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Full Length Research Paper

Adsorption of lead ions from aqueous solution by okra wastes

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Okra wastes from food canning processes were used as a potential adsorption of lead removal from various aqueous solutions was performed. Parameters such as pH, temperature of the solution, particle size of okra wastes and the concentrations of adsorbent and adsorbate were studied to optimize the conditions to be utilized on a commercial scale for the decontamination of effluents using a batch adsorption technique. Adsorption parameters were determined using both Langmuir and Freundlich isotherms. The optimum pH for lead removal was between 4 and 6, the percentage of lead removal at equilibrium increases with increasing the amount of okra wastes and temperature. Better adsorption at higher temperatures. The removal of Pb^{2+} ions attained 99%., this means that Pb^{2+} can be effectively removed from aqueous solutions by okra wastes. The mechanisms for adsorption of Pb^{2+} ions on to okra wastes involved ion exchange or the formation of hydroxyl complexes. The results obtained could be useful for the application of agricultural wastes for heavy metal removal from industrial wastewater.

Key words: Adsorption, Pb^{2+} ion, Agricultural wastes, okra wastes.

INTRODUCTION

Due to rapid development and industrialization in many countries, the levels of industrial pollution have been steadily rising. So the pollution problem of industrial wastewater is becoming more and more serious in the world. Consequently, the treatment of polluted industrial wastewater remain a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land. Moreover, contamination of ground water is today a major concern in the management of water resources (Weber et al., 1991). Contaminants as pesticides (El-Geundi et al., 2005), heavy metals (Adesola et al, 2006) and organic substances (Khouider et al., 2004) are characterised by a wide variety of processes occurring in the soil including diffusion: mechanical dispersion, chemical reaction, decay, adsorption and biodegradation. The presence of cupper, zinc, lead, iron, nickel and others metals, has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. Many methods of treatment for industrial wastewater have been reported in literature (Periasany and Namasivayam, 1995; Dimitrova and Mehandgiev, 1998). Amongst these methods are neutralisation, precipitation, ion exchange and adsorption. For low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal. The process of adsorption implies the presence of an “adsorbent” solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap.

Activated carbon (A.C.) is widely used as an effective adsorbent in many applications. It is the most commonly used adsorbent in the adsorption process for the treatment of wastewater (Mckay et al., 2000) but metal ion removal by adsorption with activated carbon is relatively expensive. The process for removing metal ions from aqueous solutions by different activated carbon obtained from agricultural by-products has been published Orhan and Buyungor (1993) and Mckay (1984). Due to the high cost of activated carbon and 10 – 15% loss during regeneration, alternative low cost adsorbents have attracted

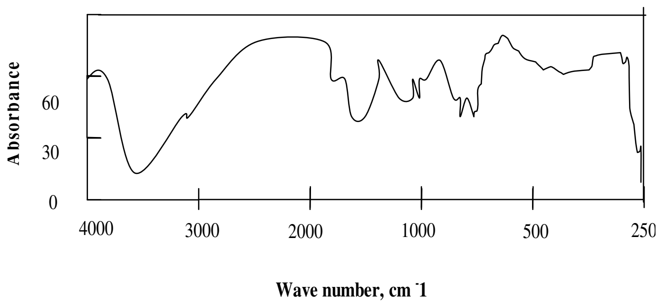

Figure 1. Infra red spectra of okra

the attention of several investigators to provide an alternate for the high cost activated carbon. Though several studies were available explaining the utilization of several low cost adsorbents, most of these work stand at the laboratory level and only a very few cases have been directly implemented in practical applications at industrial level (Abia et al., 2003).

Agricultural by-products could be heavy metal adsorbents which could be selective for some metal ions (Al Duri, 1995). Agricultural material such as banana and orange peels. (Annadurai et al., 2002) bagasse pith, sawdust wastes (Asfour et al., 1995; Zarraa, 1995), maize cob, coconut husk fibres (Tan et al., 1993; Babarinde, 2002), nut shells (Demirbas, 2003), soybeans and cotton seed hulls have been evaluated for their adsorptive properties. These materials have been reported to adsorb different pollutants such as heavy metal ions, dyestuff and other toxic pollutants (El-Geundi, 1997). Refined corn hulls, ground nut husks (Okiemen et al., 1991), and rice hulls (Roy et al., 1993), and have been also evaluated for the adsorption of heavy metal ions from wastewater.

Research in the use of agricultural by-products (Abia and Asuquo, 2006) has included metal binding studies with Datura innoxia, dyed cellulosic materials, wheat and rice bran, oat fiber, sugarcane bagasse, maize cob (El-Geundi, 1997; Al-Duri, 1995; Magdy, 1992; Nassar and El-Geundi, 1994) and sawdust to mention a few (Drake et al., 1996; Shukla and Sakhardane, 1992; Weber et al., 1991; Weber and Morris, 1964).

In this study lead has been chosen because of its environmental importance related to its well known toxicity (Hepple, 1972) and intensive use in industries such as storage-battery manufacture, printing, pigment manufacturing, petrochemicals, fuel combustion and photographic materials (Carson et al., 1986). Assimilation in the human body of relatively small amounts of lead over a long period of time can lead to malfunctioning of certain organs and chronic toxicity (Khurshid and Qureshi, 1984). Lead pollution in water has been increasing progressively in Egypt. This gives rise to concern over health problems in man and animals. Therefore it is of great relevance to develop a new method for its removal from water, and this is the aim of the present work.

This study may generate useful information for the utilization of native agricultural by-products for the removal of Pb^{2+} from wastewater. Okra wastes, as agricultural by-products from food canning industries, could be heavy metal adsorbents which could be selective for some metal ions. No information is available for metal removal by these agricultural by-products. In this study the capabilities of okra wastes for lead ion adsorption were tested at several experimental conditions. The effect of pH, lead concentration, adsorbent dose, particle size and temperature on the rate of removal of lead was investigated. The equilibrium data is described by Freundlich and Lamgnuir adsorption isotherms.

MATERIALS AND EXPERIMENTAL WORK

Materials

The sorption of Pb^{2+} ion has been studied by batch experiments using agricultural wastes (okra wastes). These wastes are obtained from food canning processes. The okra wastes were sun dried, after washing with water. The dried amounts are ground and screened to the desired size. Four fractions groups, from 180 to 60 µm with different particle sizes, d_{pm}, were used as follows:

G_1	d_{pm} = 180	µm	G_2	d_{pm} = 130	µm
G_3	d_{pm} = 90	µm	G_4	d_{pm} = 60	µm

The results of chemical analysis of okra wastes are shown in Table 1. The infrared (I.R.) absorption spectrum apparatus was used to investigate the chemical structure of okra wastes. A double beam I.R. Perkin–Elmer Model 598 has been applied over a different wave number. The absorption spectrum of okra wastes is represented in Figure 1.

Experimental work

A stock solution of lead nitrate (1000 mg/l) was used as adsorbate and solutions of various concentrations were obtained by diluting the stock solution with distilled water. The pH adjustments were made with nitric acid or sodium hydroxide depending on the pH value required. Lead concentration was determined by UV spectrophotometer and some experimental data points are confirmed by titration using EDTA. All the chemicals used were of analytical grade reagent and all experiments were carried out in 300 ml sealed glass bottles at the laboratory ambient temperature 25ºC ± 2.

The bottles were placed in a temperature controlled shaker bath. A solution (200 ml) with known initial lead concentration and pH value was mixed with a definite amount of okra wastes. After shaking the sample at constant speed for 1.5 h in order to reach equilibrium, the suspension was filtered and the lead concentration in the filtrate was determined spectrphotometerically. The adsorbed phase concentration was calculated using the following equation (Nassar, 1997):

$$Qe = V(C_i - C_f) / W$$

where C_i is the initial lead concentration, C_f is the final lead concen-

Table 1. Chemical analysis of dry okra wastes

Chemical composition of dry okra		Chemical groups present in okra	
Compound	%	Wave number of bonds cm^{-1}	Chemical groups
CaO	3.8	3700-3200	OH
P_2O_5	3.8	3000-2900	C-H
MgO	1.5	1800-1650	C=O
Carbohydrate	64.4	1620	Aromatic ring
Fat	2.3	1550-1500	N
Protein	18.9	1485-1440	CH_2 and CH_3
Fibre	7.6	1390-1360	CH_3
		1300-1200	C-O-C
		1200-1000	C-O
		900-960	Cyclic comp.
		850-800	C=C
		800-700	Alkyl group
		700-400	Sub. in arom. ring

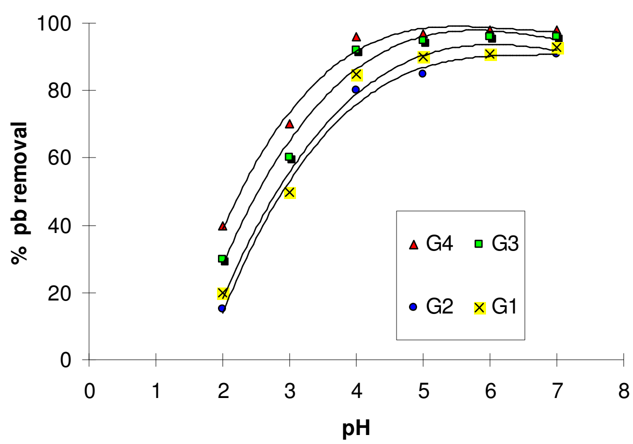

Figure 2. Dependence of the lead ion removal on pH at different particle size of okra waste (C=100 mg/l)

tration in the liquid phase, Q_e denotes the equilibrium concentration of lead in the adsorbate phase, V is the volume of the solution and W is the weight of the adsorbate.

RESULTS AND DISCUSSIONS

Effect of pH

The adsorption behaviour of Pb (II) was studied from the aqueous solution at different pH values. The pH values are the principal factors influencing the adsorptive capacities of Pb^{2+} ion on okra wastes. The removal of lead from solutions presents several difficulties, mainly due to the fact that a precipitation process is not possible by simple pH regulation of the solution as in the case of polyvalent metallic cations (Xu et al., 2006).

The results obtained are shown in Figure 2 which shows the effect of pH on the adsorption of pb^{2+} ion from the aqueous solution on okra wastes, expressed in terms of the metal ions removed percent. It is clear that Pb^{2+} ion was effectively adsorbed in the pH range 4-6 and the maximum adsorption of pb^{2+} ion on okra wastes occurred at pH = 5, thus, pH = 5 was chosen for all experiments. The dependence of percent lead removal on pH is similar to the heavy metal ion sorption on agricultural wastes sorbents (Rodda et al., 1993). The results in Figure 3 showed that the equilibrium capacity of lead removal by okra wastes increased significantly as the pH of the solution increased. If the initial pH was too high, lead ions precipitate out and this defects the purpose of em-ploying the sorption process. The sorption process is kinetically faster than the precipitation (Appel and Lena, 2002).

The adsorptive capacities of Pb^{2+} ion increased rapidly as the pH value increased. At pH value above the range 5 - 6 the adsorptive capacities of pb^{2+} ion increased but at slower rate because of the competitive adsorption between hydrogen ion and the heavy metal cation. The continuation increases in the adsorptive capacities of Pb^{2+} ion with increasing the pH value is due to the decreases in the hydrogen ion concentration as the pH value decrease. The adsorption at near neutral pH value (pH = 7) could be attributed to the cellulose component of the okra wastes where site- binding adsorption might be occurring. This could be due to the surface complexation phenomenon of functional groups present in the okra wastes (Table 1). The removal of lead therefore is probably due to the mixed effect of ion exchange and surface complexation on the surface of okra wastes and

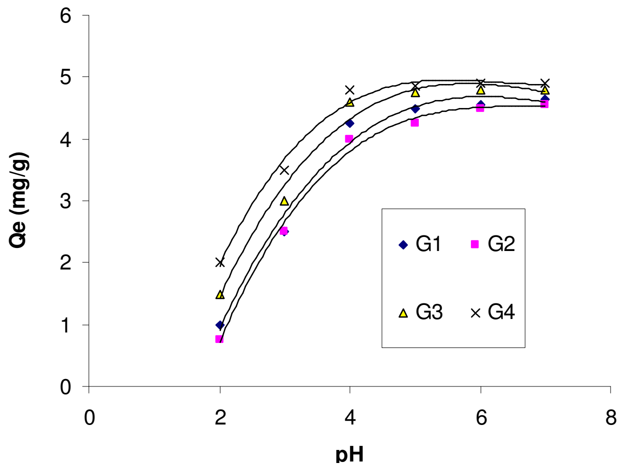

Figure 3. Effect of pH on the adsorptive capacities of pb2+ ion on okra waste (C= 100 mg/l)

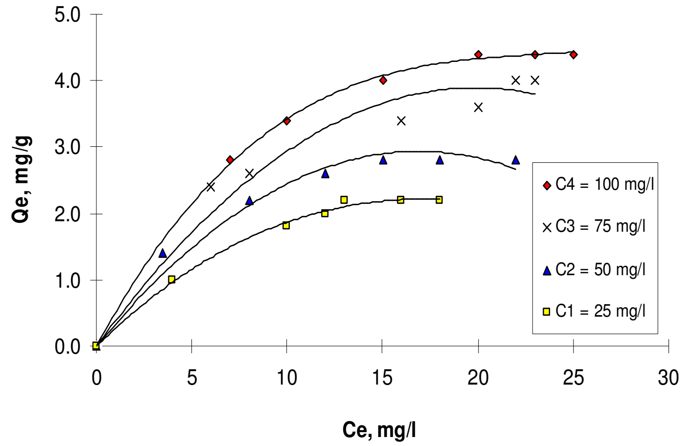

Figure 4. Effect of initial concentration of Lead ions on equilibrium.

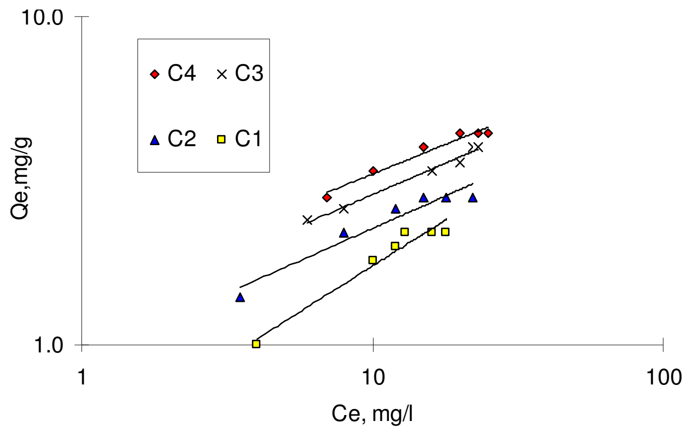

Figure 5. Lineariztion of the Freundlich isotherm of Pb(II) using okra wastes

the decrease in adsorption at pH grater than 7 is probably due to the formation of hydroxide. This is in agreements with the results obtained by (Kalid and Ahamed, 1998) for adsorption of lead on rice husk. All other fractions show almost the same pH dependence. Maximum lead removal is achieved with all okra fraction within 98 - 99% at pH = 5. The above results suggest that the okra wastes can be used as a potential decontami-nant for the removal of lead ions from aqueous solution.

Effect of the initial concentration

The effect of lead ion concentration was studied by batch adsorption experiments carried out at 25ºC using a concentration range of 25 – 100 mg/l. The results obtained were analysed using both Freundlich and Langmuir isotherms. These two models are widely used, the former being purely empirical and the latter assuming that maximum adsorption occurs when the surface is covered by one layer of adsorbate. The adsorptions of lead ion on okra wastes with different initial concentrations are shown in Figure 4. The adsorption capacity increases with an increase in the initial ion concentration. This is in agreements with the results obtained by other investigators (Dimitrova and Mehandgiev, 1998).

Since the adsorption isotherms are important to des-cribe how adsorbates will interact with adsorbents and so are critical for design purposes, therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation (Hashem et al., 2007). Two isotherm equations were adopted in this study i.e.

The Freundlich isotherm is defined as

$$Q_e = KC_e^{1/n}$$

Where K and n are Freundlich constants and Qe is the amount of lead adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage. The plots of Q_e against C (Figure 5) for adsorption of lead ion gave a straight line. The correlation coefficient (Table 2) indicates that the adsorption process conforms to the Freundlich isotherms (Akhtar and Qadeer, 1997), Salam, and Adekola, 2005). The values of Freundlich exponent, n, are greater than unity (Nassar et al., 1995), indicating that lead ions are favourably adsorbed by the okra wastes investigated.

The Langmuir isotherm is defined as

$$Qe = x/m = (a\ b\ Ce) / (1 + b\ Ce)$$

and in linearized form is

$$Ce / Qe = 1/ab + 1/a(Ce)$$

Table 2. Freundlich constants of okra wastes

Group number	Freundlich constants		Correlation coefficient, r^2, -
	$K, dm^3/g$	n,	
C_1	0.67	1.79	0.955
C_2	0.91	2.53	0.9327
C_3	1.19	2.62	0.9879
C_4	1.45	2.78	0.9557

Where C_1 = 25 mg/l, C_2 = 50 mg/l, C_3 = 75 mg/l, C_4 = 100 mg/l

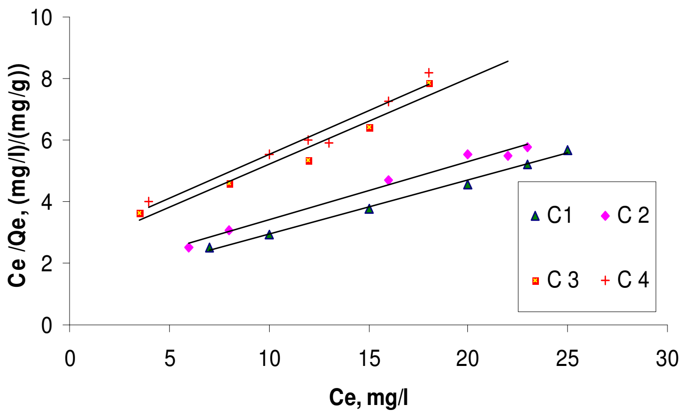

Figure 6. Lineariztion of Langmuir adsorption isotherm of pb(II) using okear waste

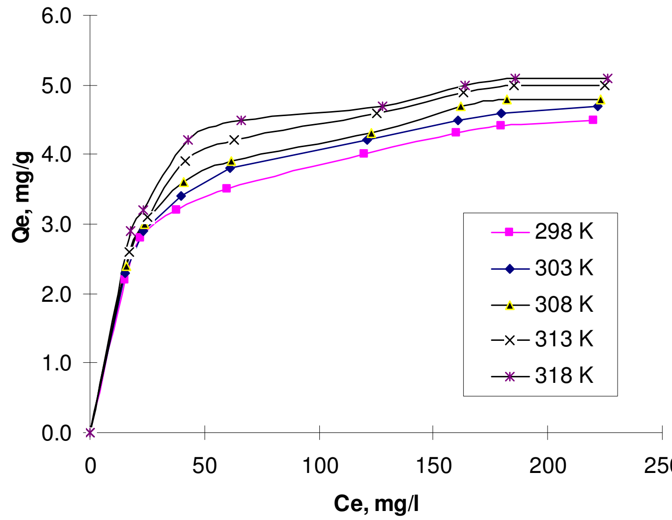

Figure 7. The Adsorption Isotherms at different temperature

Table 3. Langmuir constants of okra wastes.

Group number	Langmuir constants		Correlation coefficient, r^2, -
	ab	a	
C_1	0.378	5.74	0.9942
C_2	0.665	5.26	0.9834
C_3	0.414	3.58	0.9596
C_4	0.378	3.47	0.961

where a and b are Langmuir coefficient related to the affinity between the sorbent and sorbate, and Qe is the maximum sorbate uptake under the given condition. The plots of Ce/Q_e against Ce (Figure 6) for adsorption of lead ion gave a straight line. It is seen that the linear fit is fairly good and enables the applicability of the Langmuir model to lead ion adsorption on the okra wastes. The isotherm constants and their correlation coefficients, r^2, are listed in Table 3. Where C_1 = 25 mg/l, C2 = 50 mg/l, C_3 = 75 mg/l, C_4 = 100 mg/l.

Effect of temperature

The effect of temperature on the adsorptive capacity of Pb (II) on okra wastes is illustrated by the results depicted in Figure 7. It is clear that the uptake of Pb^{2+} ion increased with an increase in temperature, indicating better adsorption at higher temperatures. The increase in the amount of Pb^{2+} adsorbed at equilibrium with increases in temperature may be due to the acceleration of some originally slow adsorption steps or to the creation of some active sites on the adsorbent surface (Nassar and Magdy 1999). The enhanced mobility of Pb^{2+} ions from the bulk solution towards the adsorbent surface should also be taken into account (Yubin et al., 1998). Similar results have been obtained in studies of the adsorption of lead on rice husk (Khalid and Ahmad, 1998). The adsorption of Pb^{2+} ion may involves chemical bond formation and ion exchange since the temperature is the main parameter affecting the above two processes (Yubin et al., 1998).

Effect of adsorbent amounts

The amount of adsorbent employed was found to influence the efficiency of the adsorption process. This parameter was optimized in conjunction with the other optimized parameters (100 mg/l lead at a pH = 5) by shaking different amount of okra wastes (D) and the results are depicted in Figures 8 and 9. The percentage of lead removal (Figure 8) increases with increasing the okra amount for groups of different particle size. The mechanism of lead removal by the okra is complex and it is not determined by the process of precipitation. Dimitrova and Mehandgiev (1998) considered that the observed effect is connected with the redislodgement of calcium from the

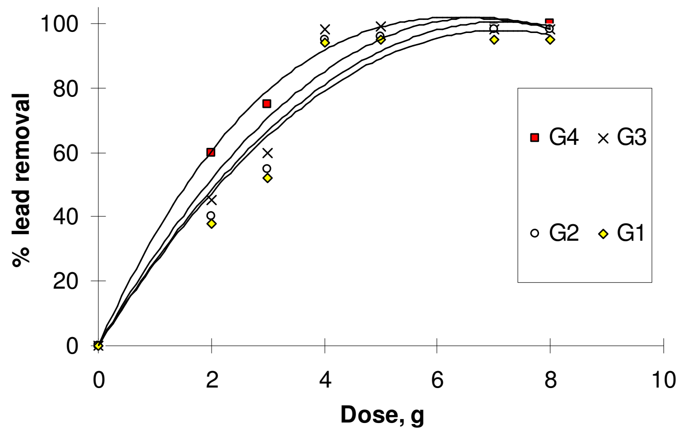

Figure 8. Effect of okra waste dose on the percentage of removal of lead (II)

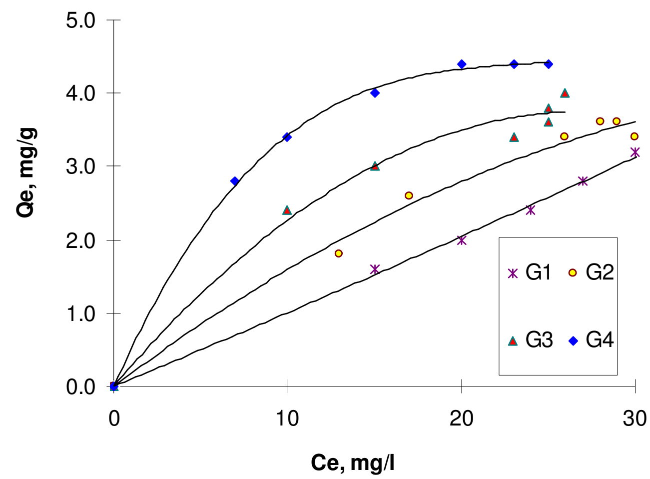

Figure 9: Effect of wastes particle size on the equilibrium capacities of lead (II)

agricultural wastes into the solution and thereby the sites for the sorption of Pb^{2+} ions are set free. The adsorption of metal ion on agricultural by-products may involve metal interactions (Kumar, 2006) or coordination to functional groups present in natural proteins, lipids, and carbohydrates positioned on cell walls (Drake et al., 1996).

Conclusions

The okra wastes are adsorbents of great potential and have proven appropriate adsorbent for lead removal from aqueous solution, percentage of lead removal reach 99%. The sorption isotherms of both Freundlich and Langmuir are obtained and they well described the sorption process indicating favourable adsorption of lead onto okra wastes as a monomolecular type. Removal of lead is highly pH dependent, the best results being obtained at pH 5. The sorption capacity was found to increase significantly with increase in the adsorbate pH, temperature and adsorbent dose. The adsorption mech-anism of Pb2 ion on okra wastes involves either cation exchange or complexation between the metal cation and the hydroxide ion in the solution.

Based on the experimental conditions, it is concluded that the removal of Pb^2 ion from their aqueous solution could attain 99%. This shows a new trend for using a agricultural wastes from food canning processing as well as a mean for wastes disposal for the benefit of environmental pollution control.

Nomenclature

C_e = equilibrium lead concentration, mg/l
D = amount of okra wastes added, g/l
d = okra wastes particle size, µm
d_{pm} = mean particle diameter, µm
G = group of okra particle size d_{pm} , µm
K, n = constants in Freundlich equation
Q_e = equilibrium capacity of the okra, mg/g

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