Full Length Research Paper

Determination of best blend of zeolite 4A-metakaolin matrices for heavy metal removal from synthetic wastewater

Nwafulugo F. U.[1]*, Adefila S. S.[2], Olawale A. S.[2] and Ajayi O. A.[2]

[1]Department of Chemical Engineering, Kaduna Polytechnic, Kaduna, Kaduna State, Nigeria.
[2]Department of Chemical Engineering, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.

Nigeria is blessed with abundant solid mineral deposits scattered in different parts of the country. As a measure to curtail the total dependence of imported commercial adsorbent for the treatment of our petroleum wastewater, Kankara kaolin from Katsina state, Nigeria was pretreated and blended with a commercial zeolite 4A from UOP, New Jersey, USA. The determination of the best blend of matrices of zeolites 4A and metakaolin was based on the adsorption capacities of the blends. It was found that Matrix 4 composed from 75% metakaolin and 25% zeolite 4A yielded a unique and best matrix, with removal efficiency of almost 100%, except for lead. The compositions of the spectrum of matrices are: Matrix 1 – 0% metakaolin and 100% zeolite 4A; Matrix 2 – 25% metakaolin and 75% zeolite 4A; Matrix 3 – 50% metakaolin and 50% zeolite 4A; Matrix 4 – 25% metakaolin and 75% zeolite 4A; and Matrix 5 – 100% metakaolin and 0% zeolite 4A. The treatment profile suggested enhanced ion exchange ability as the key lever force.

Key words: Crude oil, petroleum wastewater, zeolite 4A, pollution, heavy metals.
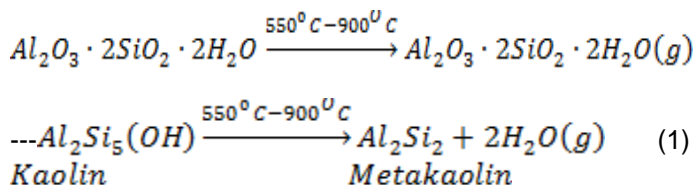
INTRODUCTION

The ability to adjust the pores to precisely determine uniform openings allows for molecules smaller than its pore diameter to be adsorbed whilst excluding larger molecules. The different pore sizes of synthetic zeolites open up a wide range of possibilities in terms of "sieving" molecules of different sizes or shapes from gases and liquids (Adel et al., 2010).

Zeolites are microporous crystalline solids with well-defined structures that contain silicon, aluminum and oxygen in its framework and cations (Atlas of zeolite framework type, 2001). The chemical inertness of zeolites, modifications, unique properties and selectivity, can provide effective solutions for environmental pollution by minimizing or removal of the pollutants by secondary treatment of the petroleum wastewater. Due to its unique and special properties which are suitable for various kinds of chemical reactions, zeolites 4A has been widely used in many applications such as in ion exchange separation processes. Inglezakis et al. (2000) reported that pre-treatment leads to a high effective capacity of a zeolitic material. Inglezakis et al (2004) also observed

that modification of the natural zeolite sample is favorable, leading to an increase of removal efficiency by 32-100%, hence blending with kaolin became necessary to reduce the cost of using high cost commercial zeolite 4A for the treatment of our petroleum wastewater. Kaolin is one of the industrial minerals that can be found in commercial quantity. Nigeria has an estimated reserve of about two billion metric tons of kaolin deposit scattered in different parts of the country including Ogun, Edo, Plateau, Nassarrawa and Katsina. The market for kaolin is large, sustainable and expanding because of the numerous applications of the products. As a measure to improve industrial dependant on local kaolin, there is an outright ban on the importation of kaolin into the country (http:www.foramfera.com/index.php/market-research-reports). The raw form of kaolin is less reactive and forms hydrosodalite when reacted with sodium hydroxide.

---

*Corresponding author. E-mail: francaunoma@yahoo.com.

Kaolinite has to undergo the processes of metakaolinization to improve the reactivity. The process of metakaolinization involves beneficiation and calcination processes to form metakaolin. Calcination occurs within the temperatures of 550 to 900°C (Kovo, 2011). This process involves the loss of hydroxyl group and this is followed by rearrangement of the octahedral layer to tetrahedral structure in the calcined clay:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{550^0C-900^UC} Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O(g)$$

$$---Al_2Si_5(OH) \xrightarrow{550^0C-900^UC} Al_2Si_2 + 2H_2O(g) \quad (1)$$
Kaolin   Metakaolin

The importance of this calcination process is to remove the presence of undesirable volatile matter and to make the product as aforementioned more reactive and a quest for metallic ions during ion exchange process.

To achieve high performance, the adsorbent must have high abrasion resistance, thermal stability and small pore diameters which are a gateway to high surface area for adsorption. The distinct pore structure enhances fast transport of the metallic ions. Myzaurah et al. (2013) stated that the adsorption of metal ions depends on the nature of the adsorbent surface and adsorbate species in the solution. As such when there is an increase in pH, there will be less positive charges producing an increased electrostatic attraction between the metal and the acid group. This could be attributed to electrostatic effect that causes the adsorption capacity to increase with decrease in radius. According to Mulu et al. (2013), metal adsorption efficiency increases with increase in adsorption sites available for adsorption. At higher concentration, there could be saturation of adsorption sites thus the available sites for adsorption becomes fewer and the percentage removal which depends on concentration decreases (Gharbani et al., 2011). This research will show the interaction effects of the parameters pH, contact time and adsorbent dose on the percentage metal removal as a function of the best blend of zeolite 4A-metakaolin matrix.

MATERIALS AND METHODS

Procedure

Here, this study gives a detailed description of the process of procuring and processing the commercial zeolites 4A, kaolin, and transformation to sodium base metakaolin, blending with commercial zeolite 4A and then the adsorption of ion exchange processes.

Procuring zeolite and kaolin

The commercial zeolite 4A was purchased from UOP, a subsidiary of Honeywell group of companies, New Jersey, USA while the kaolin was procured from Kankara,

Katsina State, Nigeria.

Beneficiation of kaolin

About 2 kg of white kaolinite clay was procured from Kankara village in Katsina State of Nigeria. This was mixed with 10 L of tap water to form slurry and was allowed to age for four days. At each day of sedimentation, decantation of the overflow was done and replaced with fresh tap water to the fourth day when the overflow has become less milky and free from suspended particles. The thick slurry was sieved and carefully spread out to dry at atmospheric condition for two days. The now beneficiated kaolin was gathered and stored. The lumped kaolin clay was milled with a ball miller and sieved with a 150 μm mesh.

Calcination of kaolin

The powered dried kaolin was placed in locally fabricated crucibles and charged into an already heated furnace at 750°C for 3 h where according to Ugal et al. (2010), decomposition occurs leading to the destruction of the structure and removal of the undesirable volatile matter. By this process, kaolin was converted to metakaolin.

Conditioning of metakaolin to sodium base

The conditioning was done with 8 M NaOH solution which was prepared by dissolving 400 g of sodium hydroxide pellets in 1250 mL of deionized water. 300 g of metakaolin was added to 1.5 L of the 8 M NaOH and well mixed to form slurry. The mixture was then heated up to 90°C with continuous vigorous stirring for 4 h. The slurry was allowed to cool for several hours, washed for about 5 times to remove excess NaOH, after which it was allowed to settle overnight, oven dried at 110°C for 1 h, packed and stored in a nylon bag.

Particle size analysis and blending

Particle size analysis for both the commercial zeolite 4A and metakaolin was carried out by ball milling and sieving with the same mesh of aperture 150 μm to ensure similar particle size distribution. The specified ratios in Table 1 were measured, mixed and properly blended with a domestic blender to ensure homogeneity forming zeolites 4A-metakaolin matrix.

Preparation of standard solution

The procedure from Delloyd's (2000) laboratory technological resource (2000) was adopted. This provides a method of preparing 1000 mg/L (ppm) atomic absorption standard of a metal from its pure element or from its salt using deionized water.

Nickel

To prepare 5 mg/L of nickel metal from nickel nitrate,

Table 1. Nomenclated blends of Metakaolin and Zeolite 4A.

Description	Nomenclature (Matrix)
0% metakaolin + 100% Zeolite 4A	1
25% metakaolin + 75% Zeolite 4A	2
50% metakaolin + 50% Zeolite 4A	3
75% metakaolin + 25% Zeolite 4A	4
100% metakaolin + 0% Zeolite 4A	5

according to the aforementioned procedure, 4.9530 g of nickel nitrate [Ni $(NO_3)_2.6H_2O$] was dissolved in 1 L of deionzed water in a volumetric flask and was diluted to 5 ppm using this correlation:

$$C_1V_1 = C_2V_2 \qquad (2)$$

where C_1, V_1 and C_2, V_2 were the initia and final concentration and volume respectively. Similar methods were used for lead, nickel and cadmium.

Lead

An accurate measurement of 1.5980 g of lead nitrate [Pb $(NO_3)_2.4H_2O$] was dissolved in 100 mL of deionized water and dilute to 1 L in a volumetric flask and further diluted to 5 mg/L.

Cadmium

Accurate measurement of 2.1032 g of cadmium [Cd $(NO_3)_2.4H_2O$] was dissolved in 250 mL of deionized water and vigorously stirred to dissolve then diluted to 1 L in a volumetric flask and further diluted to 5 mg/L.

Manganese

Correct measurement of 1.000 g of manganese powder was dissolved in 50 mL of concentrated hydrochloric acid. The solution was diluted to 1 L in a volumetric flask with deionized water and was further diluted to 5 mg/L.

Procedure for removal of heavy metal from simulated wastewater

The best matrix was determined by using the different matrices for removal of nickel, lead, cadmium and manganese from the simulated wastewater. The simulated wastewaters were prepared with the standard solutions in accordance with the procedure presented in this study's materials and methods. Different samples of the simulated wastewater were prepared by dosing ultimately all metals together. The rate of removal of individual metals from the wastewater samples was determined using different contact time, matrix dose and pH. The adsorption of the four heavy metal ions were carried out in 50 mL stopper conical flask by taking

appropriate amounts of the wastewater sample and adsorbent (zeolite 4A/metakaolin). The pH values of the solutions were adjusted from 2 to 12 with 0.5 M NaOH and 0.5 M HCl, and controlled with a pH meter according to Barakat (2008) batch adsorption process.

Determination of effect of the various variables on adsorption capacity

Accurate measurement of 0.5, 1.0, 1.5, 2.0 and 2.5 g of zeolites 4A-metakaolin matrices were dispensed separately into each of the five 250 mL Erlenmeyer flasks simulated wastewater samples. 50 mL of the samples were added to the content of the five flasks in turn and stoppered. This was followed by agitation at constant speed, for a period of 3 h and pH of 4. The mixtures in each flask were filtered by suction pump through a sintered glass crucible and the different filtrates were collected and analyzed using Atomic Absorption Spectrometer (AAS). The same procedure was used at varying contact time from 0 to 60 min at pH of 4 and at the optimal Blend dose and finally varying pH from 2 to 12 at the best contact time and the optimal Blend dose.

RESULTS AND DISCUSSION

### Effect of contact time on adsorption of heavy metals removal

Figures 1 to 5 for Matrix 1, 2, 3, 4 and 5 show the effects of contact time on the removal of Ni, Pb, Cd and Mn ions. The optimal contact time to attain equilibrium with Matrix 1 (0% metakaolin and 100% zeolite 4A) was experimentally found to be 5 to 10 min and 60 min for Matrix 5 (100% metakaolin and 0% zeolite 4A). It is evident from the results that contact time required to attain equilibrium is dependent on the initial concentration of heavy metals and the type of resin used as reported by Taha et al. (2010). The longer contact time of 60 min for metakaolin could be reasoned to the fact that raw clay was used which might indicate limited ionic sites due to collapsible pores. The kaolin could not be structurally rigid as zeolites 4A, as such there could be the possibility of collapsed pore structures as it comes in contact with water thereby hindering immediate diffusion into the ionic sites.
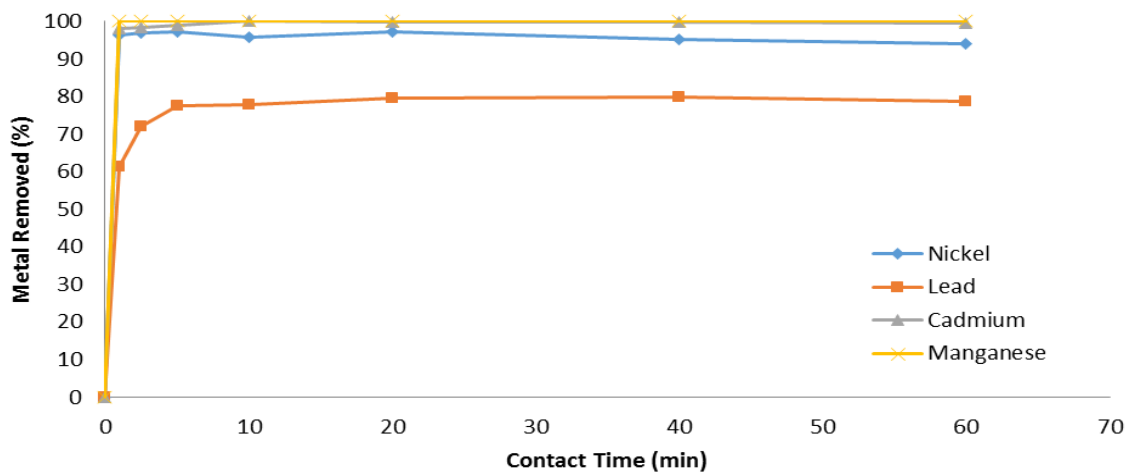
Effect of pH on heavy metal removal

From Figures 6 and 7 for blends 1 and 5 respectively was used to establish the pH. The removal is significant at a basic medium. At high values of pH of 10 for lead as shown in Figure 6, there may be the possibility of hydroxides formation or formation of complexes which might clog the pores leading to partial destruction of the structure (Inglezakis et al., 2000). The insignificant uptake at pH of 2 and 4 for blend 5 (Figure 7) could probably be as a result of attack of the buffering acid on
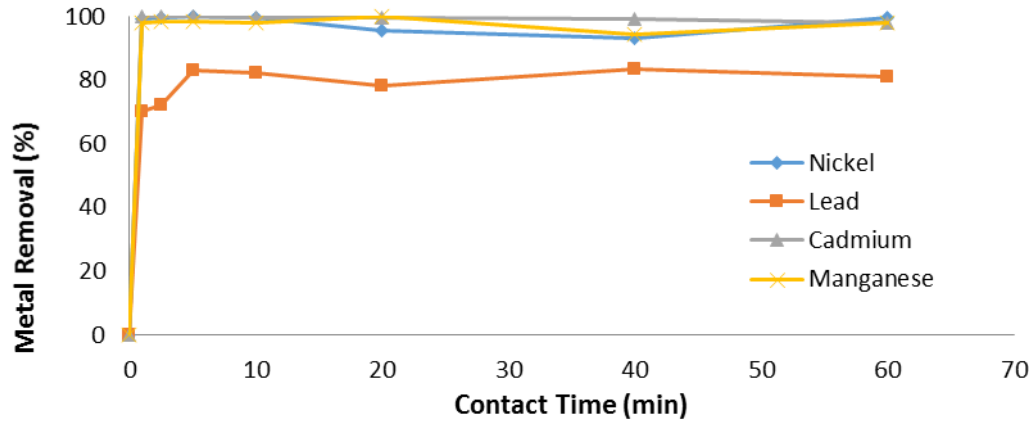
Figure 1. Effect of contact time on heavy metal removal for Matrix 1 (0% metakaolin and 100% zeolite 4A).
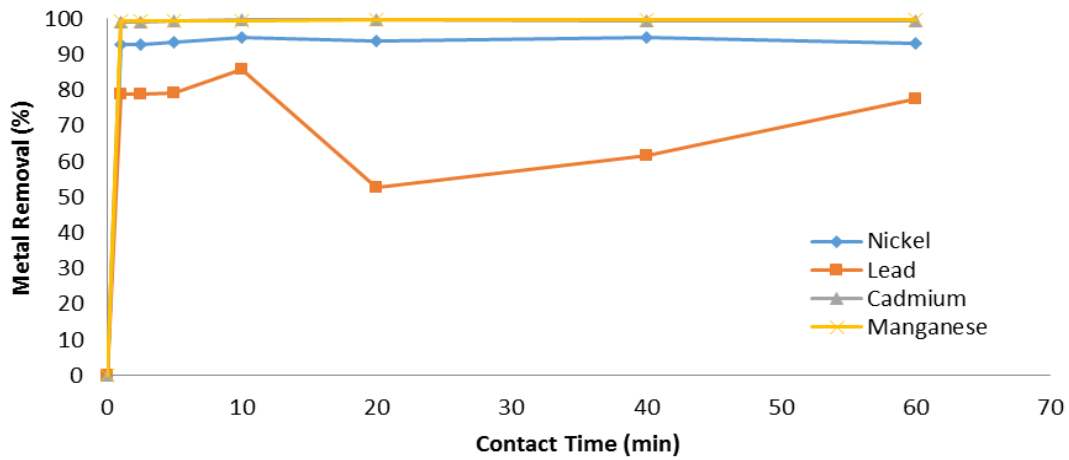
*Figure 2. **Effects of contact time on heavy metal removal by Matrix 2 (25% metakaolin and 75% zeolite 4A***

Figure 3. Effect of contact time on heavy metal removal by Matrix 3 (50% metakaolin and 50% zeolite 4A).
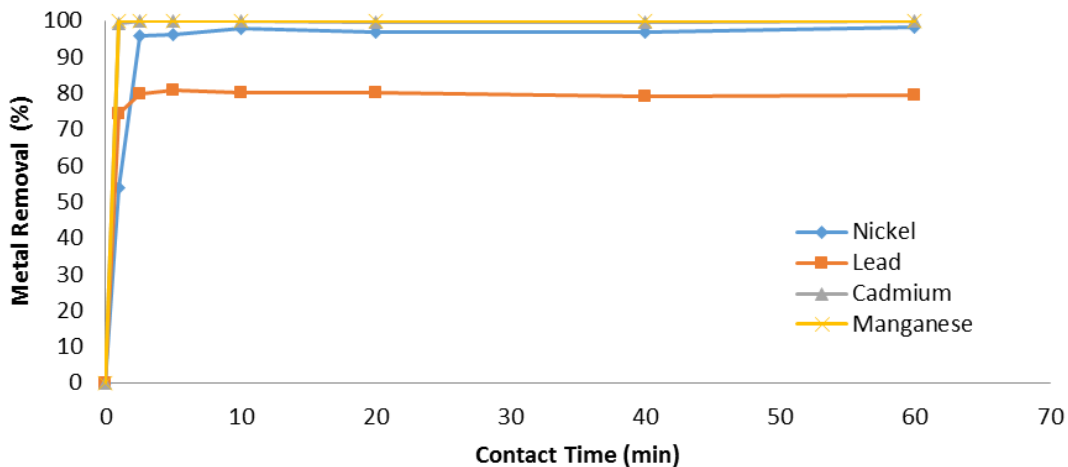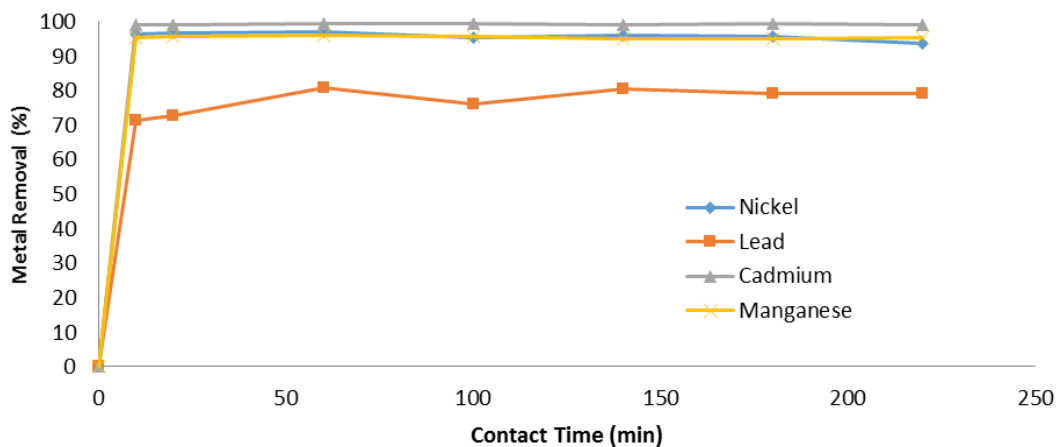
Figure 4. **Effect of contact time on heavy metal removal by Matrix 4 (75% metakaolin and 25% zeolite 4A).**

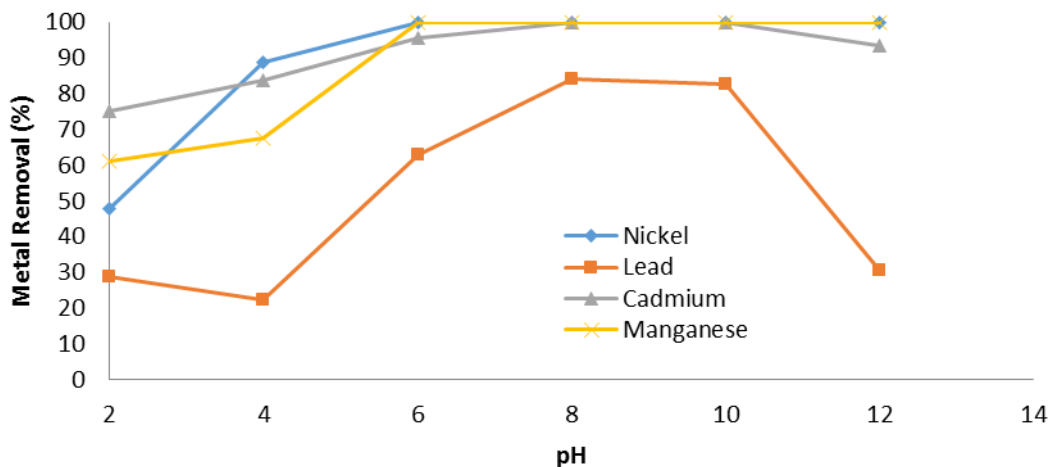**Figure 5.** Effect of contact time on metal removal by Matrix 5 (100% metakaolin and 0% zeolite 4A).

Figure 6. Effect of pH on heavy metal removal for Matrix 1 (0% metakaolin and 100% zeolite 4A).
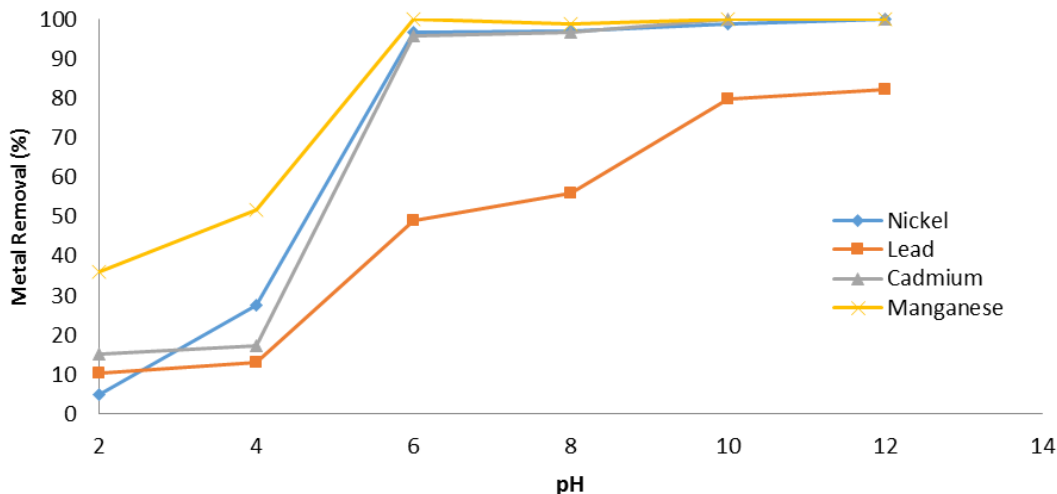
Figure 7. Effect of pH on heavy metal removal for Matrix 5 (100% metakaolin and 0% zeolite 4A).
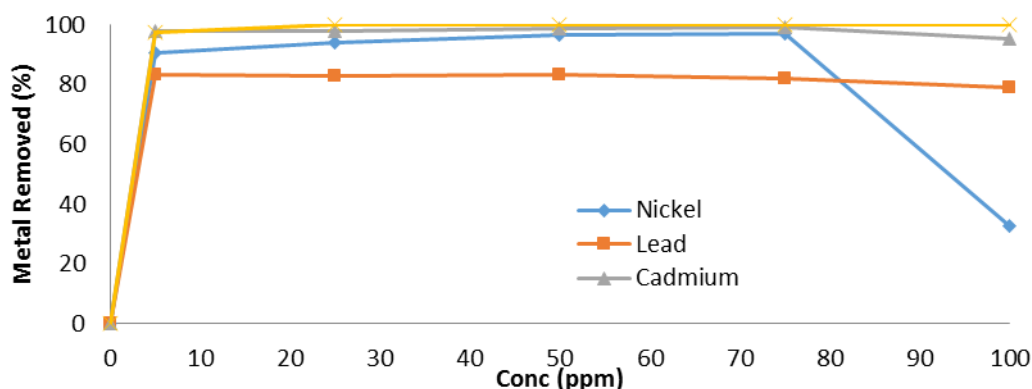

Figure 8. Effect of initial concentration on heavy metal removal for Matrix 1 (0% metakaolin and 100% zeolite 4A).

the clay and the leaching behavior of the acid and raw clay. An optimal pH range of 8 to 10 was obtained for all the metals. The mechanism of adsorption at the surface reflects the nature of the chemical interaction between the metal ions in the solution and adsorbent active sites, thus at pH lower than 4, more H^+ ion concentration may be produced which could compete with metal ions for exchange sites (Hui, 2000). The pH value at which the heavy metal ions were adsorbed could also be a measure of the relative affinity of metal cations for adsorbent surfaces.

Effect of initial concentration of heavy metals on adsorption

It can be seen that percentage removal decreases with decrease in initial concentration as shown in Figure 8. For Ni, Cd and Mn ion, it recorded a sharp uptake to nearly 100% removal. It can then be deduced that fractional adsorption is dependent of the initial metal ion

concentration. At higher concentration, the number of heavy metal ions is relatively higher and the zeolite 4A/metakaolin is saturated with sodium ions, so further increase has no effect (Inglezakis et al., 2000), thus the percentage removal still depends on the initial concentration and electron affinity of the metals under considerations. Ni ion recorded a sharp drop to almost 25% removal. This could be due to increasing driving force of metal ions towards active sites on the adsorbent, but when the percentage of metal ion adsorbed decreased with increasing initial metal ion concentrations, it indicates that there is decrease in active sites on the adsorbents as more metal ions were adsorbed (Ismail et al., 2013), thus leading to limited ionic sites.

Effect of adsorbent dose on blends

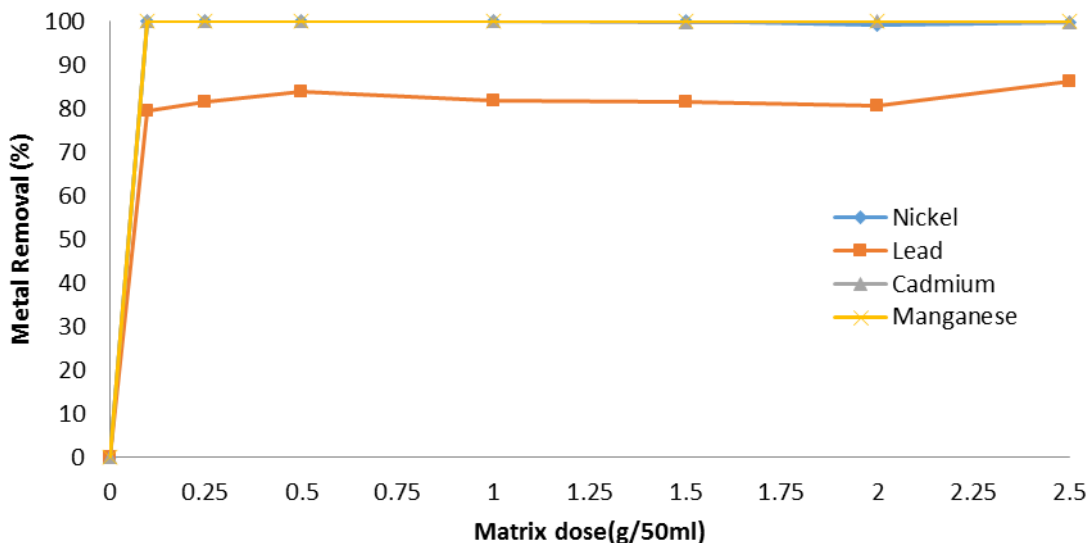Figures 9 to 13 represent the removal of Ni, Pb, Cd and Mn ions as a function of adsorbent dose at a sample pH

Figure 9. Effect of Matrix 1 (0% metakaolin and 100% zeolite 4A) dose on heavy metal removal.
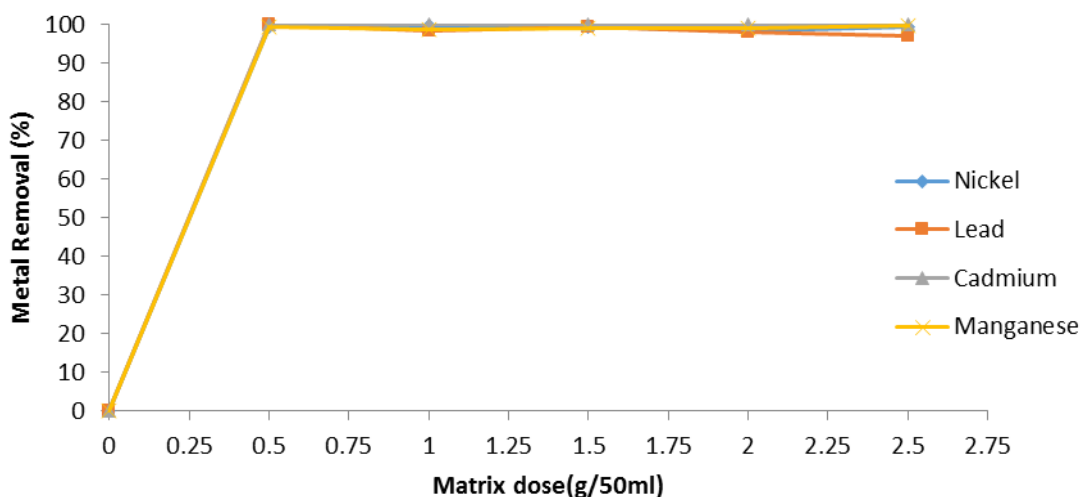

Figure 10. Effects of Matrix 2 (25% metakaolin and 75% zeolite 4A) dose on heavy metal removal.

of 8 contact time of 10 min (Figure 9) and 60 min. The adsorbent dose was varied from 0.5 to 2.5 g and equilibrated for 60 min for metakaolin and 10 min for zeolite 4A. Thus increasing the adsorbent dosage, led to a sharp percentage removal for almost all the metal ions except for lead whose ionic radius is large compared to Ni, Cd and Mn. The results also indicate that the removal efficiency increases up to the optimum dosage of 1 g/50 ml for the matrices, beyond which the removal efficiency has little significant change with the matrices dose as indicated in Figure 12 which agrees with observations made by Selverj et al. (2003). It is apparent that the percentage removal of heavy metals increases rapidly with increase in the dosage of the adsorbents due to the

greater availability of the exchangeable sites and surface area, thus available sites relates to the equilibrium behaviour whereas accessibility relates to the kinetic behavior of the ion exchange system as also reported by Edison et al. (2011).

The parameters, contact time and adsorbent dose were used to get the optimal Blend from Matrix 2 (25% metakaolin and 75% zeolite), Matrix 3 (50% metakaolin and 50% zeolite) and Matrix 4 (75% metakaolin and 25% zeolite). It was observed that at contact time of 10 min and 1 g Matrix dose, equilibrium was attained probably because of the high reactivity of zeolite 4A–metakaolin matrix with well enriched sodium base which led to high ionic sites for ion exchange as indicated in Figure 13.
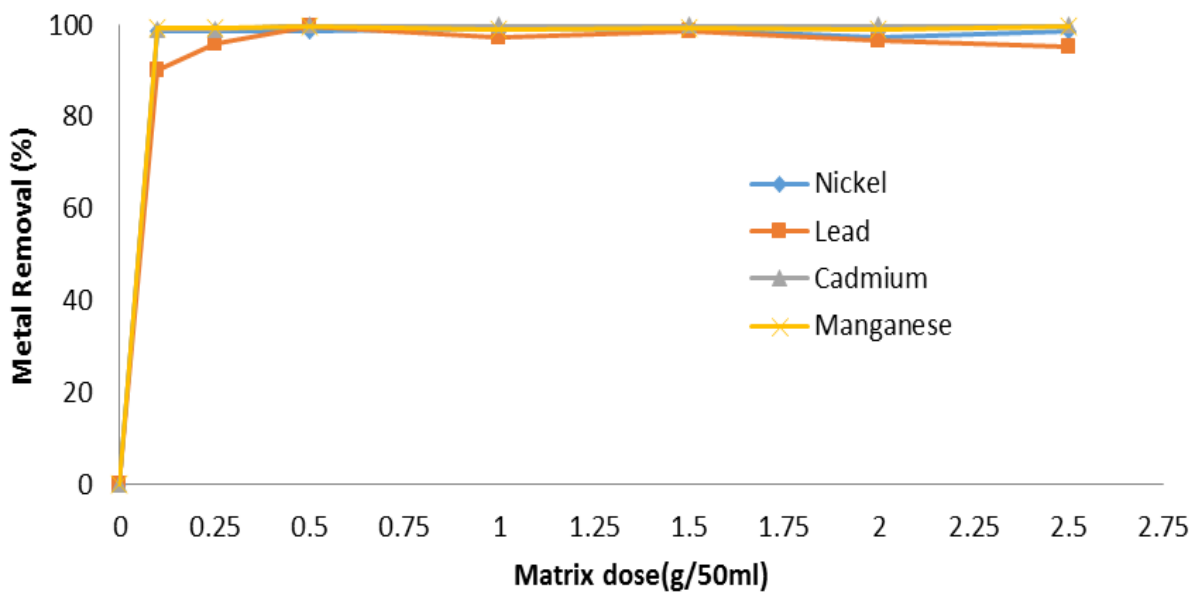
Figure 11. Effects of Matrix 3 (50% metakaolin and 50% zeolite 4A) dose on heavy metal removal.
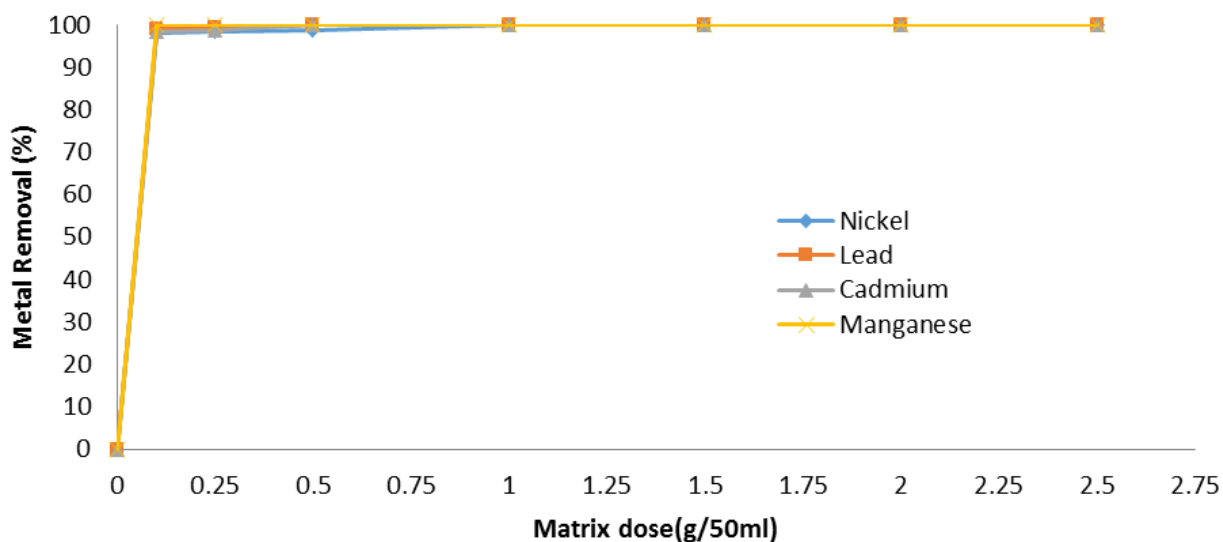

Figure 12. Effects of Matrix 4 (75% metakaolin and 25% zeolite 4A) dose on heavy metal removal.

The unique properties of zeolites 4A was further exploited to enrich metakaolin obtained from raw clay. The three different matrices were treated at same conditions of 5 mg/L initial concentration, contact time of 10 min and at its initial pH of 8. The Matrix 2, 3 and 4 (Figure 14) depicts high significant removal of nearly 100% except for Lead, using Lead as the bases of comparison for Matrix 2, 3 and 4. Matrix 4 was considered as the optimal matrix with the best bend of 75% metakaolin and 25% zeolite 4A because it almost achieved aggregate removal of all the metals under consideration and has less quantity of the

expensive zeolite 4A and more locally available metakaolin.

Conclusion

The heavy metal removal profile proved that efficient zeolites 4A – metakaolin matrix were achieved after the calcinations, metakaolinization and conditioning processes. The difference in percentage removal of different heavy metal ions at the same initial metal concentration, zeolite dose and contact time may be
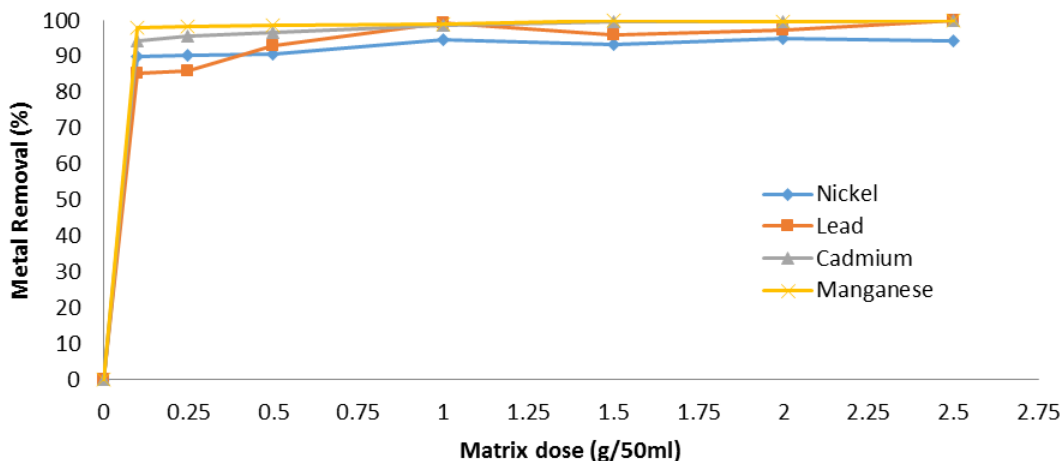
Figure 13. Effect of Matrix 5 (100% metakaolin and 0% zeolite 4A) dose on heavy metal removal.
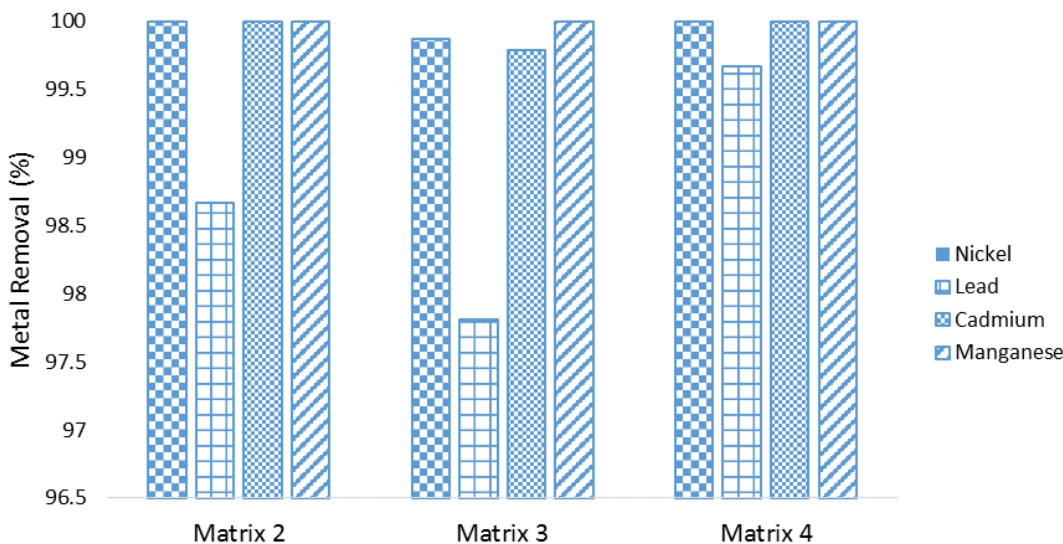

Figure 14. Determination of the optimal blend.

attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent. Matrix 4 with the relatively larger pore size and higher ionic sites, with corresponding enhancing accessibility and attraction, respectively, proved to be the best blend. This is apart from the blend's relatively higher surface area per unit mass.

REFERENCES

Adel AI, Mohameda R, Ibrahima IA, Kinib G, Koopman B (2010). Synthesis, optimization and characterization of zeolite A and its ion-exchange properties. Advanced

Materials Department, Central Metallurgical Research and Development Institute, CMRDI, Cairo, Egypt. Physicochemical. Eng. Aspects 366 (2010) 80–87.

Atlas of Zeolite Framework Types (2001), Fifth Revised Edition.

Barakat MA (2008). Adsorption of Heavy metals from aqueous solutions on synthetic zeolite. Res. J. Environ. Sci., 2: 13-22.

Delloyd Analchem Resouces (2000). sourced from PyeUnicam Atomic absorption Data   Book.

Edison M, John K, Freeman N, Mansoor M, Antoine F, Mulaba B (2011). Cu (II) Removal   from   Synthetic Wastewater by Ion Exchange Process. Proceedings of the World Congress on Engineering and Computer Science Vol. II WCECS, San Francisco, USA.

Gharbani P, Tabatabael S. M, Dastmalachi S, Mosenharzandi A, Mahrizad A, (2011). Adsorption of Choloform from Aqueous Solution by Nano Tio$_2$" Int. J. Heavy Metal ions in Wastewater by Zeolite 4A and Residual Products from recycled Coal fly ash. Department of Mechanical Engineering. The Hong Kong University of Science and Technology, Hong Kong China.

Hui KS, Chao CYH, Kot SC (2005). Removal of Mixed

Inglezakis VJ, Grigoropoulou H (2004), Effects of operating conditions on the removal ofheavy metals by Zeolite in fixed bed reactors. Department of Chemical Engineering, Process Analysis and Plant Design, Laboratory of Chemical Process Engineering, Zografou Athens, Greece.

Inglezakis VJ, Hadjiandreou KJ, Loizidou MD, Grigoropoulou HP (2000).   Pretreatment of Natural Clinoptilolite in a Laboratory-scale ion-exchange Packed Bed. Department of Chemical Engineering, National Technical University of Athens, Zografou Campus, Athens, Greece.

Ismail MA, Eltayeb MAZ, Abdel Mages SA (2013). Elimination of Heavy Metals from Aqueous Solutions using Zeolite LTA Synthesized from Sudanese Clay   Department of Chemistry, Faculty of Science and Technology, Al Neelain University, Khartoum 11121, SUDAN.

Kovo AS (2011). Development of Zeolites and Zeolite Membranes from Ahoko Nigerian kaolin University of Manchester Faculty of Engineering and Physical Sciences School of Chemical Engineering and Analytical Science pp 160-194.

Mulu BD (2013) "Batch Sorption Experiment, Langmuir and Fredulich Isotherm Studies for the Adsorption of Teff Straw (Ercgrostistef) Agricultural Waste. Department of Chemistry, College of Natural and Computational Sciences Mekelle University. Mekelle Ethopia J. Thermdynamics Hindew.

Myzaurah H, Hamdzah ZU, Mohamed M, Gustaf N, Tony HH, Nurfarhain MR (2013) "Optimization of Parameters Affecting Adsorption of Nickel (II), Zinc (II), Lead (II) on Dowex 50 W Resin using a Response Surface Methodology Approach. J. Environ. Sci. Technol., 6: 106–118.

Nano Dimension (IJND).

Selvaraj R, Younghun K, Cheol KJ, Kyunghee C, Jongheop Y (2003). .Batch Adsorptive Removal of Copper Ions in Aqueous Solutionsby Ion Exchange Resins: School of Chemical Engineering, Seoul National University, Kwanak-gu, Seoul: 151-742, Korea.

Taha A, Waly A,Dakroury M, El-Sayed GO, El-Salam AG (2010). Assessment Removal of Heavy Metals Ions from Wastewater by Cement Kiln Dust; J. Am. Sci., Egyptian Fuel Manufacturing Pilot Plant (FMPP), Benha, Egypt.

Ugal JR, Hassan KH, Ali IH (2010). Preparation of Type 4A Zeolite from Iraq kaolin: characterization and properties measurement. Department of Chemistry, College of Science for Women, university of Diyala, Iraq: 142   –   146. http://www.foramfera.com/index.php/market-reseach-reports.