African Journal of Science and Technology (AJST)
Science and Engineering Series Vol. 6, No. 2, pp. 55 - 66

THE INFLUENCE OF PH AND ADSORBENT CONCENTRATION ON ADSORPTION OF LEAD AND ZINC ON A NATURAL GOETHITE

Abdus-Salam, N. and Adekola, F. A.

Department of Chemistry, University of Ilorin, P. M. B. 1515, Ilorin,Nigeria.

ABSTRACT:- *Adsorption characteristics of Pb and Cd were conducted on a natural goethite from Kaduna (Niperia) and compared same with a synthetic goethite. The adsorption data was fitted into Langmuir model which gave Langmuir constants k and* X_m *for Pb and Cd as 4.99 & 2.40 and 1.43 & 1.05 respectively. The adsorption behavior was essentially the same, although, synthetic goethite sorbed a little more metal ion than the natural goethite. This was attributed to the higher proportion of goethite in synthetic than natural goethite per unit mass of sample rather than greater chemical reactivity of the synthetic goethite. The influence of variable pH and adsorbent concentrations on the sorption of Pb and Cd by the natural goethite was studied. Sorption efficiency was greatly governed by pH with nearly 100% adsorption of Pb occurring at initial pH of 5. Generally, Pb was sorbed more strongly with increasing pH from 3 to 5 than Cd and thus poses less environmental threat. Efficient removal of Pb was achieved at lower dose of goethite, as there was no appreciable increase in the amount of Pb adsorbed when the adsorbent dose was increased.*

INTRODUCTION

Metals and their compounds are indispensable to the industrial, agricultural and technological advancement of any nation. The numbers of applications of metals for commercial uses continue to grow with the developments of modern Science and Technology. Inevitably, industrial processes and spent commercial (metallic) products generate large quantity of metallic waste products, which are discharge into the water or land-dump sites. It has been estimated that the toxicity due to metallic discharge annually, into the environments far exceeds the combined total toxicity of all radioactive and organic wastes as measured by the quantity of waste required to dilute such wastes to the drinking water standard. (1, 2) This gives rise to the growing concern on the gradual build-up of toxic metals in the ecosystem.

Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment (3, 4). Research on Pb has become a dominant topic for environmental and medical scientists for two obvious reasons: (1) It has no known biological use and (2) It is toxic to most living things (4). Lead readily bioaccumulates in the human-rich surface layer of the soils due to its complexation with organic matter. It is the least mobile heavy metal in soils under reducing or non-acidic conditions. Furthermore, it is one of the most common trace metal contaminants in urban soils due to atmospheric deposition from industries and automobile emission.

When Pb is ingested, there is rapid uptake into red blood cells forming PbB, then into soft tissues (kidney, bone marrow, liver and Brain) and followed by a slower-redistribution to mineralizing tissues (bones and teeth) (1, 3, 5).

Hydrous oxides have long been recognized as reactive soil materials that control the availability of metal nutrients and toxins to plants. Goethite (α-FeOOH) is the most abundant and most stable of all forms of iron-oxides in soil and its surface chemistry affects the distribution of soluble species in soil (6). Synthetic goethite have been extensively study and applied for the removal of heavy metal contaminants from industrial solutions (7), radionuclides from nuclear reactor plants (8, 9) and for municipal water treatment (10). Despite successes recorded at batch equilibration level, recent researches have shown that synthetic goethite, which commonly occurs as fine powders or as hydroxides gel, is not desirable as column packing material (11). In order to overcome this setback, sand-coating goethite preparation was recently introduced. It was found to be suitable for column operation (10, 12).

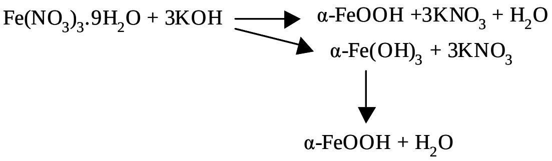
The process of preparation of sand-coating goethite is cumbersome, technical and expensive. A substitute, which provides comparative advantage in terms of adsorption property, column conditions and cost, will be desirable. Kaduna goethite was found to contain quartz and silica in its natural structure (Ph.D thesis Abdus-Salam 2005). This present study investigated the comparative sorption of lead and cadmium on a natural goethite from Kaduna (Nigeria) and a synthetic goethite with a view to evaluate the efficiency of the natural goethite for the removal of Pb and Cd from aqueous solution. The influence of pH as well as adsorbent loading on the sorption capacity was also studied.

MATERIALS AND METHODS

Goethite Preparation

A natural goethite was obtained from a deposit in Kaduna, Kaduna state, Nigeria. The goethite sample was earlier characterized and its quantity in terms of amount of goethite per unit mass of sample was determined (Ife J. Sci.-accepted for publication).

Synthetic goethite was prepared following literature method (13, 14). 100.0g of analytical grade of $Fe(NO_3)_3.9H_2O$ was dissolved in 1L of de-ionised water in a 2L plastic container, which was previously sterilized. The solution was hydrated for 24hrs at pH 1.6 with continuous stirring with teflon-coated magnetic stirrer. Then, 2.5M KOH solution was added drop-wise until solution attained a pH of 12. The resulting thick suspension was aged for 5 days in a thermostated oven at 60°C. This was followed by dialysis for 7 days using de-ionised water, which was changed twice daily until the conductivity of the wash solution equals to that of de-ionised water. The goethite paste was then oven dried at 60°C. The schematic equation of reaction is



The point of zero charge (pzc) of both natural and synthetic goethite was determined by pH drift method using sodium nitrate as reference indiferent electrolyte. The graph of 6pH versus the final pH was plotted separately for natural and synthetic goethite. The point of intersection of the curve on the final pH axis, where 6pH is zero, is the point of zero charge.

Lead and Cadmium Adsorption Experiments

Analytical grade $Pb(NO_3)_2$ and Cd $(NO_3)_2$ salt were used for the preparation of the stock solutions of Pb^{2+} and Cd^{2+} respectively. The adsorption experiments were carried out in 0.1M $CaCl_2$ background electrolyte solutions to ensure a relatively constant and defined ionic strength of the solution during the adsorption of the metals. Dilutions were appropriately made with 0.1M $CaCl_2$ solution, which serve as background electrolyte to the working concentrations ranging between 5 – 750ppm and 0.05 – 15ppm for Pb^{2+} and Cd^{2+} respectively. The reactor for the equilibration reaction was basically a 100ml conical flask holding 1.0g air-dried goethite sample and 25ml of the working concentration. The fraction of the natural goethite passing through 90μm was used. The reactor content was mechanically agitated on an orbital shaker, Mk V Lh fermentation type, for 8hr at 120 rpm and at room temperature (27 ± 1°C). The contact experiment was done in triplicates and the reactor contents were separately filtered into plastic vials using Whatman 110mm Ö filter paper. An Alpha 4 Chem Tech Analytical Atomic Absorption Spectrometer (AAS) with graphite atomizer was used to determine Pb and Cd concentration in the filtrate. The triplicates AAS values were averaged and the amount of Pb^{2+}/ Cd^{2+} was calculated from the difference between the added and equilibrium concentration of Pb^{2+}/ Cd^{2+} (15).

Sorption Kinetics

The batch reactor consists of a 250ml 3-neck round bottom flask, which is fitted with a reflux condenser, a 0-100°C graduated thermometer and the 3rd neck was permanently corked except when aliquot sample were withdrawn. 250ml of 300ppm Pb^{2+} (or 6ppmCd^{2+}), was thermostated at 30°C before 1g – goethite was added. The content was electromagnetically agitated for 3hr while clear aliquot sample were withdrawn at various time intervals with a 5ml plastic syringe and filtered into plastic vials. Filtrates were analyzed for residual Pb^{2+}/Cd^{2+}.

Effect of pH on Pb^{2+}/Cd^{2+} Adsorption.

On the basis of previous experimental experience (Abdus-Salam, 2004), 1.0g goethite was added into the batch reactor containing 25ml of 10 – 750ppm of Pb^{2+} (or 0.05 – 15ppm Cd^{2+}). The Pb^{2+}/Cd^{2+} stock solution was prepared using distilled water and the pH of the reactor was adjusted to between 3 and 5 with either HNO_3 or NaOH to the desired pH. The choice of pH range (3-5) was informed partly by the initial Pb^{2+}/Cd^{2+} concentrations in which its hydrolytic products are completely soluble and partly by a condition that confer a predominantly negative surface charge on the goethite. The whole lot was agitated on an orbital shaker for 8hr at 27 ± 1^0C. Equilibrium concentrations of Pb^{2+} and Cd^{2+} were determined by AAS.

RESULTS AND DISCUSSIONS

pH Selection

Goethite has variable surface charge characteristics, which gave it a surface charge that is pH dependent. The pH of the medium in which goethite is suspended, like other tropical soils, affects not only the magnitude of the surface charge but also metal hydrolysis and organic matter solubility (16). It has been observed that when the pH increases, divalent metal retention on the surfaces via adsorption, inner sphere surface complexation and/or precipitation increases (17).

Pb and Cd sorption in our experiments followed the expected trend of increasing metal retention with increasing medium pH as shown in Figures 1 and 2. When the pH of the adsorbing medium is increased from 3 – 5, there was a corresponding increase in deprotonation of the goethite surface leading to a decrease in H^+ ion on the goethite surface. This creates more negative charges on the goethite surface, which favours adsorption of positively charge species as a result of less repulsion between the positively charge species and the positive sites on the goethite surface (18, 19). At initial pH 5, adsorption of Pb^{2+} was practically total (100%) for all concentrations range studied while it decreased to as low as 37% adsorption at pH3 and at the highest concentration

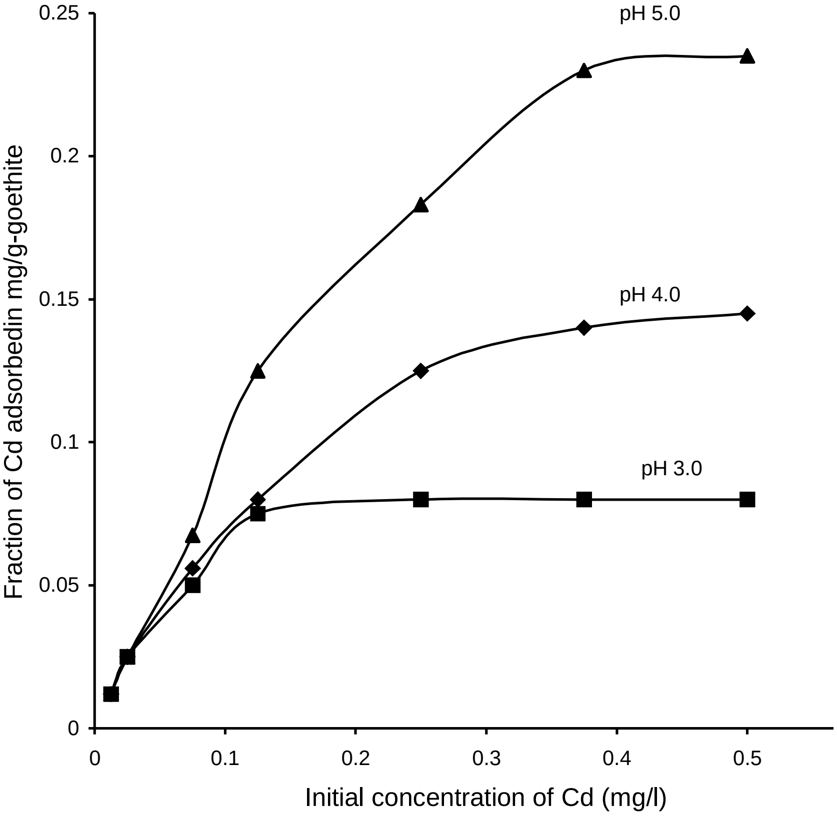


Figure 1: Adsorption of Cd on Kaduna goethite at pH 3.0, 4.0 and 5.0

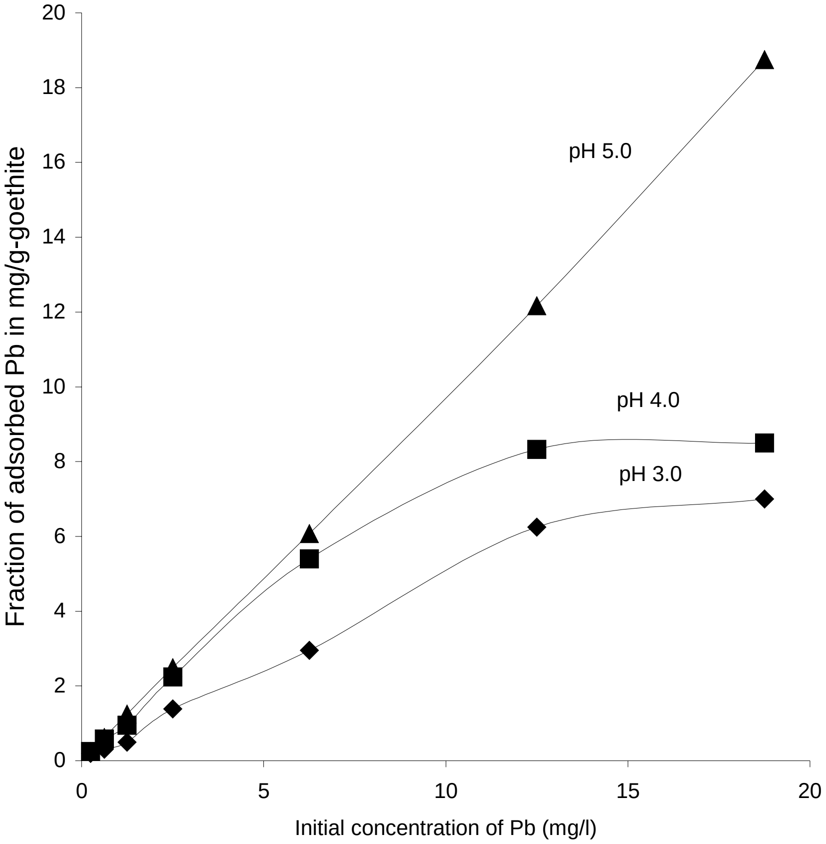


Figure 2: Adsorption of Pb on Kaduna goethite at pH of 3.0, 4.0 and 5.0

(750ppm Pb^{2+}). A comparable trend had earlier been reported for synthetic goethite (20) in which the greatest proportion of Pb^{2+} (~60%) was adsorbed at pH4.5 and 100% adsorption at pH6. In a related experiment carried out at pH5.5, up to 90% of the initial lead concentration was adsorbed by a synthetic goethite (21). Thus, the behaviour of Kaduna (natural) goethite with respect to Pb^{2+} and Cd^{2+} adsorption is similar to that of synthetic goethite used by some other researchers.

The dependence of metal ion adsorption on pH as observed by some researchers over a wider range of pH (3-12) has an S-like adsorption curve (22, 23, 24). The S-like curve describing fractional adsorption, as a function of pH was not obtained probably due to lower pH range used (pH 3-5) where these metal ions are still sufficiently soluble. Even where it was reported, there is the likelihood of the precipitation of the hydroxide forms of these metals (at pH > 8). The solubility of metals is known to be lowered at higher pH values (24, 25). Thus, results that gave S-like curve were reflection of adsorption and precipitation processes on goethite rather than adsorption only.

If all adsorption sites on goethite surface are equally available and energetically the same for adsorption, the fractional metal adsorption versus pH curves, Figures 1 and 2, would have been independent of initial metal concentration, but this was not the case. This characteristic that is more apparent at higher concentration is a departure from Langmuir behaviour and is suggestive of the presence of different site types with different adsorption characteristics. From our infrared results of this goethite (an Ife J. Sci. article already accepted for publication), 3–different OH coordination groups were identified. Each group may correspond to different adsorption energy. Consequently, adsorption sites with greatest reactivity are filled first before sites with lower reactivity. Fractional metal adsorption at lower concentration was independent of pH and this was particularly shown with adsorption of Cd at the various pH values where fractional adsorption was essentially the same (Figure 4.43). This differential surface reactivity of goethite, was also observed by some researchers who worked on synthetic goethite and related minerals (24, 26, 27).

The Influence of adsorbent (goethite) dose on adsorption of lead at constant adsorbate concentration was studied for the purpose of determining the right goethite mass that will bring about a better decontamination of Pb - contaminated effluent. Figure 3 is the plot of the fractions of lead adsorbed versus adsorbent dose. Although, there was an increasing Pb adsorption as adsorbent dose increases, the percentage of Pb adsorbed per g-goethite decreases. Efficient removal of Pb was attained at lower dose of goethite, as there was no appreciable gain in the amount of Pb adsorbed commensurate with the increasing quantity of adsorbent.

Lead and Cadmium Adsorption

The initial pH of the reacting medium (~ 7.0) was slightly lower than the pH_{pzc} of all the goethite samples. At this pH of 7.0, most of the adsorption sites on the goethite surface are positively charged with some neutral charge sites. Under this condition, adsorption is expected to be unfavourable by electrostatic forces. The only plausible reason for the observed metal ions adsorption is for the process to be by other factors. The point of zero charge, pzc, of Kaduna goethite was found to be 7.8. At pH below the pzc, the goethite surface had a net positive charge. The adsorption of positive species will be electrically unfavourable. When adsorption takes place below the pzc then, the adsorption may be attributed to either (i) metal adsorption on to the few negatively charge surface sites and/or (ii) an adsorption of anionic species preceding cationic species, which increases the net negative on the goethite surface.

The influence of metal ion concentration was noted on the percentage metal adsorbed (data not shown). As initial metal ion concentration increased, the percentage metal ion adsorbed decreased while the total amount of metal adsorbed per g-goethite increased. Adsorption of Pb^{2+} and Cd^{2+} involve higher energy sites on goethite surface, and as initial concentration of metal ion increases the higher energy sites are first saturated and thereafter, adsorption to the lower energy (the less energetically favourable) sites begins resulting in a decrease in the adsorption efficiency and percentage metal ion adsorbed (19). The amount of Cd and Pb adsorbed on the goethite is a function of the metal ion affinity for goethite surface and the type of the surface complex formed. The affinity observed followed the order Pb > Cd and this order is

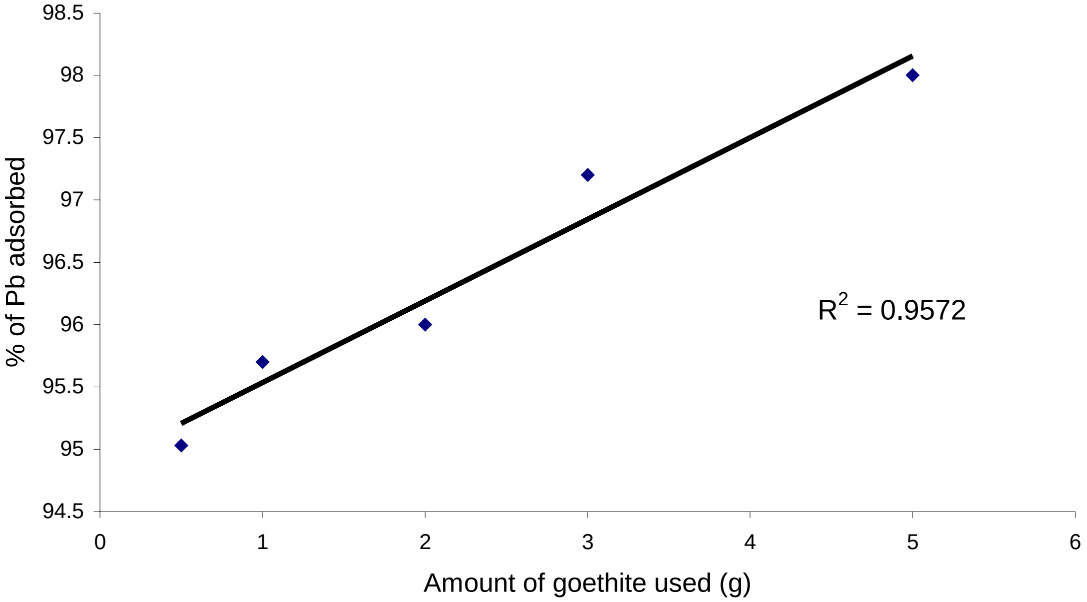


Figure 3: Effect of adsorbent (Kaduna goethite) dose on adsorption of Pb

reflected in the Langmuir bonding energy coefficient, K, which is highest for the most adsorbed metal ions. Although, the quantity of metal ions adsorbed by the natural goethite was different from the previous results obtained by other researchers working on synthetic goethite, the order is essentially the same (28, 29). The differences in the quantities of metals adsorbed by this natural goethite and goethite synthesized by other workers could be attributed to a number of factors. These include the metal loading concentrations or volume, the contact time and the amount of adsorbent used, which varied among various researchers. Essentially, there was an agreement, between our results and the results obtained by others who worked with synthetic goethite, at lower loading concentrations where a total (100%) adsorption was recorded.

Recent spectroscopic evidence has demonstrated that these metals (Cd and Pb) form inner-sphere surface complexes on iron oxide, which is a more specific type of reaction (30) rather than diffusion process. There is a preferential adsorption pattern on the goethite that favours Pb than Cd, which was also observed on some permanently, charged soil surfaces (31). The chemistry of this trend may be attributed to the differences in behaviour among these metals or their ions in solution. Whereas, Pb (II) is adsorbed as hydrolyzed species, Cd (II) is not. This behaviour is attributed to a number of factors which include (i) the smaller hydrated radius of lead (II) (0.401nm) compared to cadmium (II) (0.426nm) (32); (ii) the higher electronegativity of Pb than Cd (2.10 and 1.69 respectively); (iii) the pK_{oH} (negative log. of hydrolysis constant) of 7.78 and 11.70 for $Pb(OH)_2$ and $Cd(OH)_2$ respectively; and (iv) the strength of acidity of these metals (Pb is a border line hard Lewis acid while Cd is soft Lewis acid). These factors make Pb to be more preferentially adsorbed through inner-sphere surface complexation reactions than Cd.

Figures 4 and 5 illustrate the adsorption isotherms for Pb and Cd on Kaduna goethite. Although, initial metal concentrations varied, the metal behaviour on goethite was essentially the same. As initial adsorbate concentration was increase, there was corresponding increase in the amount of metal adsorbed. This was followed by a little increase in the amount of metal adsorbed irrespective of the initial metal concentration. The adsorption data for Cd and Pb fitted well into linearized form of Langmuir adsorption isotherm as shown in Figures 6 and 7. The Langmuir constants K and X_m obtained for Cd and Pb are 1.43 & 1.05 and 4.99 & 2.40 respectively.

It is interesting to note that the adsorption capacity of natural goethite is similar to that of synthetic goethite as shown in Figure 10 for Pb adsorption isotherm. The higher adsorption capacity of synthetic goethite to natural may be due to percentage active substrate in the material used. While the proportion of goethite in Kaduna sample was 63.60% only, as obtained from its mineralogical determination (Ife J. Sci.), as compared to 100% in a

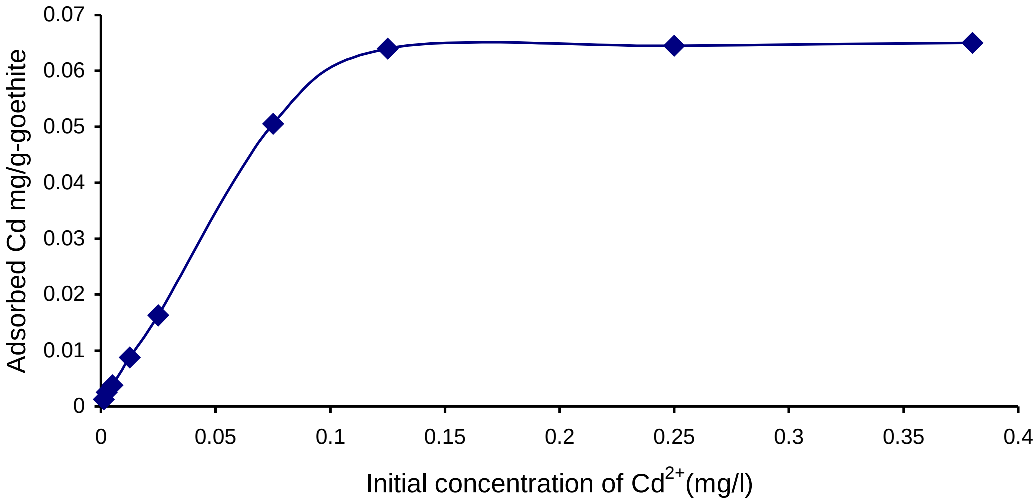


Figure 4: Adsorption isotherm for Cd on Kaduna goethite

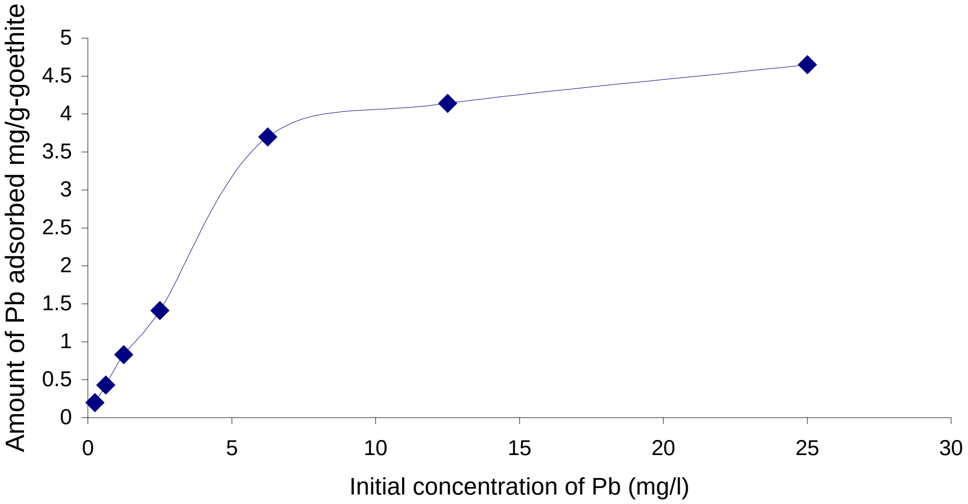


Figure 5: Adsorption isotherm for Pb on Kaduna goethite

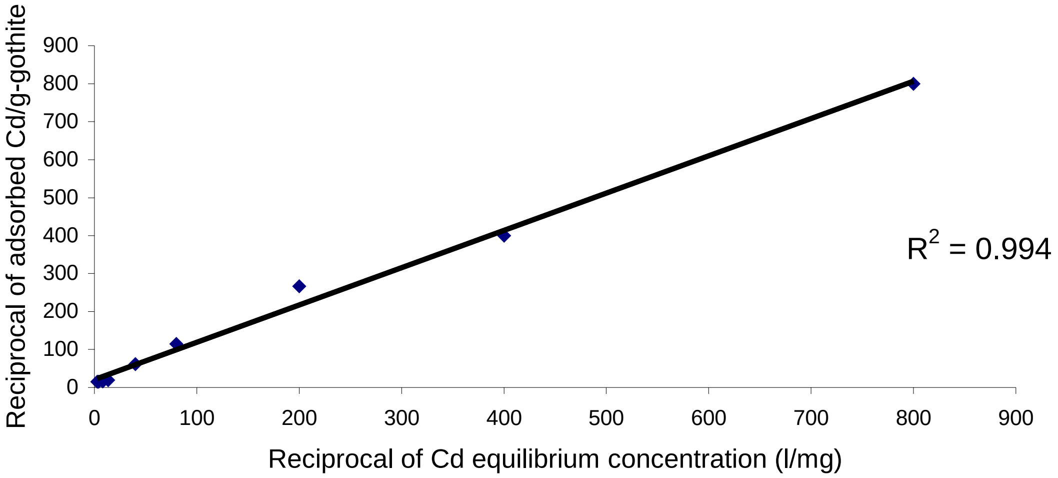


Figure 6: Langmuir adsorption isotherm of Cd on Kaduna goethite

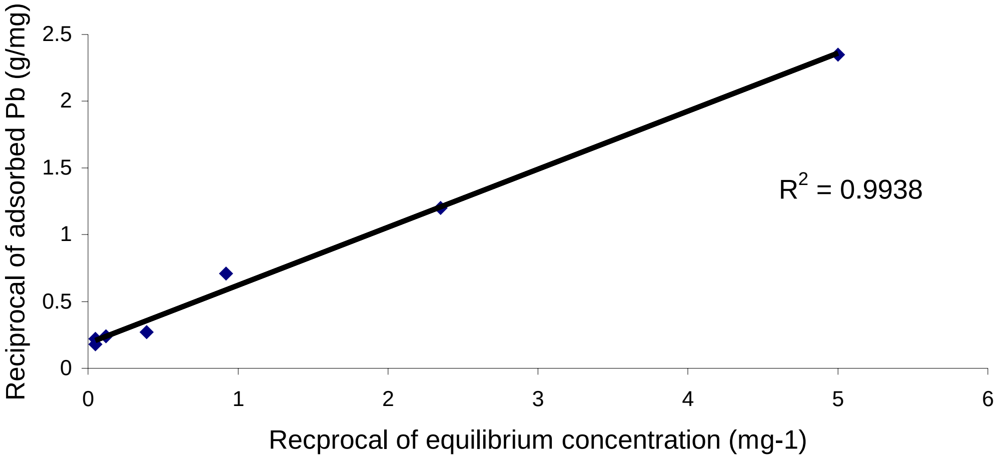


Figure 7: Langmuir adsorptin isotherm of Pb on Kaduna goethite

carefully synthesized pure goethite. Thus, the slight difference particularly observe at higher metal concentration (> 1.25mg/l) was due essentially to the effective number of adsorption sites available as a function of actual amount of goethite per gramme of substrate used.

Adsorption Kinetics

The results of batch equilibration of Cd and Pb adsorption were used to obtain metal adsorption isotherms as illustrated in Figures 4 and 5 respectively. The isotherms are essentially the same and are typical of L2 curve isotherm according to Gile's adsorption isotherm classification (33). This form of isotherm is characteristic of adsorbent with mono-functional ionic substances with very strong intermolecular attraction. The adsorption data obtained for these metal ions were converted to linearised form of 1-site Langmuir adsorption equation with correlation, R^2, values of 0.994 for Cd and Pb. The Langmuir adsorption isotherms are shown in Figures. 6 and 7.

The adsorption kinetics was studied at a constant metal ion concentration corresponding to the maximum adsorbed concentration on the increasing portion of the metal adsorption isotherms (i.e. before equilibrium was established). The adsorption of the two metal ions were characterized by initial rapid adsorption which was

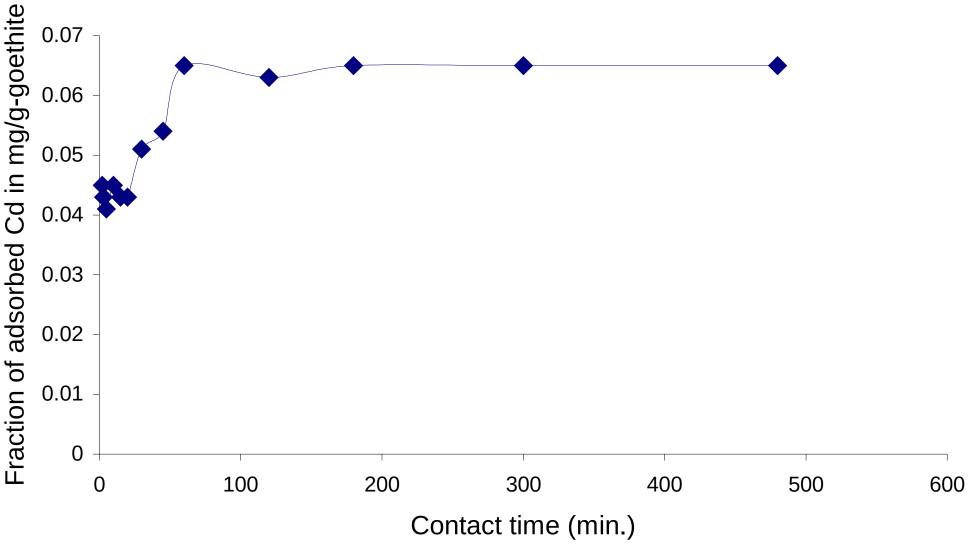


Figure 8: Kinetics of adsorption of Cd on Kaduna goethite

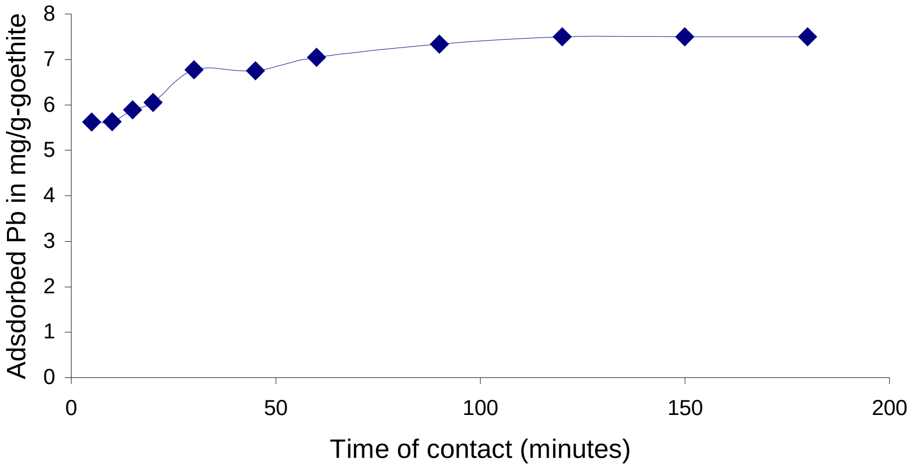


Figure 9: Kinetics of Pb adsorption on Kaduna goethite

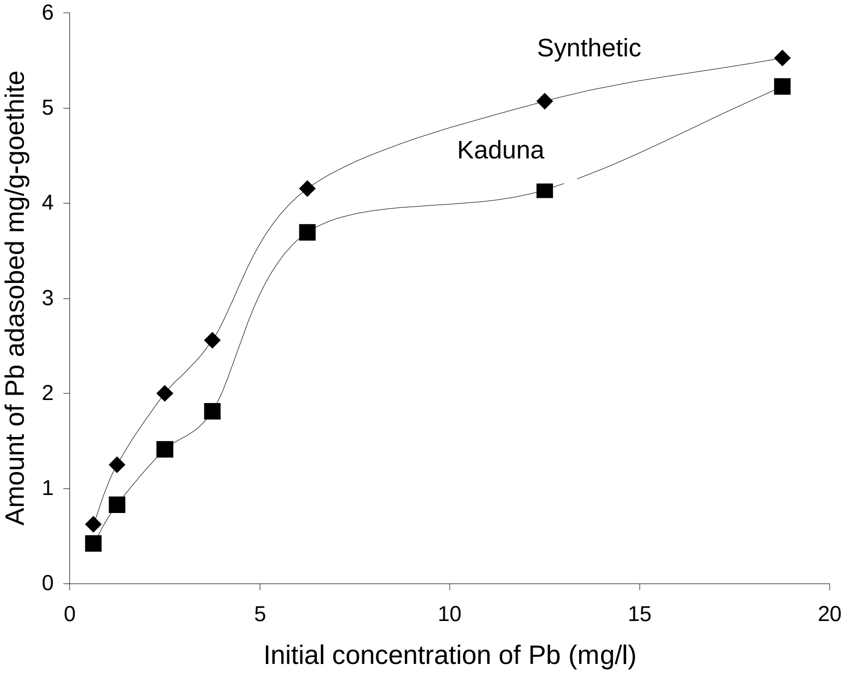


Figure10: Pb Adsorption Isotherm for Synthetic and Kaduna goethites

followed by slow but steady increasing adsorption and reaching about 90% of adsorption maxima within the first 90 minutes of experiment (Figures 8 and 9). The adsorption was later slowed down with minimal incremental adsorption. This is the general characteristic of adsorption of these metal ions on iron oxides (17, 23). About 90% of the metals were adsorbed within the 90 min of contact time as evident from metal adsorption isotherms (Figures 4 and 5). The metal adsorption takes place at the more reactive surface sites. As these sites are progressively filled the more difficult the sorption becomes, as the sorption experiment tends to be more unfavourable. The differences in surface reactivity of goethite are due to differences in OH coordination on goethite surface (35).

CONCLUSION

Experiments conducted on the sorption of Pb and Cd by synthetic and natural (Kaduna) goethites showed similarity in quantity of metal ions adsorbed. The slightly higher adsorption capacity of synthetic goethite was attributed to the higher proportion of goethite in synthetic than natural per unit mass of sample used, rather then greater chemical reactivity of the synthetic goethite. Consequently, natural goethite can compete favourably with synthetic goethite for decontamination of Pb or Zn from polluted effluents.

Sorption efficiency was greatly governed by pH with nearly a total adsorption of Pb occurring at initial pH of 5. The results of effect of temperature showed significant increase in the fractional adsorption for slight increase in temperature; consequently, these factors (pH and Temperature) can be manipulated to enhance adsorption capacity of the goethite. The reaction scheme for the adsorption process of the goethite can be represented by the following equilibria,

$$M^{2+} + SOH \rightleftharpoons SOM^{+} + H^{+}$$

$$M^{2+} + SOH + H_2O \rightleftharpoons SOMOH + 2H^{+}$$

where M represents Cd, Pb or Zn while OH represents the surface hydroxyl group on goethite, S.

REFERENCES

1. Nriagu, J. O. (1988). “A silent Epidemic of Environmental metal poisoning?” Environ.l pollut., **50**, 139 -161.

2. Bready, N. and Weil, R. (1999). “The nature and properties of soils”. Prentice Hall. Upper saddle River, New Jersey, pp 74 – 92.\

3. Environmental health criteria 165 (1995). Inorganic Lead. Jointly publish by U. N. Environmental programme, WHO and International labour organization, Geneva, pp 26 – 33 and 232 - 233.

4. Amdur, M. O., Doull, J. and Klaasen, C. (1991). “Casarett and Doull’s Toxicology, the Basic science of poisons”. Pergamon press, New York PP.639 - 643.

5. Lum Max., Orti, D. and Poindexter, P. (1994). “Lead – Toxicity”. Agency for Toxic substances and Disease registry. Biological Sciences Division Academic computing, University of Chicago, CHICAGO, IL Lead- Toxicity / September 1994 /BSDAC / mmaskay @ Uhs bsd. uchgago .edu

6. Grossl, P. R., Eick, M., Sparks, D. L., Goldberg, S. and Ainsworth, C. C. (1997). “Arsenate and chromate retention mechanisms on Goethite. 2. Kinetic evaluation using a pressure – jump relaxation technique”. Environ. Sci. Technol., **31**, 321 – 326.

7. Grossl, P. R., Eick, M., Sparks, D. L., Goldberg, S. and Ainsworth, C. C. (1997). “Arsenate and chromate retention mechanisms on Goethite. 2. Kinetic evaluation using a pressure – jump relaxation technique”. Environ. Sci. Technol., **31**, 321 – 326.

8. Moyes, L. N., Parkman, R. H., Charnock, T. M., Vaughan, D. J., Livens, F. R., Hughes, C. R. and Braithwaite, A. (2000). “Uranium Uptake from Aqueous Solution by Interaction with Goethite, Lepidocrocite, Muscovite and Mackinawite: An X – ray Absorption Spectroscopy Study”. Environ. Sci. Technol., **34**, 1062 – 1068.

9. Giammar, D. E. and Hering, J. G. (2001). "Time scales for sorption-desorption and surface precipitation of uranyl on Goethite". Environ. Sci. Technol., **35**, 332 – 3337.

10. Benjamin, M. M.; Sletten, R. S.; Bailey, R.P. and Bennett, T. (1996). "Sorption and filteration of metals using iron-coated sand". Water Res., **30**, 2609 – 2619.

11. Lai, C. H., Chen, CY., Wei, BL., Yeh, SH. (2002). "Cadmium adsorption on goethite – coated sand in the presence of humic acid". Water Res., **36**, 4943 - 4950.

12. Lai, CH, Chen, CY, Shih, PH, and Hsia, TH (2000). "Competitive adsorption of copper and lead ions on an iron coated sand from water". Water Sci. Technol., **42**, 149 - 154.

13. Johnson, B. B. (1990). "Effect of pH, Temperature and Concentration on the adsorption of Cadmium on Goethite". Environ. Sci. Technol., **24**, 112 – 118.

14. Zhenghua, W., Jun, L., Hongyan, G., Xiaorong, W. and Chunsheng, Y. (2001). "Adsorption isotherms of lanthanum to soil constitutions and effects of pH, EDTA and fulfic acid on adsorption of Lanthanum onto goethite and humic acid. Chemical Speciation and Bioavailability, **13 (3)**, 75 – 81.

15. Salami, N. and Adekola, F. A. (2002). "A study of sorption of cadmium by goethite in aqueous solution". Bull. Chem. Soc. Ethiop., **16**, 1 - 7.

16. Sauve,S., McBride, M and Hendershot, W. H. (1988b). Soil solution speciation of lead (II): Effects of organic matter and pH. Soil Sci. Soc. Am J., 62, 618-621.

17. Appel, C. and Lena, M. (2002). "Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils". J. Environ. Qual., **31**,581 – 589.

18. Ghanem, S. A. and Mikkelsen, D. S. (1988). "Sorption of Zn on iron hydrous oxide". Soil Sci., **146**, 15 – 21.

19. Kadirvelu, K. and Namasivayam, C. (2003). "Activated carbon from coconut coirpith as metal adsorbent: Adsorption of Cd (II) from aqueous solutions". Adv. Environ. Res., **7**, 471-478.

20 . Glover II, L. J. (2000). "The influence of resident time and organic acids on the desorption of trace metals from goethite". An unpublished M.Sc. thesis submitted to the faculty of Virginia Polytechnic, Blacksburg, Virginia pp 1 - 54.

21. Glover II, L. J., Eick, M. J. and Brady, P. V. (2002). "Desorption kinetics of cadmium^{2+} and lead^{2+} from goethite: Influence of time and organic acids". Soil Sci. Soc. Am. J. (SSSAJ), **66 (3)**, 1 - 14.

22. Bruce J. 200. Soils: "Our interface with environment". Worner research Lecture series La Trobe University, Bendigo, Australia, pp 1 - 20.

23. Johnson, B. B. (1990). "Effect of pH, Temperature and Concentration on the adsorption of Cadmium on Goethite". Environ. Sci. Technol., **24**, 112 – 118.

24. Inbaraj, B. S. and Sulochana, N. (2002). "Basic dye adsorption on a low cost carbonaceous sorbent". Ind. J. Chem. Technol., **9**, 201 - 210.

25. "Partition coefficient for lead". Appendix F. Retrieved on the 5th May 2004 from http://www.epa.gov/radiation/docs/Kdreport/vol2/appf.pdf

26. Teik-Thye, L., Joo-Hwa, T. and Cee-Tng, T. (2001). "Influence of metal loading on the mode of metal retention in a natural clay". J. Environ. Engr., **127 (6)**, 539 - 545

27. Benyahya, L. and Garnier, J. (1999). "Effect of salicylic acid upon trace metal sorption (Cd, Zn, Co and Mn) on to alumina, silica and kaolinite as a function of pH. Environ. Sci. Technol., **33**, 1398 - 1407.

28. Schwertman, U. and Taylor, R. N. (1989) "Iron oxides: Minerals in soil environments". Soil Sci. Soc. Am. (SSSA Book Series No 1), Madison, Wisconsin, USA, pp 379 - 427.

29. Kusuyama, T., Tanimura, K. and Sato, K. (2002). "Adsorption Properties of Mn-Substituted Goethite Particles for Aqueous Solutions of Lead, Copper and Zinc". Mater. Trans., **43 (3)**, 455 – 458.

30. Spandini, L., Manceau, A., Schindler, P. W. and Charlet, L. (1994). "Structure and stability of Zn^{2+} surface complexes on ferric oxides I. Results from EXAFS spectroscopy". J. Colloid Interface Sci., **168**, 73 - 86.

31. Pardo, M. T. (2000). “Sorption of lead, copper, zinc and cadmium by soils: Effect of nitriloacetic acid on metal retention”. Commun. Soil Sci. Plant Anal., **31**, 31 - 40.

32. Jeanjean, J., Fedoroff, M., Faverjon, F. and Vincent, U. (1996). “Influence of pH on the adsorption of cadmium ion on calcium hydroxyapatite”. J. Mater. Sci., **31**, 6156 - 6160.

33. Giles, C. H., McEwan, T. H., Nakhwa, S. N. and Smith, D. (1960). “Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids”. J. Am. Chem. Soc., **82**, 3973 - 3993.

34. Smith, K. L. and Eggleton, R. A. (1983). “Botryoidal goethite: A transmission electron microscope study”. Clays Clay Miner., **31 (5)**, 392 - 396.

35. Parafitt, R. L., Russel, J. D. and Farmer, V. C. (1976). “Confirmation of the surface structure of goethite (á - FeOOH) and phosphate goethite by ir spectroscope”. J. Chem. Soc. Faraday Trans., **I (72)**, 1082 - 1087.