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Removal of Cadmium from Aqueous Solution using Ripe Plantain Peels and Clay Composite

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Abstract This research was aimed at using locally sourced materials for the removal of Cadmium from aqueous solution. Locally sourced ripe plantain peels and clay were collected from Port Harcourt, Rivers State. A mixture of powdered peels and clay was used as adsorbent by a batch experiment in determining the effects of pH, contact time and initial concentration in the removal of Cadmium from aqueous solution. The effects of pH indicated that the optimum pH for adsorption of Cadmium from the composite sample was 5.0. The effects of contact time on the adsorption process indicated that the three composite showed a % removal of 96, 97.5 and 98 respectively of the metal ions at optimum time of 50mins. The kinetic model for the adsorption was a Pseudo-Second-Order which was the best fit for the adsorption. The ripe plantain peels and clay composite showed good adsorbent potential for the removal of Cadmium from aqueous solutions.

Keywords Ripe plantain peels, clay, Adsorption, Cadmium, composite

Introduction

Management of water shortage has posed serious threat to access to water as a result of the imbalance between water supply and demand. It has also been associated with issues of climate change and population growth which has made water reuse an important method for water conservation. Researchers have reported that, there is an increasing environmental and public health concern associated with water containing heavy metals used by industries [1]. These metals are discharged into the environment through mechanical dispersion, which have been reported to affect cellular organelles such as cell membrane, lysosome and endoplasmic reticulum. They interact with nuclear protein and DNA causing changes that may lead to cell modulation or carcinogenesis [2, 3].

Most of these heavy metals are soluble in water and form aqueous solutions which are not easily separated by ordinary physical methods. The methods used to remove heavy metals from water to ensure its safety include, precipitation, ion exchange, reduction, reverse osmosis, adsorption and electrochemical reduction. Most of these methods are not suitable for small-scale industries for the reason that they involve high capital cost. Adsorption is effective and has advantages among other methods of wastewater treatment because it is sludge free, simple design and not expensive [4].

Consequently, researchers have continually sourced for an alternative low-cost material that can adsorb heavy metals from water. Such efforts have been made towards using locally sourced materials which has low carbon footprints and are sustainable. Such materials include clay, plant biomass which is used to remove heavy metals from an aqueous environment. Amongst the agricultural wastes, peels of different fruits can serve as potential adsorbents for the removal of heavy metals from water. The removal of cadmium from wastewater has been reported using clay [5] and other agricultural by-products such as orange bark, coffee residues, banana peels, olive core, [6, 7, 8].

Plantain (*Musa Sapientum*) is a stable food in Nigeria and some part of Africa. It has also been graded as the tenth most staple food cultivated in tropical parts of the world [9]. The major waste associated with plantain consumption is the peels, it is not edible and it contributes to the volume of refuse generated. They are usually part of agricultural waste generated from kitchens, food vendors and industries which depends on them for flour processing. These peels are often disposed in waste-dumps or littered in the environment thereby making the environment untidy. Plantain peels contain starch which has high retention capacity and selectivity to heavy metals [9].

According to [10], clay is a fine grain, earthly material that becomes plastic and hard when moist and becomes permanently hard when baked or fired. Clay is becoming important among the low-cost adsorbent because of their abundant availability and their adsorption capabilities which result from a net charge of fine- grained silicate minerals. The negative charge is neutralized by the adsorption of positively charged species giving clay the ability to attract and hold cations such as heavy metals [11].

Methodology

1000mg/l of cadmium stock solution was prepared from nitrates of cadmium and diluted to obtain a working solution. The reagent was of analytical grade. The concentration of cadmium was obtained using an Atomic Adsorption Spectrophotometer (Agilent Technologies 4210 MP-AES model).

The ripe plantain peels and clay used for the analysis were obtained in Port Harcourt. The peels and clay were washed, cleaned and sundried after which they were pulverized into fine powder, thereafter it was kept in an airtight bag for further use. Composite mixtures were prepared by mixing 50% clay to 50% ripe plantain peels, 80% clay to 20% ripe plantain peels and 20% clay to 80% ripe plantain peels.

The effects of pH on the rate of Cd removal was done by placing 0.2g of the composite mixtures into10ml aqueous solution of adjusted pH values of 3.0, 5.0, 7.0, 8.0 and 9.0 respectively using 0.1M HCl or 0.1M NaOH. The mixture was agitated at 100 rpm with a mechanical shaker for 90mins.The suspension was allowed to stand and was filtered using Whatman No.1 filter paper to remove suspended particles.

The adsorption process was also achieved by varying concentrations (10, 20, 30, 40 and 50 mg/l) of the metal ions and varying contact time of (10, 30, 50, 70 and 90minutes) maintained at optimal pH by pouring 0.2g of the composite mixtures in 10ml of each aqueous solution that has been measured into each of 250ml conical flasks and agitated at 100 rpm with a mechanical shaker. The samples were allowed to stand and thereafter, filtered using Whatman No.1 filter paper to remove suspended adsorbent.

The data generated were subjected to the Pseudo-First-Order and Pseudo-Second-Order kinetic models. The models were applied to the experimental data obtained from the contact time study. The models are expressed in equations (i) and (ii) respectively as pseudo-first-order and pseudo-second-order models [12, 15].

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad \text{(i)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(ii)}$$

Where:

q_e and q_t are the amount absorbed per unit of solute absorbed at equilibrium at any time

k_1 is the pseudo - first - order rate constant(min^{-1}) for adsorption process

k_2 is the pseudo – second - order rate constant ($gmmol^{-1}min^{-1}$) for adsorption

Results and Discussion

The effect of pH on the adsorption efficiency of Cadmium onto the composite mixtures was examined by varying the pH from 3.0 - 9.0. Figure 1a of the 20% composite shows that the percentage removal of cadmium increased at a steady rate as pH increased to 9.0, attaining optimum pH of 7.0 and a maximum percentage removal of 99.98%. The results of the 50% composite from figure 1a shows that the percentage removal of cadmium increased at a steady rate as pH increased to 9.0, having optimum pH of 5.0 and a maximum percentage removal of 95.99%. For the 80% composites, the percentage removal of cadmium increased at a steady rate as pH increased to 9.0, attaining an optimum pH of 5.0 and a maximum percentage removal of 98.98%. Increasing pH also reduces the competition between metal ions and protons for adsorption sites on the particle surface [13]. The adsorption of the cadmium ions onto ripe plantain peels and clay composite mixtures waste adsorbent were largely influenced by pH.

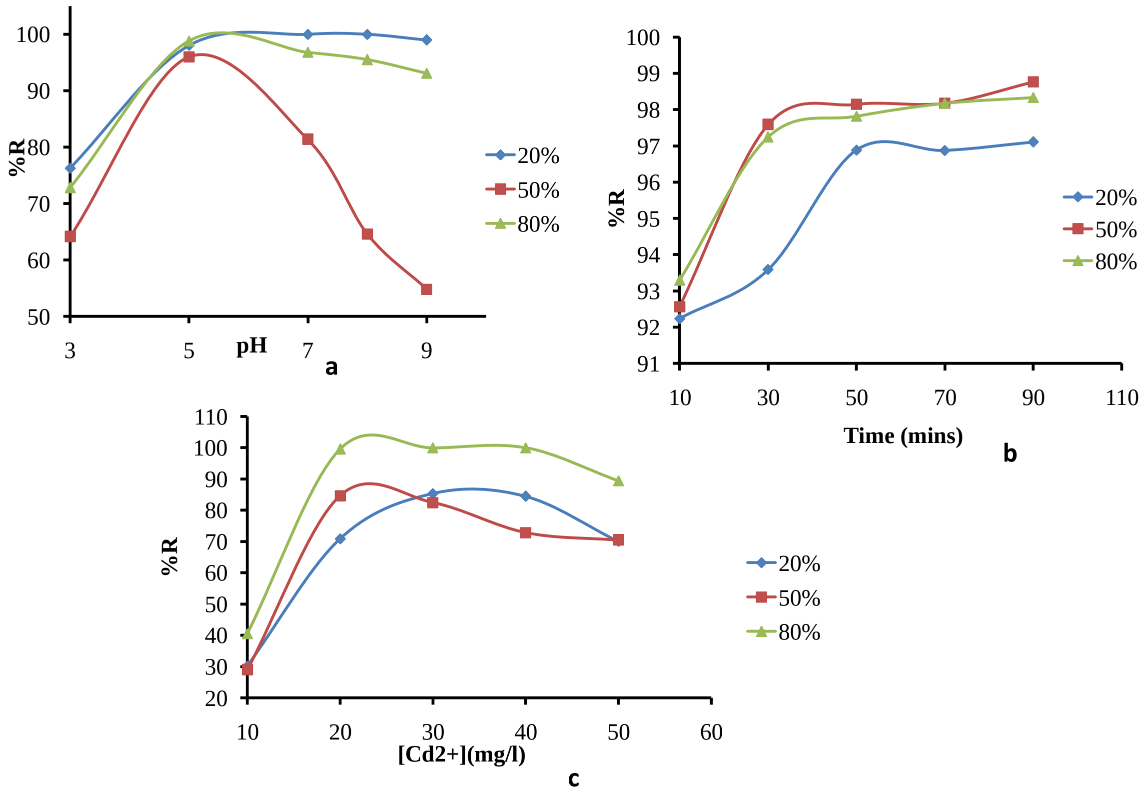

Figure 1: Effect of pH, contact time and concentration on the percentage removal of cadmium

The results of the contact time showed that for all the adsorbent, the removal rate was rapid and gradually increased to 90 minutes. Fig. 1b shows that the percentage removal of cadmium ions increased at a steady rate as the contact time increased up to 90mins attaining a maximum value of 97.11% for 20% composite mixtures, 98.77% for 50% composite mixtures and 98.34% for 80% composite mixtures at an optimum contact time of 50mins.

The initial faster rate was due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depends on the surface area of the adsorbents [14]. The cadmium adsorption takes place at the more reactive sites. As the sites are progressively filled the more difficult the adsorption becomes.

The result of initial metal ion concentration showed that removal of Cd increased at a steady rate as initial concentration increased up to 50 mg/L. The percentage removal of cadmium (fig. 1c) showed an increased at a steady rate as initial concentration was increased up to 50 mg/L, attaining a maximum value of 85.36% for 20% composite mixtures, 84.66% for 50% composite mixtures and 99.97% for 80% composite mixtures.

With increasing metal ion concentration, there is increase in the amount of metal ion adsorbed due to an increased in the driving force of the metal ions towards the active sites on the adsorbent [14].

The study of adsorption kinetics explains the rate of solute uptake at the solid – solution interface. Pseudo-Second-Order reaction is based on the assumption that adsorption follows a second order mechanism and a plot of t/q_tvs t gives linear plots. According to [15], if the plots are linear, then the adsorption process may be described as chemisorptions.

Pseudo-Second-Order kinetic and Pseudo-First-Order model were applied to the experimental data and Pseudo-Second-Order gave relatively high R^2 value (> 0.990) indicating that the model successfully describes the adsorption of the cadmium onto the composite mixtures in this study and the adsorption process may be a chemical reaction.

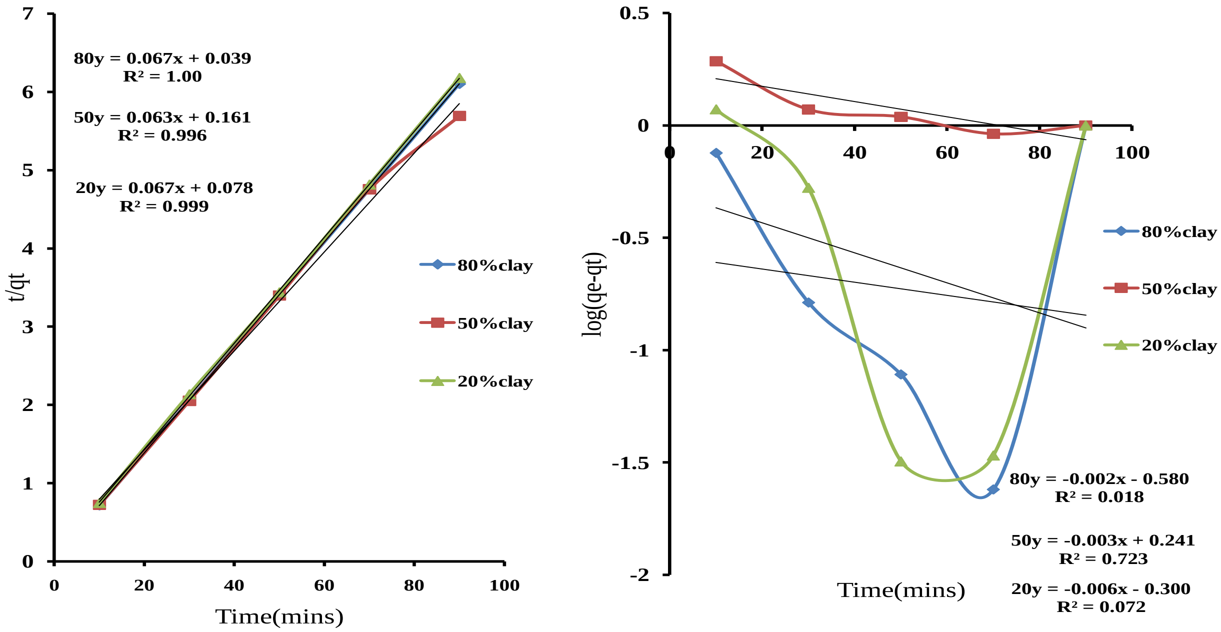

Figure 2: Pseudo-Second-Order Model and Pseudo-First -Order Model for the Adsorption of Cd ions

Conclusions

From the analysis of the result, it is evident that irrespective of the various composite mixtures, clay and ripe plantain peels have great potential for the uptake of cadmium from aqueous solution. It was also observed that the adsorption process of the composite mixtures depends on conditions such as pH, initial metal ion concentration and contact time. Plantain peels which are a problem to the environment could be used to remove heavy metals and help to reduce its menace in the environment and enhance effective waste management.

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