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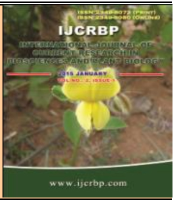

Original Research Article

Adsorption of Heavy Metals from Aqueous Waste Water Using Unmodified and Ethylenediaminetetraacetic Acid (EDTA) Modified Maize Cobs

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Abstract

The adsorption of heavy metals (Zn, Fe, Pb, Cu and Cr) ions from aqueous waste water using unmodified and EDTA modified maize cob was modeled. The influence of contact time and temperature on the adsorption efficiency was studied using batch equilibrium assays. From the results, it was observed that, adsorption capacity was highest at 40 min (the contact time). Further observation showed that, adsorption efficiency decreases and increases with temperature using unmodified and modified cobs respectively. Thermodynamic parameters such as ΔG, ΔH, ΔHr and ΔS were obtained from the experimental data which indicated the feasibility and spontaneity of the adsorption process with physisorption mechanism using unmodified cob and combined physisorption, ion exchange and chemisorptions using modified cob. The EDTA modified cob showed the highest adsorption capacity and thus suitable for heavy metals removal from aqueous waste water.

Keywords

Adsorption
Heavy metals
Maize cobs
Thermodynamic parameters

Introduction

The problems of the ecosystem are increasing with developing technology; Heavy metals pollution is one of the main problems (Uzun and Guzel, 2000). Toxic metal compounds coming to the earth's surface not only reach the earth's Waters (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow. Therefore, the earth's waters may contain various toxic metals (Uzun and Guzel, 2000).

Heavy metals are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment. High concentrations of heavy metals may accumulate in human body once they interrupt in human food chain and possibly cause severe health problems if the metals exceed the permitted concentrations (Siti Nur et al., 2013). The presence of these metals in effluents may increase fertility of the sediment and water column, this may eventually lead to eutrophication, which in open waters may results to oxygen deficiency, algal bloom and death of aquatic life (Asamudo et al., 2006; Igwe and Abia, 2007)

Water contaminated with metallic effluent can cause several health problems. Lead for instance, can interfere with enzyme activities and formation of red blood cells. It can affect nerves and brain at low concentration. Heavy metals such as mercury, cadmium and chromium can accumulate and through the food chain to toxic levels in man. Cadmium is responsible for kidney tubular impairment and osteomalacia (Igwe and Abia, 2007). Cadmium, zinc and manganese are reported to affect ion regulation if present in sufficient concentrations. Cadmium and manganese arealso known to affect calcium metabolism, development and skeletal calcification as well as long term effect, spawning and recruitment of fish and other aquatic lives (Igwe and Abia, 2007).

A number of physico-chemical processes are used world- wide to depollute water loaded with heavy metals. These methods however, are inherently problematic in their application and are not economically feasible (Volesky, 2001; Sharma, 2003). For this reason, low cost adsorbent have been evaluated for the removal of heavy metals in aqueous solutions. The search for new technologies to remove toxic metals from waste waters has directed attention to biosorption which is based on metal binding for various biological materials (Hanan et al., 2010). A variety of agricultural waste materials that are environmentally friendly and low cost has been used by many researchers to depollute the menace of heavy metals in aqueous solutions. For instance, a variety of low-cost biomass has been studied by various workers for controlling pollution from diverse sources in different parts of the world (Kar and Misra, 2004). They include anaerobically digested sludge, bacteria and fungi (Tokcaer and Yetis, 2006; Lu et al., 2006; Garcia et al., 2005). Agricultural materials have also been used; these include rice bran, soya bean and cottonseed hulls, and crop milling waste (Saeed et al., 2005), groundnut husk, maize cob meal, coir, jute and sawdust (Shukla and Pai, 2005).

The objectives of this work are to evaluate the sorption capability of heavy metals by maize cobs, study the effect of modification on the sorption properties of the maize cobs and determine the thermodynamic parameters related to the adsorption.

Materials and methods

In the preparation of reagents, chemicals of analytical grade purity and doubly distilled water were used. All apparatus were thoroughly washed with detergent solution followed by tap water and lastly, distilled water was used for the rinsing.

Sampling and Pre-treatment

Maize cobs were freely obtained from the farm in Dutsinma, Katsina State, Nigeria. These were milled and sieved through a 1mm mesh size. Waste water was obtained from five sampling sites labeled as B1-B5 from river Getsi-Kano, Nigeria. Samples were transported to the laboratory for further analysis.

Experimental

To evaluate the effectiveness of agro waste material in the sorption of heavy metals in aqueous solutions, maize cob was used in two ways. First the maize cob was used without any modification, and in the second experiment the maize cob was modified using ethylenediaminetetraacetic acid (EDTA).

Analysis of water sample

Measured quantity (100 cm^3) of the water sample was taken in a 250 ml beaker. To this $30cm^3$ of concentrated nitric acid was added, the mixture was digested in a fume cupboard until the digestion was complete with an evolution of a colorless gas. The digest was cooled, washed with distilled water, filtered and transferred to a 100 ml volumetric flask. The solution was made up to the mark with distilled water. The solution was analyzed for heavy metals using Atomic Absorption Spectrophotometer (Buckmann Model 4) (APHA, 1998).

Sorption experiment

The adsorption experiment was carried out in a $250cm^3$ conical flask capped with aluminium foil first to determine the contact time and at varying temperatures (25, 40 and 55 °C) to study the effect of temperature. Weighed quantity (2 g) of the maize cob (adsorbent) was added to each 100 cm^3 of the water sample (whose metal concentration was evaluated as described above), and agitated with a Stuart flask shaker for the contact time. At the end of the contact time, the reaction mixture was filtered through what man filter paper and the metal ions in the filtrate were determined using an atomic absorption spectrophotometer. The amount of the metal adsorbed by the maize cob was calculated as the difference between the initial and final metal ion concentration of the solutions. The procedure was repeated for the adsorption using modified maize cob (Abdel-Ghani et al., 2007).

Results

The results were expressed as the removal efficiency *(%ad)* of the adsorbent towards metal ions or percentage (%) removal, which is defined by equation 1.

$$\%ad = \left[\frac{co-cf}{co}\right]X100 \qquad \text{-------- (1)}$$

Where, C_o and C_f are the initial and equilibrium concentration (mg/L) of metal ions in solution, respectively (Abdel-Ghani et al., 2007). Tables 1 and 2 present the results of the experimental run for the adsorption of Cu, Pb, Fe, Cr and Zn ions on modified and unmodified maize cobs.

Note:

Throughout the course of this work, any quantity or parameter with asterisk (*) describes the use of modified maize cob**,** HMI in full is heavy metal ion and **Ci** = initial concentration (mg/L) of heavy metal ions in aqueous solution.

Table 1. Equilibrium concentrations in mg/L of heavy metal ions for adsorption using unmodified (Ce) and modified (*Ce) maize cobs at different temperatures.

HMI	Temperature (°C)						
	Ci	25		40		55	
		Ce	*Ce	Ce	*Ce	Ce	*Ce
Zn	0.81	0.07	0.04	0.1	0.009	0.17	0.008
Fe	1.57	0.7	0.63	0.73	0.59	0.76	0.58
Pb	0.67	0.07	0.05	0.14	0.02	0.2	0.012
Cu	1.55	0.65	0.6	0.68	0.56	0.74	0.51
Cr	0.72	0.09	0.07	0.17	0.053	0.22	0.045

HMI - heavy metal ion; Ci - initial concentration (mg/L).

Table 2. Adsorption efficiencies for adsorption using unmodified (%ad) and modified (%ad*) maize cobs at different temperatures.

HMI	Temperature (°C)					
	25		40		55	
	%ad	%ad*	%ad	%ad*	%ad	%ad*
Zn	91.36	95.06	87.65	98.89	79.01	99.01
Fe	55.41	59.87	53.50	62.42	51.59	63.06
Pb	89.55	92.54	79.10	97.01	70.15	98.21
Cu	58.06	61.29	56.13	63.87	52.26	67.10
Cr	87.5	90.28	76.39	92.64	69.44	93.75

HMI - heavy metal ion.

Effect of surface modification

From tables 1 and 2, it can be shown that in all the heavy metal ions, the modified cob gave the highest adsorption capacity, showing that there was enhancement of adsorption by modifying with EDTA. EDTA is a chelating agent. Therefore, the modification of the maize cob with EDTA was to change the surface characteristics of the adsorbent and then, to find out the effect this will have on the sorption process (Okuo et al., 2014).

Effect of contact time

It was observed that the maximum time for the adsorption capacity of the metals uptake by the maize cob was 40 min due to the large surface area available for adsorption. Further increase in time resulted in desorption of the metal ions from the adsorbate surface.

Effect of temperature

It has been observed from Table 2 that, adsorption decreases with increasing temperature for the same mass of unmodified maize cob and metal ion concentration but increases with increase in temperature for adsorption using modified maize cob. The decrease is as a result of the tendency of the heavy metal ions to evaporate from the solid phase to the bulk phase or due to weak adsorptive forces between the active sites and the adsorbed species and also between close by molecules of adsorbed phase. This suggests that the adsorption process using unmodified maize cob is physisorption (Ladan et al., 2013). The reason for the enhanced adsorption at higher temperature using modified maize cob may be attributed to the increase in number of active sites on the adsorbent. The adsorption of the metal ions increased with rise in temperature which indicates endothermic nature of the adsorption process (Deosarkar, 2012).

Thermodynamic study

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not (Jing et al., 2010). The changes of Gibb's free energy, enthalpy, entropy and isosteric heats of adsorption were all calculated from the data generated from the experiments and were presented in Tables 3 and 4.

Table 3. Gibbs free energy change (kJ/mol) for heavy metal ions adsorption onto maize cob at varying temperatures.

HMI	Temperature (°C)					
	25		40		55	
	ΔG	ΔG*	ΔG	ΔG*	ΔG	ΔG*
Zn	-5.85	-7.28	-5.1	-7.7	-6.63	-12.57
Fe	-0.55	-0.99	-0.36	-1.33	-0.17	-1.45
Pb	-5.33	-6.24	-3.46	-9.06	-2.32	-10.9
Cu	-0.82	-1.14	-0.65	-1.46	-0.25	-1.94
Cr	-4.83	-5.52	-3.04	-6.58	-2.24	-7.39

HMI - heavy metal ion.

As seen from Table 3, the overall standard free energy changes during the adsorption process were negative for the experimental range of temperatures, corresponding to a spontaneous process of heavy metal ions adsorption onto the two forms of maize cob (Solener et al., 2008). The decrease in the negative value of ΔG* with an increase in temperature indicates that the adsorption process of heavy metal ions on modified maize cob becomes more favorable at higher temperatures (Zaki et al., 2000). However, adsorption process of heavy metal ions on unmodified maize cob followed the opposite trend.

From Table 4, the negative values of enthalpy change (**ΔH)** for adsorption of heavy metal ions using unmodified maize cob indicates an exothermic process whereas, positive values of enthalpy change (**ΔH***) for adsorption using modified maize cob indicates an endothermic process. The negative values of entropy change (**ΔS)** for adsorption of heavy metal ions using unmodified maize cob indicates less randomness at the solid/solution interface whereas, positive values of entropy change (**ΔS***) for adsorption using modified maize cob corresponds to the increasing randomness at the solid/liquid interface during the sorption process. However, a negative value for ΔS was also reported for the adsorption of Methylene Blue by cereal chaff (Han et al., 2006) and fallen phoenix tree's leaves (Han et al., 2007).

Table 4. Enthalpy change (kJ/mol), Isosteric heat of adsorption (kJ/mol) and Entropy change (kJ/mol/K) for heavy metal ions adsorption onto maize cobs.

HMI	Temperature (°C)					
	25		40		55	
	ΔH	ΔH*	ΔHr	ΔHr*	ΔS	ΔS*
Zn	-21.41	34.71	-14.38	62.00	-0.053	0.14
Fe	-3.24	2.70	-1.74	2.73	-0.0092	12.64
Pb	-27.00	30.76	-28.81	38.10	-0.074	0.13
Cu	-4.99	5.20	-1.86	2.87	-0.014	0.021
Cr	-23.49	9.98	-26.44	11.56	-0.064	0.053

HMI - heavy metal ion.

The values of Isosteric heat of adsorption (Δ**Hr**) for adsorption using unmodified maize cob are below 8kJ/mol, indicating a physisorption process. For adsorption in the presence of modified maize cob, some energy values are less than 8 kJ/mol, a value fall between (8 and 16) kJ/mol, a value is less than 40 kJ/mol and one greater than 40 kJ/mol corresponding to a combined physical adsorption, physisorption, chemical ions exchange and chemisorption process (Al-Anber, 2010).

Conclusion

This work described the adsorption studies of heavy metals, Zn, Pb, Cr, Cu and Fe from the aqueous solution using modified EDTA and unmodified maize cob. The results revealed that maize cob which is a waste agricultural product is effective in the sorption of the heavy metals in aqueous solution. The sorption of all the five metal ions onto unmodified maize cob is a physisorption process while the use of EDTA modified maize cob is a combined physisorption, chemical ion exchange and chemisorptions process. The sorption efficiency (% removal) was found to be higher with the modified EDTA maize cob compared to unmodified form probably due to the chelating ability of EDTA. Thus, maize cob can be used in the removal of heavy metals from aqueous solutions.

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