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Metal Ions Adsorption Affinity of Clayey Materials from the North West Province of South Africa

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Abstract Local clays that are abundant in the periphery of Potchefstroom in South Africa were characterized and investigated as potential sorbents for the removal of metal ions from effluents. The clay samples mostly contained illite-montmorillonite and had a buffering capacity suitable for increased interaction with metal ions in solution. The use of these clays showed adsorption capacities above 35 mg/g for Pb^{2+}, Cu^{2+} and Zn^{2+}. Prediction of their adsorption behaviour with the Langmuir model revealed a higher binding affinity for Pb^{2+}. These clays are potential sorbents that will be further investigated to design and construct a treatment plant for mine effluents in the area.

Keywords clayey materials, mine effluents, adsorption affinity

Introduction

Metal ion sorption has been identified as one of the most suitable techniques for the mitigation of mine effluents impacting on surface water as it allows for removal and recovery of metal ions, reducing the potential for waste by-products formation. The selection of a sorbent is mainly determined by its adsorption capacity, its overall cost, its availability and environmental friendliness. Clay is among the most attractive adsorbents so far investigated because of the high surface reactivity and the ubiquitous occurrence in the geological sphere.

Metal ion binding on the clay is a physico-chemical process depending on the porosity of the clay and the chemistry of the solution and the metal ion. Typical binding mechanisms include ion exchange, precipitation, adsorption and complexation (Roehl and Czurda. 1998). Metal ion adsorption by clay, predominantly occurs through an ion exchange mechanism, implying that the electrochemical properties and therefore the source of the clay may determine its affinity for the metal ion. Electrochemical properties related to the mineralogy of the clay may often be specific to the source of clay; the isomorphic substitution on the clay structure determines the permanent charge located at the interlayer basal surfaces (Proust et al. 2013). The clay mineral montmorillonite is more reactive than kaolinite because of higher isomorphic substitution which contributes to a higher cation exchange capacity (CEC) (Srodon and McCarthy. 2008).

The improvement of metal ions removal processes could be achieved if suitable sorbents are selected and it is therefore important to determine the affinity of these sorbents for a range of metal ion pollutants. To investigate the metal ion adsorption affinity of three clay samples, they were exposed to Zn^{2+}, Cu^{2+} and Pb^{2+}ions in aqueous solutions under various conditions.

Methodology

Preparation and characterization of clay adsorbent

Two clay samples from the Potchefstroom areas in the North West Province of South Africa (fig. 1), were ground in a mortar and the particle sizes separated by a sieving technique to selectively recover particles with a size of -75 µm. X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to determine the mineralogy of the clay samples and their elemental composition, respectively.

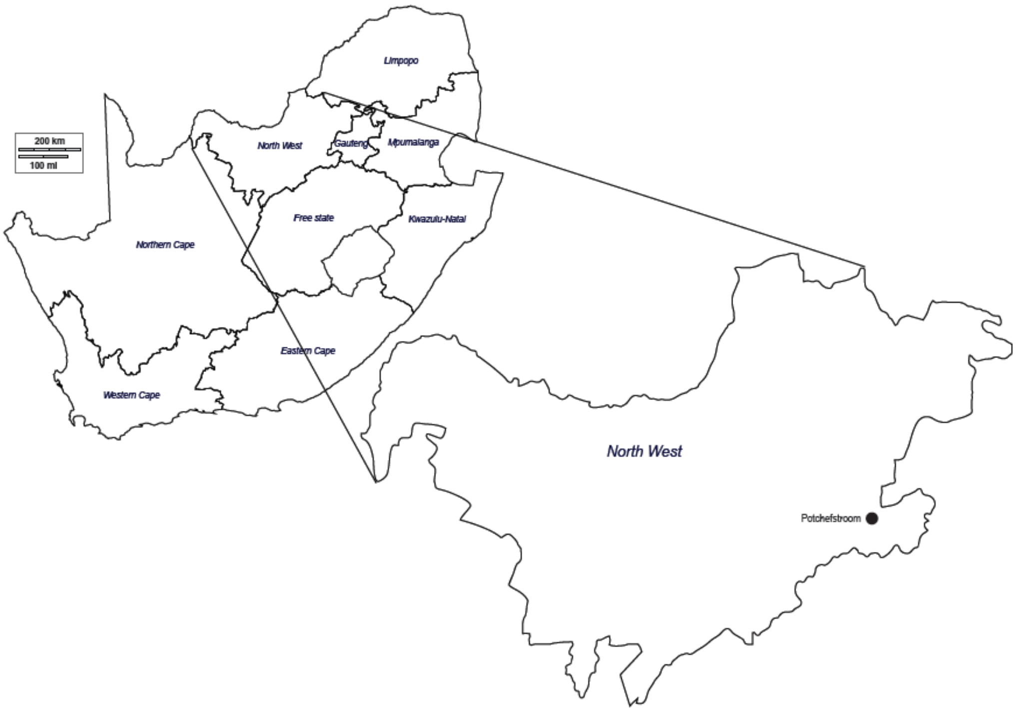

Fig. 1 *Location of Potchefstroom in South Africa*

The determination of the cation exchange capacity of the soil samples was done through a modified method, of the $BaCl_2$-compulsive exchange procedure using 1 M of NH_4Cl in replacement of $BaCl_2$.

The pH of the clay samples was determined in a 1:5 clay-water solution ratio after one hour incubation.

Adsorption batch tests

Chemicals used for preparation of metal ion solutions were $Pb(NO_3)_2$, $CuSO_4.5H_2O$ and $ZnSO_4 \cdot 6H_2O$, which were dissolved in distilled water. Adsorption was carried out using a batch equilibrium system in a 250 mL glass reactor. A solution of 10, 20, 30 and 40 mg/L of metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) was prepared in 100 ml distilled water and exposed to 0.1 g of clay A and B in the 250 mL glass reactor, put on an orbital shaker for pre-determined times. The contact between the adsorbates and the adsorbents was maintained by shaking at a speed of 160 rpm for 2, 4, 5, 6 and 8 hours at room temperature (25 ℃). After exposure to the clay, the mixture was centrifuged at 10000 rpm for 5 min and the supernatant was collected for measurement of the residual metal ion using the Atomic Absorption Spectrophotometer.

The adsorption capacity of the clay samples was determined using the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V$$

Where qe is the adsorption capacity (mg/g), C_0 is the initial concentration of metal ion (mg/L), C_e is the concentration of metal ion at equilibrium (mg/L), V is the volume of the solution (*L*) and m is the mass of the clay (*g*).

The adsorption isotherm models of Langmuir and Freundlich were studied using 0.1 g of clay samples and various initial concentrations of Pb^{2+}, Cu^{2+} and Zn^{2+}.

Results and discussion

Mineralogical and elemental composition

The XRD analysis showed that clay A and B mainly contained illite-montmorillonite; but with various concentrations of other minerals such as quartz and grossite in clay A, as well as pigeonite and ferrobustamite in clay B. Metals such as Na, Ca, Mn, Mg, K, Ni, Zn, Cu and Fe were present in both clay A and B at relatively the same concentrations. The pH values of clay A and B were found to be in the alkaline zone and very similar, 7.9 and 7.6 respectively. The CEC values of clay A and B were 62.1 and 59.6 cmol/kg, respectively. The pH and CEC are always reported as soil characteristics to show good association to the soil adsorption capacity (King. 1988). The buffering capability of the clay samples reduces the solubility of metal ions and increases the possibility of interaction with the clay surface.

Adsorption behaviour of the clay samples

The Langmuir and Freundlich models allow for the determination of the adsorption capacity and affinity of the clay, characteristics which are necessary prior to consideration of adsorbents and prediction for the performance in large remediation plants.

The linear form $\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{C_e}{q_m}$ of the Langmuir isotherm model allows the derivation of the equilibrium constant from the plot (C_e/q_e vs C_e), where, q_m is the maximum adsorption capacity (mg/g) of the adsorbent and b is the Langmuir constant related to the adsorption energy.

The Freundlich constants can be calculated by the logarithmic form of the linearized equation

$$\log q_e = \log K_F + \tfrac{1}{n} \times \log C_e$$

where, q_e is the equilibrium adsorption concentration of adsorbate per unit mass of the adsorbent (mg/g), C_e is the concentration of adsorbate left in the solution (mg/L), K_F and 1/n are the Freundlich constants related to the adsorption capacity and intensity of adsorption.

Table 1 shows the isotherms' parameters for the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} on clay A and B.

Table 1 *Isotherm parameters for the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} on clay A and B*

Model	Parameter	Clay A			Clay B		
		Pb^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cu^{2+}	Zn^{2+}
Langmuir	k	0.161	0.1099	0.026	0.04	0.05	0.008
	q_m (mg/g)	39.15	35.73	70.33	82.86	41.06	141.3
	R^2	0.9404	0.9494	0.6147	0.9612	0.9808	0.8948
Freundlich	k_F	6.821	4.9481	2.393	3.702	2.64	0.61
	R^2	0.9926	0.9962	0.9855	0.9999	0.99	0.9596
	$1/n$	0.547	0.558	0.761	0.803	0.698	1.194
% removal in mine water		70	10.4	41	81.8	42	88

The best possible fit of the model for the adsorption study undertaken is determined by the values of the coefficient of determination (R^2). It can be observed that the values of R^2 are close to unity, except in the case of the adsorption of Zn^{2+} which cannot be predicted with the Langmuir model. The k value has been reported to positively correlate to the strength of the binding sites (Fosso-Kankeu et al. 2011). The sorption affinity of the clay samples could therefore be illustrated by higher values of k. It is observed that clay A and B both have higher affinity for Pb^{2+} than Cu^{2+}. Metal ions with higher atomic weight can generate higher momentum energy, which may promote the adsorption of the metal ion by increasing the probability of effective cohesion between the metal ion and the sorbent surface (Sag et al., 2002); it therefore ensues that a higher atomic weight leads to higher adsorption preference by the sorbent. This explains the preferential binding of Pb^{2+} on the clays.

In the Freundlich model, the value of $1/n$ predicts the applicability of the adsorbent and the favourability of the adsorption process. If the value of $1/n$ is less than 1.0, the adsorption process is favourable over the entire range of concentrations of the adsorbate studied and if the value of $1/n$ is larger than 1.0 then the adsorption process is favourable at higher concentrations but not favourable at lower concentrations (Mittal et al. 2013). It is observed in this study that the values of $1/n$ for the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} by clay A and B are <1, except in the case of adsorption of Zn^{2+} by clay B, which implies the adsorption is mostly applicable for the range of concentrations considered. The removal of metals from real mine solution showed that clay B was much effective, but both clays had lower affinity for copper as predicted by the models. During the removal of metals from mine solution, the adsorption capacity of the clays were lower than predicted which was certainly due to competitions for the binding sites by other metals present in solution

Effect of time on the adsorption capacity

The determination of the adsorption rate of the metal ion on the adsorbent is very important in the prediction of the adsorption capacity. The effect of time on the adsorption capacity is shown in figs. 2 and 3. It can be observed that the adsorption capacity of both clay A and B increases with time. It can also be observed that more Pb^{2+} is adsorbed over time than any other metal ions.

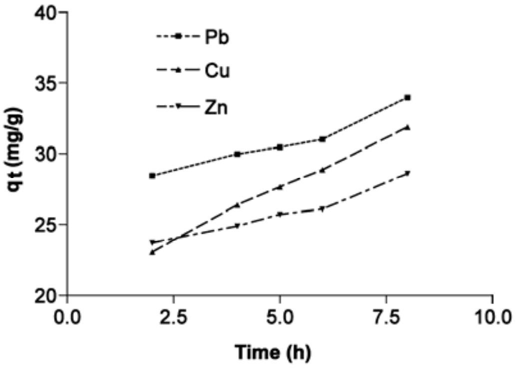

Fig. 2 *Effect of time on the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} by clay A*

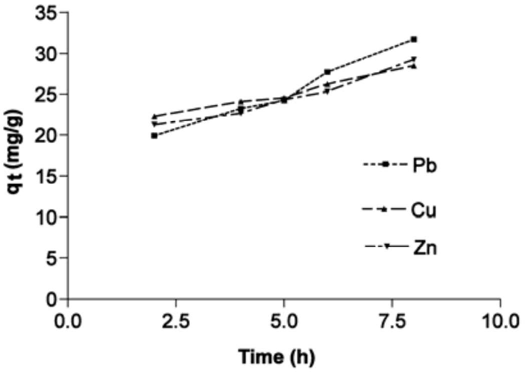

Fig. 3 *Effect of time on the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} by clay B*

However, the adsorption capacity does not reach stability, indicating that the clay samples were not saturated and therefore were not used to their full potential. This means that, these clays can adsorb more metal ion if the time is prolonged.

Conclusion

The clayey materials which are abundant in the Potchefstroom area in the North West Province of South Africa, were found to have relatively similar characteristics, and could effectively remove the studied metal ions from solution. It was found that the adsorption behaviour of these clays during removal of Pb^{2+} and Cu^{2+} from solution could be predicted using isotherm models such as Langmuir and Freundlich. The affinity of these clays for Pb^{2+}, suggest that in a multi-metal ions system, Pb^{2+} could be preferentially removed; however the investigation of the performance of these clays in a larger range of multi-metal ions systems will clearly indicate their suitability for the treatment of the more complex environmental solutions.

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References

Fosso-Kankeu E, Mulaba-Bafubiandi AF, Mamba BB, Barnard TG (2011) Prediction of metal-adsorption behaviour in the remediation of water contamination using indigenous microorganisms. Journal of Environmental Management 92 (10):2786-2793

King LD (1988) Retention of metals by several soils of the southeastern United States. Journal of Environmental Quality 17:239-246

Mittal H, Fosso-Kankeu E, Mishra SB, Mishra AK (2013) Biosorption potential of Gum ghatti-g-poly (acrylic acid) and susceptibility to biodegradation by B. subtilis. International Journal of Biological Macromolecules 62: 370-378

Proust D, Fontaine C, Dauger N (2013) Impact of weathering and clay mineralogy on heavy metals sorption in sludge-amended soils, Catena 101:188-196

Roehl KE, Czurda K (1998) Diffusion and solid suspension of Cd and Pb in clay liners. Applied Clay Science 12: 387-402

Sag Y, Akcael B, Kutsal T (2002) Ternary biosorption equilibria of chromium (VI), copper (II) and cadmium (II) on Rhizopus arrhizus. Separation Science and Technology 37(2): 279-309

Srodon J, McCarthy DK (2008) Surface area and layer charge of smectite from CEC and EGME/H20-retention measurements. Clays and Clay Minerals 56:155-174