ion concentration of 5 mg/L, contact time of 3 hrs, particle size of 150 μ m, solution pH 6 at 27 °C and batch volume of 25 mL.

The results indicated an increase in percentage adsorption with increase in adsorbent weight until equilibrium was achieved. This observation is supported by the presence of greater number of active adsorption sites available on the surface of RMK, which ultimately increases the ratio of

number of adsorption sites to the number of heavy metal ions to fill those vacant spaces in the adsorbent (Shukla et al. 2002). The maximum heavy metal removal when RMK sample weighing 0.8 g was used as an adsorbent was found to be 95.12 and 93.31% for Cd²⁺ and Co²⁺, respectively. After the equilibrium was reached, the adsorption process remained constant due to limited number of active sites on the surface of adsorbent, which become occupied with Cd²⁺ and Co²⁺ ions with time. This observation is in agreement with the work of Badmus et al. (2007).

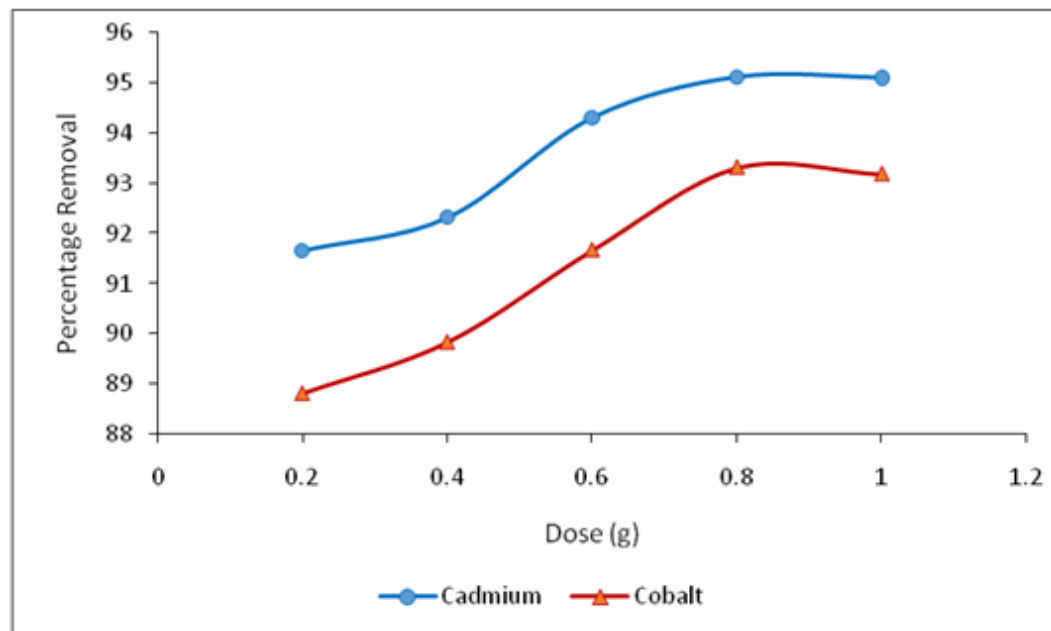


Figure 6: Effect of Adsorbent Dose on the Removal of Cd^{2+} and Co^{2+} Ions

The Effects of Contact Time

The results on the effects of contact time on the adsorption of Cd^{2+} and Co^{2+} ions by the studied RMK adsorbent are shown in Figure 7. From these results, apparently, the rate of percentage removal was observed to be higher in the initial stages because adequate surface area of the adsorbent is considered to be available for the adsorption of heavy metal cations. However, as time progressed, adsorption process and hence its rate was decreasing implying that the adsorption sites were decreasing also. The decrease in adsorption sites and then slow adsorption rate is probably due to the formation of a thin monolayer surface which covers the surface of the adsorbent material causing saturation of active sites and exhaustion of the capacity of the adsorbent as time lapses (Asrari et al. 2010). It can therefore be concluded from this study that adsorption is a function of contact time and it is expected to level up despite longer duration due to

adsorption-desorption equilibrium soon established in the process (Tchobanoglous et al. 1991).

The Effects of Initial Metal Ion Concentrations

The uptake of any particular heavy metal cation by an adsorbent material strongly depends on the initial metal ion concentration available in solution, which makes it an important factor that needs to be determined for an effective adsorption process. The results for the effect of initial metal ion concentration shown in Figure 8 indicate that the percentage adsorption of Cd^{2+} and Co^{2+} ions decreased with the increase in initial metal ion concentration from 5 to 25 mg/L, after which no significant decrease was observed. The decrease in percentage adsorption is due to saturation of a fixed number of adsorbent active sites as the concentrations of heavy metal ions are increased (Tsia and Chan 2010, Salam et al. 2011). The highest

percentage removal of Cd^{2+} and Co^{2+} ions were observed to be 95.29 and 88.56%, respectively, both at initial metal ion concentration of 5 mg/L.

Although the percentage adsorption of Cd^{2+} and Co^{2+} ions decreased with the increase in initial metal ion concentration, Figure 9 revealed that the total adsorption capacity for all adsorbents of both metal ions increased with increase in the initial metal

ion concentrations. The increasing concentration gradient which acts like a driving force to overcome the resistance to mass transfer of the metal ions between the adsorbate and adsorbent species could be the reason for this observation (Das and Mondal 2011). The results of this work are in agreement with that already reported by Dawodu and Akpomie (2014).

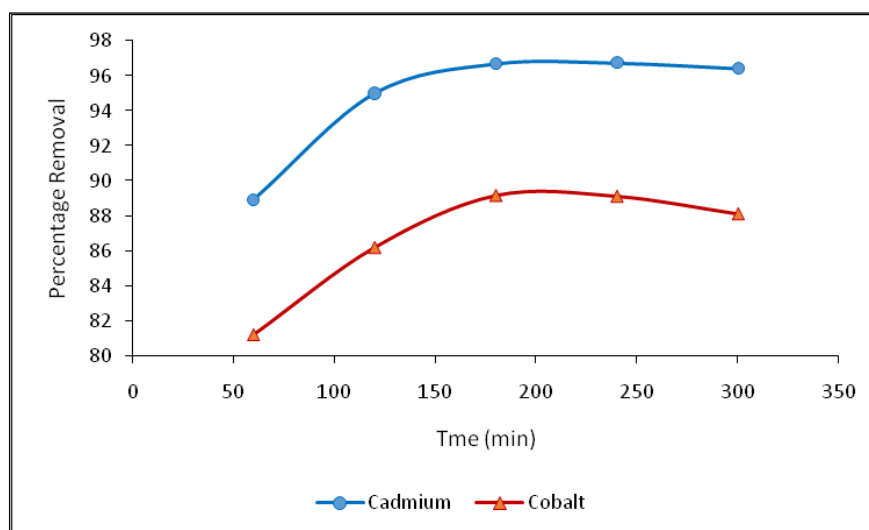


Figure 7: Effects of Contact Time on the Removal of Cd^{2+} and Co^{2+} Ions

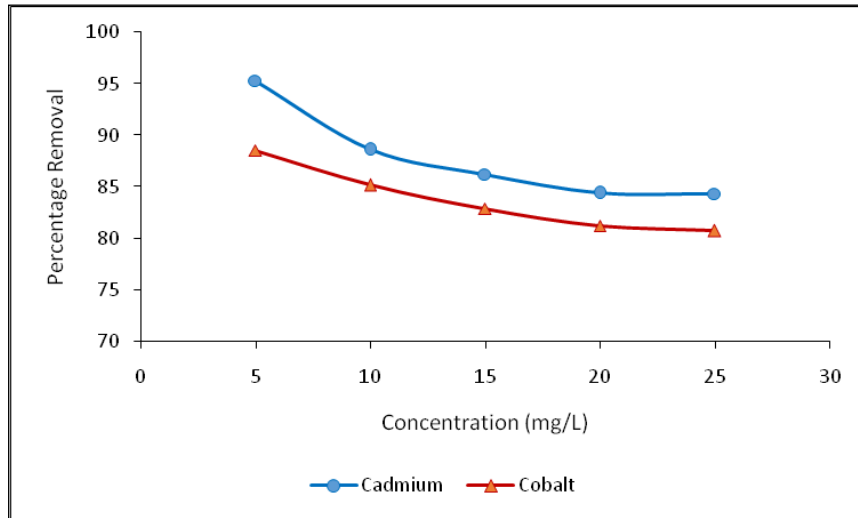


Figure 8: Effects of Concentration on the Removal of Cd^{2+} and Co^{2+} Ions

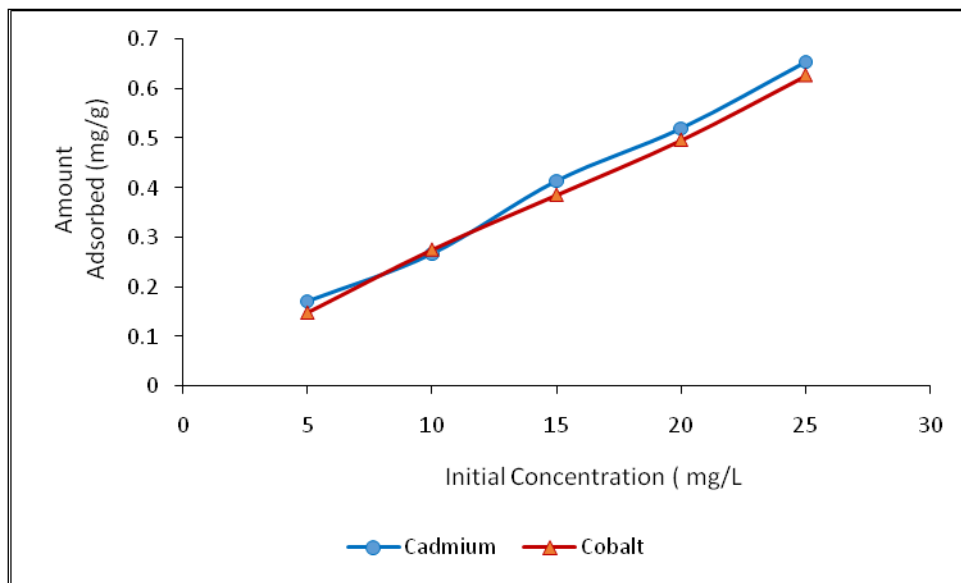


Figure 9: Effects of Concentration on the Adsorption Capacity of RMK

Effects of pH

The initial pH of the solution has also a significant impact on the removal of heavy metals by adsorption process since it determines the surface charge of the adsorbent material and the degree of

ionization of the adsorbate (Imamoglu and Tekir 2008). The manipulated data were used to plot Figure 10 which shows the results of percentage removal of both heavy metal ions. It was observed that the adsorption efficiency was low at lower pH

values (pH 2) probably due to the presence of high number of hydrogen ions in solution that compete with $\text{Cd}^{2+}/\text{Co}^{2+}$ ions for available adsorption sites on the surface of RMK and so adsorption capacity is limited (Hashem 2007). With increasing pH from 4 to 8, the adsorption efficiency was observed to increase due to decrease in concentrations of protons in solution, thereby reducing the competition between hydrogen ions and heavy metal cations for the active sites (Ofomaja et al. 2010). Low adsorption of the metal ions at higher pH values greater than 8 may have been caused by the formation of complexes between heavy metal and OH^- ions, which are likely to precipitate onto the kaolinite structure and therefore inhibit further adsorption (Lisa et al. 2004, Ofomaja et al. 2010). The observed trend in this study is consistent with that observed in previous studies (Rashed and Soltan 2002, Veli and Alyuz 2007, Karapinar and Donat 2009). The maximum percentage removals were observed to be 93.27 and 91.59% for Cd^{2+} and Co^{2+} ions, respectively, at pH 6.0.

Effects of Adsorbent Particle Sizes

The processed data were plotted in Figure 11 and the highest adsorption efficiency for both heavy metals was achieved with particle sizes of 75 μm where 99.20 and 87.17% of Cd^{2+} and Co^{2+} ions, respectively, were adsorbed onto RMK. It was observed that the percentage removal of Cd^{2+} and Co^{2+} ions decreased with increase in the particle size of the adsorbent. This observation was expected because the increase in the adsorbent particle size usually causes a substantial decrease in the surface area of the powder, and as a result, the numbers of active sites on the adsorbent are less exposed to the adsorbate and the metal ions uptake would therefore be decreased (Karapinar and Donat 2009). Thus, smaller particle sizes and hence greater surface areas correlate with greater adsorption as observed in this study.

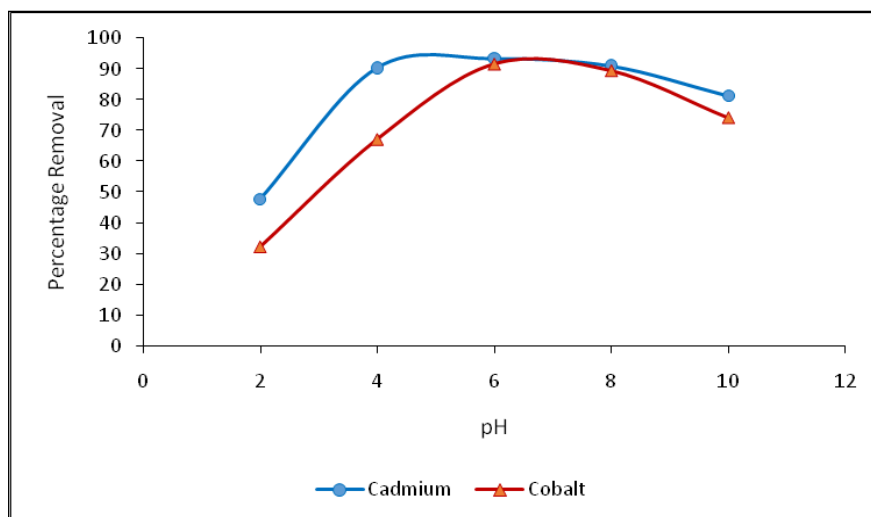


Figure 10: Effects of pH on the Removal of Cd^{2+} and Co^{2+} Ions

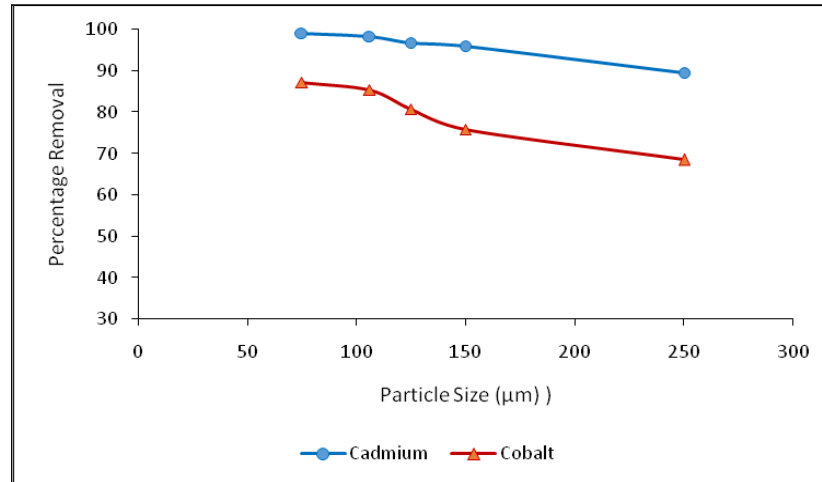


Figure 11: Effects of Particle Sizes on the Removal of Cd^{2+} and Co^{2+} Ions

Adsorption Isotherms

Adsorption isotherms express the relationship between the amounts of adsorbate removed from the liquid phase by unit mass of adsorbent at a constant temperature. The parameters of equilibrium isotherms often give useful information on adsorption mechanism, surface properties and affinity of the adsorbent and they are basic requirements for the design of adsorption systems.

Langmuir and Freundlich adsorption isotherms were tested to analyze the equilibrium data derived from the adsorption of Cd^{2+} and Co^{2+} ions from water on RMK. The equilibrium studies were conducted at initial metal ion concentration ranging from 5 to 25 mg/L using RMK clay sample.

The Langmuir isotherm parameters and their corresponding correlation coefficients R^2 listed in Table 2 were calculated by manipulating equations (3) and (4).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where, q_e is the monolayer adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively reflects the affinity between the adsorbent and adsorbate, and q_m is the maximum monolayer adsorption capacity of adsorbent (mg/g). The constants, q_L and K_L , can be determined from the slope and the intercept of the linear plot of C_e/q_e against C_e .

The equilibrium data obtained from this study were tested against Langmuir model as shown by linear plot of C_e/q_e versus C_e in Figure 12 for both metal ions. From the aforementioned figure, the adsorption of both Cd^{2+} and Co^{2+} ions on RMK gave a straight line suggesting clearly that the linear fit is fairly good and therefore enables the applicability of Langmuir adsorption model. For the initial Cd^{2+} ions concentration from 5 to 25 mg/L, the values of R_L ranged from 0.033 to 0.007 and 0.270 to 0.0705 indicating a favorable adsorption of Cd^{2+} and Co^{2+} ions onto RMK, respectively.

The quality of the isotherm fit to the experimental data was evaluated based on

the magnitude of the correlation coefficient (R^2) for the regression. From Table 2, it was seen that, the correlation coefficient (R^2) of both Cd^{2+} and Co^{2+} ions were 0.999 and 0.966, respectively, indicating a good fit of the monolayer Langmuir isotherm to the adsorption of both heavy metal ions by RMK clay sample.

The Freundlich isotherm model is applied to non-ideal sorption taking place on heterogeneous surfaces where the linear form of the equation is given by equation (5) (Freundlich 1906).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where; K_F and n are Freundlich adsorption constants related to the adsorption capacity and intensity of the adsorbents, respectively. The linear plot of $\log q_e$ versus $\log C_e$ determines these constants. Furthermore, it was experimentally determined that, the

value of n between 1 and 10, is indicative of favourable adsorption (Slejko 1985).

The applicability of Freundlich adsorption model was analyzed by testing the equilibrium data obtained from this study using the plot of $\log q_e$ versus $\log C_e$ represented by Figure 13 for both Cd^{2+} and Co^{2+} ions. The values of n and K_F listed in Table 2 were determined from the slope and the intercept of a linearized form of equation (5). The results show that the values of n range between 1 and 10 indicating that both Cd^{2+} and Co^{2+} ions are favourably adsorbed on RMK clay (Slejko 1985).

Nevertheless, Langmuir isotherm displayed a better fitting model than the Freundlich isotherm because of higher correlation coefficients than the latter, indicating the applicability of monolayer coverage of Cd^{2+} and Co^{2+} ions on the surface of RMK adsorbent.

Table 2: The Langmuir and Freundlich Parameters for Adsorption of Cd^{2+} and Co^{2+} Ions on RMK Clay

Metal Ion	Langmuir Parameters				Freundlich Parameters		
	q_m	K_L	R_L	R^2	K_F	N	R^2
Cd^{2+}	0.949	5.890	0.033 to 0.007	0.999	1.061	1.905	0.955
Co^{2+}	0.803	0.526	0.270 to 0.071	0.966	0.261	1.871	0.909

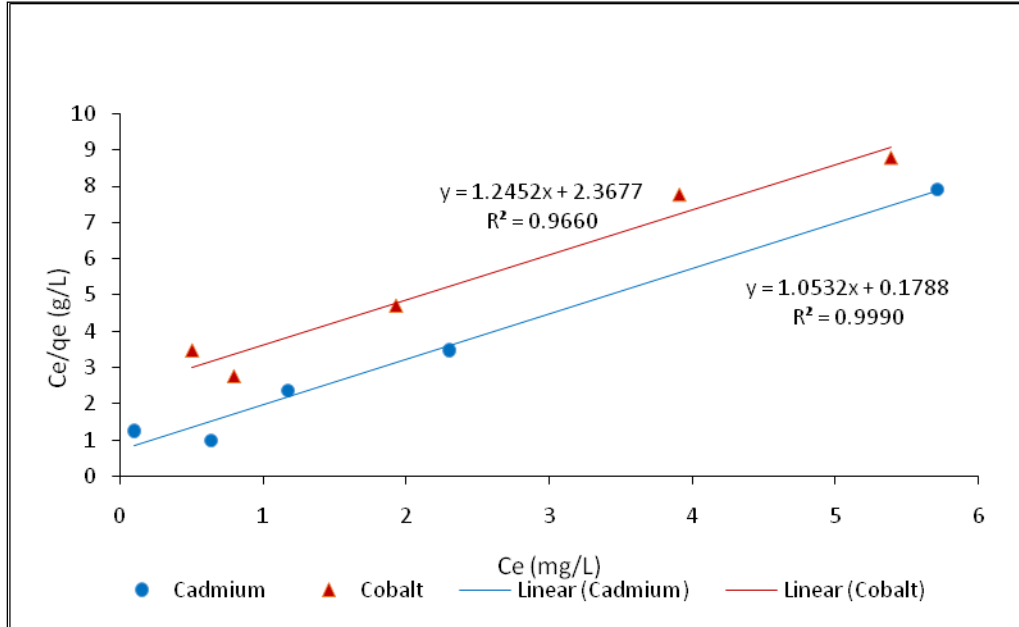


Figure 12: Langmuir Plot for the Adsorption of Cadmium and Cobalt on RMK

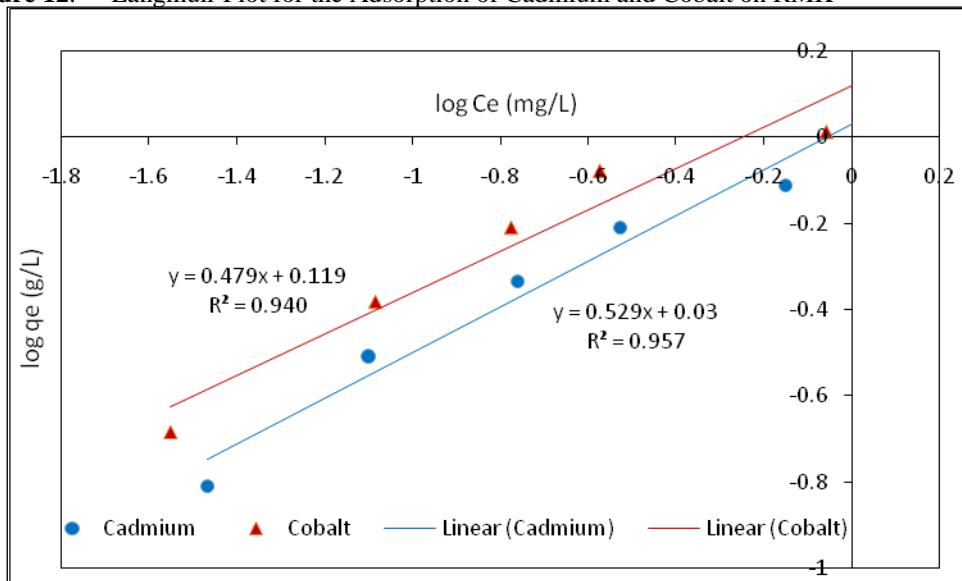


Figure 13: Freundlich Plot for the Adsorption of Cadmium and Cobalt on RMK

CONCLUSIONS

Raw Malangali kaolin clay was found to be useful as a potential and an effective adsorbent for adsorptive removal of Cd²⁺

and Co²⁺ ions from water. The optimum conditions for batch adsorption of both Cd²⁺ and Co²⁺ ions were investigated and obtained at initial metal ion concentrations,

contact time, pH, adsorbent doses and adsorbent particle sizes of 5 mg/L, 180 min, 6, 0.8 g and 75 μm , respectively.

The equilibrium data described by Langmuir and Freundlich isotherm equations showed that the Langmuir isotherm displayed a better fitting model to the experimental data than the Freundlich isotherm because of the higher correlation coefficients that the former exhibited, thus, indicating the applicability of monolayer coverage of Cd^{2+} and Co^{2+} ions on the surface of RMK. The study therefore concludes that raw Malangali kaolin clay can be used as suitable adsorbent for adsorptive removal of heavy metal ions from water.

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