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Heavy Metal uptake from Industrial Effluents using Natural Zeolitic Aluminosilicates

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Abstract

The uses of zeolites derive from their special properties: They can interact with water to adsorb or release ions (ion exchange); they can selectively adsorb ions that fit the cavities in their structures (molecular sieves). The locally available zeolite samples have been proved to have application in reducing toxic waste and causes driven by environmental concern and energy consumption. Cation-containing zeolites can differentiate molecules on the basis of their electrostatic interactions with the metal ions, size difference, shape and polarity. The adsorption properties of certain specific pore sized zeolites are useful for size selective separation of molecules. The high cation exchange capacity of zeolites as evident from our studies combined with their selective affinity for specific cations make them uniquely suited to various application in disposal of Industrial effluents like Cu, Cr, Co, Zn etc. The heavy metal ions were quantified using atomic absorption spectroscopy before and after the process of adsorption. This promising adsorbent is found to exhibit 90% adsorption efficiency with most of the heavy metals.

Keywords: Heavy metals, adsorption, cation exchange capacity, effluent treatment.

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1. Introduction

Waste water treatment is one of the environmental problems that concern the modern Industrial society. In particular, the deposition of effluents especially heavy metals produced by mining, electroplating, plastic and other industries is known to present a technological problem¹. The heavy metal concentrations are often lowered so that wastewater can be safely discharged into municipal sewers or biological wastewater treatment can take place without biomass inhibition problems. Heavy metal toxicity can result in reduced mental and central nervous function, and damage to blood composition, and other vital organs². Long-term exposure may result in slowly progressing neurological degenerative processes that mimic Alzheimer's disease and Parkinson's disease³. Several natural low cost adsorbents such as activated carbon, flyash, chitosan have been tested to reduce heavy metals present in very low concentrations⁴.

In this paper, the adsorption of heavy metals of agrofuel effluents from main Industrial area of Lusaka were studied on an untreated microporous aluminosilicate adsorbent at optimum conditions of temperature, pH and contact time. The purpose of the study is to demonstrate the efficiency of the sample as an

adsorbent. Over any other conventional adsorption techniques the advantage of the use of zeolites is that they are molecular sieves which show high specificity towards cations. The isomorphic substitution of Al^{3+} for Fe^{2+} or Mg^{2+} , and Si^{4+} for Al^{3+} generates charge deficiencies which will be compensated with inorganic cations either Na^+ or Ca^{2+} and later will be readily exchanged by other inorganic or organic cations during decontamination process⁵. Adsorbents belonging to this class can easily be regenerated keeping its initial properties intact⁶, they are environment friendly, cheap, has a simple design and is easy to operate compared to conventional processes. This aluminosilicate mineral is found to have relatively high cation exchange capacity (CEC) which explains its ability to hold cations. To be attractive commercially the adsorbents should embody features like large internal surface area and high cation exchange capacity.

An inverse relation exists between the surface area, S , density of the zeolite, ρ and particle size, l .

$$S = \frac{6}{\rho l} \quad (1)$$

The finer the particle size of a mineral the better the access to the surface area and faster the adsorption kinetics. Essentially zeolites are highly porous and high surface area should be accessible through pores which are large enough to admit the molecules to be adsorbed and small enough to exclude the unwanted molecules. Sieve action and hydration of cationic species influence a zeolites selectivity. The intra-crystalline cavities make 20% to 50% of most of the zeolites total crystal volume. Another property which dictates the advantage of this chosen sample is its high leach resistance as evident by our studies.

2 Experimental Details

The Zeolitic aluminosilicate used in this study was a grey fluffy clay which has been formed typically by the intense weathering of rocks at alkaline conditions. This was found to be highly crystalline by X ray diffraction studies and bulk of the sample consisted of SiO_2 which is derived from quartz and clay minerals like kaolinite. The zeolites are known to separate molecules based on size, shape, polarity and degree of saturation. The major components of the adsorbent and its textural class have already been reported⁷ as Calcium Aluminium Oxide and Sandy loam respectively.

The three major aspects which this study focuses is (1) leach resistance (2) Cation Exchange Capacity and (3) Extent of adsorption. It is important to note that highly toxic and non essential elements like Hg and Pb are present only in undetectable quantities in the matrix. To prove the leach resistance, the sample was crushed and soaked in demineralised water for 30 days and filtrate analyzed for trace metal ions using atomic absorption spectroscopy. The cation exchange capacity (CEC) of the aluminosilicate was determined by extracting the sample using ammonium acetate.

In order to conduct the adsorption studies, the adsorbent material was washed with distilled water to remove the impurities, dried at 120°C for 24 hours to diffuse any adsorbed particles and to maximize the active surface sites. The sample was then pulverized and screened into a particle size of 0.25 mm using a sieve of appropriate size to ensure high surface area. Adsorption experiment was performed using an optimum adsorbent concentration of 0.12 mg/l of sewerage water to ensure maximum adsorption efficiency by providing adequate adsorption sites⁸. The suspension was shaken thoroughly and after the elapse of the desired contact time of 72 hours it was filtered through Whatman 40 filter paper and the filtrate analysed using atomic absorption spectroscopy. The amount of metal ion retained in the adsorbent was calculated using the initial and final concentrations of metal ions in the effluent water.

3 Results and Discussion

The leachate obtained by soaking the adsorbent were analysed for toxic metals like Pb, Cd, Hg, Co, Zn, Cu and Cr which was quite obvious in a smelting or electroplating environment using atomic absorption spectroscopy. It was encouraging to find out that leachates have less than $10\ \mu\text{g/l}$ of Pb, Co, Zn Cu and Cr and the metals like Cd and Hg are of below detection limits. Thus this Zeolitic sample which is of volcanic origin is like a high

temperature oxide with very high leach resistance, i.e., it does not dissolve easily in water. High leach resistance is one of the most desirable properties of the solid matrix used to immobilize the heavy metal ions. Thus the leaching concentrations of all metals were maintained below $10\ \mu\text{g/l}$ throughout the experiment and the results obtained are represented graphically using sigma plot in figure 1.

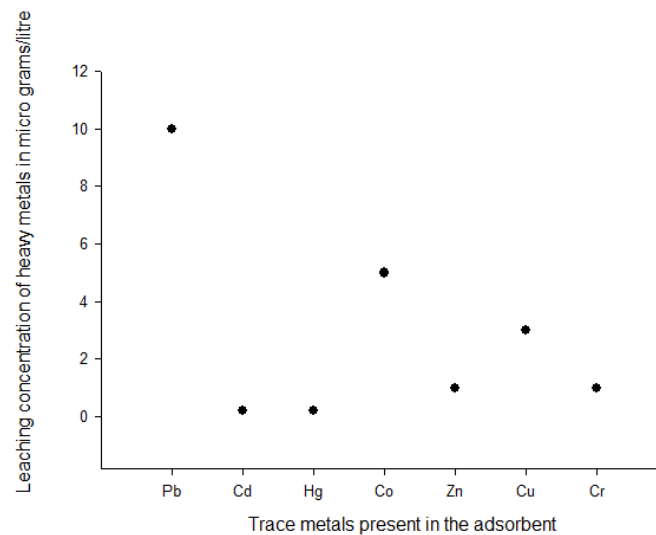


Fig 1. Trace metals from leaching process and their concentrations

The sample was extracted using ammonium acetate to find its cation exchange capacity. The capacity of the adsorbent to hold the cations is referred to as cation exchange capacity. The cation exchange capacity represents the total amount of exchangeable cations it can adsorb which in turn depends on the negatively charged clay particles present. Aluminosilicates voids have the net negative charge due to the isomorphous substitution of Si^{4+} ions with Al^{3+} ions. The cation exchange capacity of the sample was found to be 170 mmol/kg which is quite an appreciable value as far as a silicate rich oxide is concerned. This feature is going to enhance the adsorption capacity and permeability of the adsorbent.

The adsorption experiment was performed on effluent water contaminated with heavy metals like Zn, Cu, Co and Cr having initial concentrations of 0.124, 0.012, 0.132 and 0.023 mg/l respectively. The batch equilibration method was used to investigate the specific adsorption of the above metals and the trace amounts of heavy metal ions remaining in the filtrate after adsorption were analyzed using atomic absorption spectroscopy. The results reveal that the final concentrations of the above heavy metals were appreciably reduced to 0.01, 0.003, 0.005 and 0.002 mg/l respectively.

The amount of adsorbate captured by the adsorbent at equilibrium can be found out using the equation

$$Q_e = \frac{(C_i - C_e)V}{M} \quad (2)$$

Where Q_e is the amount of equilibrium adsorbate concentration on the adsorbent,

C_i and C_e are the initial and residual concentrations of metal ions, V is the volume of the aqueous solution, and M the mass of adsorbent used.

Finally percentage of adsorption efficiency with each metal was computed using the initial concentration of the adsorbate in the effluent water and the equilibrium concentration of adsorbate in the adsorbent. The adsorption efficiency was found to be highest for Cobalt with a percentage of 96 and lowest for Copper which is 75%. Zinc and Chromium are exhibiting the same efficiencies of 91%. The results are illustrated using graphical sigma plot in figure 2.

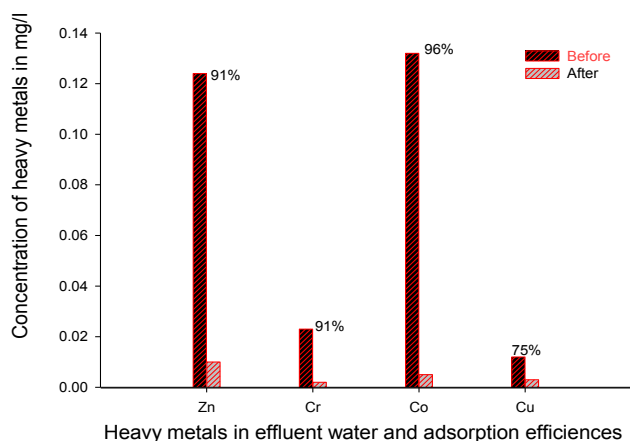


Fig 2. Concentrations of heavy metal ions before and after adsorption

The adsorbent efficiency exhibited by this adsorbent is much higher than that of many other natural polymeric sorbents. The contact time of 72 hrs provided should have been sufficient enough for the adsorption process to reach equilibria⁹ and to maximize adsorption efficiency to 96%. The 0.25mm size maintained for the adsorbent particles also was favorable for the adsorption process: adsorption rate increases as the size of the particles decrease. A much finer particle size in porous solids may result in rupturing of pores resulting in reduction of adsorption and also increases the metal concentrations in the leachates¹⁰.

Since adsorption is an exothermic process, a high experimental temperature was avoided and experiment was conducted at room temperature and pressure. At the same time very low temperatures are not advisable since low kinetic energy reduces the mobility and approach of the ions to the interface of the active sites. The optimum temperature used has ensured enhanced

adsorption by denuding the hydration sheath to some extent which is an endothermic process. Metal ions in aqueous solutions will be hydrated and large hydrated radius can dramatically reduce the rate of adsorption.

The pH of the effluent water was 7.6 and specific adsorption at a pH range 6-8 can help prevent dissolution of zeolite at a lower pH and avoids ion hydrolysis and precipitation at a higher pH. At lower pH the negative sites on the zeolites will be bound to the protons and probability of binding any other cations will also be diminished. The metal ion adsorption on to a negatively charged adsorbent is in essence an ion exchange mechanism which is essentially electrostatic in nature.

The quantity of specifically adsorbed ions on the surface of solids depends on electric charge, hydrated ion radii, hydration energy, metal electronegativity, ionic potential etc. According to literature search, there is no consistent universal rule governing the removal of cations by adsorbents. These first row transition metals have common oxidation states of +2 except for chromium which is +3 or sometimes accessing +6 state¹¹. The specific adsorption was the highest with Co^{2+} and lowest with Cu^{2+} . Since experiment was conducted at neutral pH of 7.6, extent of hydrolysis was minimized and the observed trend in efficiency $Co^{2+} > Cr^{3+} = Zn^{2+} > Cu^{2+}$ cannot be explained using Irving-Williams rule of stability of complexes. According to Irving-William series Zn^{2+} should have been adsorbed the most and Cr^{3+} the least. The above trend can be best explained on the basis of initial concentration of metal ions and their ionic radii. Initial concentration was highest with Co^{2+} and Zn^{2+} and has the highest efficiencies of 95% and 91% respectively. But Cr^{3+} also shows the same efficiency of 91% even though the initial concentration is low. This could be due to the high ionic potential ' Φ ' which is charge/radius ratio of the ion. The Cu^{2+} ions have the lowest initial concentration and lowest ionic potential and is adsorbed the least. Radii of Co^{2+} and Cr^{3+} ions are the least and they are adsorbed to a greater extent. This shows the affinity of the active sites on the matrix to small and highly charged species. Heavy metals penetrate easily into microporous solid when the ionic radii are small. The electronegativities of Chromium and Zinc ($\chi=1.6$) are same and showed an equal tendency to be specifically adsorbed. Electronegativity of Copper is the highest ($\chi=1.9$), but its adsorption efficiency was only 75% probably due to the very low initial concentration and the presence of interfering cations.

15. Conclusion

The primary goal of the research work was to find out the effectiveness of leach resistant aluminosilicate clay for the removal of selected metal ions from the effluent water. This was accomplished through laboratory experiments involving known amounts of pulverized adsorbent and predetermined concentrations of metal ions in effluent water. The

concentrations of the chosen heavy metals were reduced to nil; thus showing promising adsorption characteristics for the removal of heavy metals. The cation exchange capacity of the aluminosilicate was found to be 170 mmol/kg. The key factors found to control the adsorption efficiencies were radius of metal ions, ionic potential, presence of competing ions, electronegativity and hydration energy. The optimum removal capacity of the mineral is found to be 7.0 mg/kg of the sample. The highest amount removed was 0.132 mg/l with Co^{2+} ions while the lowest was 0.009 mg/l with Cu^{2+} ion. The overall rates of adsorption of metal ions followed the order $\text{Co}^{2+} > \text{Cr}^{3+} = \text{Zn}^{2+} > \text{Cu}^{2+}$ which is due to the combination of different factors. The merit of this green technique is to throw light on the high performance promising candidate in remediation of heavy metal poisoning. Modifications of this mineral by functionalization, acid base treatment and intercalation can boost the adsorption properties although reverse trends have been reported.

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