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Removal of Cd, Cr, and Pb from aqueous solution by unmodified and modified agricultural wastes

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Abstract The adsorption of cadmium (Cd), chromium (Cr), and lead (Pb), widely detected in wastewater, by unmodified and modified banana stalks, corn cob, and sunflower achene was explored. The three agricultural wastes were chemically modified with sodium hydroxide (NaOH), in combination with nitric acid (HNO_3) and sulfuric acid (H_2SO_4), in order to improve their adsorptive binding capacity. The experiments were conducted as a function of contact time and initial metal ion concentrations. Of the three waste materials, corn cob had the highest adsorptive capacity for Pb than Cr and Cd. The NaOH-modified substrates had higher adsorptive capacity than the acid modified samples. The chemical treatment invariably increased the adsorption capacity between 10 and 100 %. The Langmuir maximum sorption capacity (q_m) of Pb was highest (21–60 mg g^{-1} of banana, 30–57 mg g^{-1} of corn cob, and 23–28 mg g^{-1} of sunflower achene) and that of Cd was least (4–7 mg g^{-1} of banana, 14–20 mg g^{-1} of corn cob, and 11–16 mg g^{-1} of sunflower achene). The q_m was in the order of Pb > Cr > Cd for all the three adsorbents. The results demonstrate that the agricultural waste materials used in this study could be used to remediate water polluted with heavy metals.

Keywords Cadmium · Chromium · Lead · Removal · Aqueous solution · Agricultural waste material

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Introduction

The reuse of wastewater for agricultural purposes especially in peri-urban areas has become common due to its availability and high organic component at little or no cost. The rapid increase in population, coupled with high industrial scale operations, has contributed significantly to the discharge of untreated effluent containing toxic metals into municipal sewers. This wastewater, containing considerable amounts of heavy metals, is disposed of to water bodies and arable land without any pretreatment (Mahmood-ul-Hassan et al. 2012). The contamination of peri-urban soils following irrigation with untreated wastewater has been established in various studies (Ghafoor et al. 1995; Hussain et al. 2006; Mahmood-ul-Hassan et al. 2012; Suthar et al. 2014). Continuous accumulation of non-biodegradable toxic elements on arable land has a consequential and detrimental health effects to human and entire ecosystem (Kabata-Pendias and Pendias 1992; Giller et al. 1998).

Pretreatment of wastewater can substantially reduce its hazardous impact on the environment, biota, and human and animal health. Conventional techniques, which are being practiced to remove heavy metals from effluents, include lime precipitation, ion exchange, adsorption onto activated carbon (Dean et al. 1972), membrane processing, and electrolytic methods (Braukmann 1990). Among these, adsorption is a simple and relatively cost-effective method that has been widely used (Leung et al. 2000; Kurniawan and Babel 2003a). Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and bounded by physical and/or chemical interactions (Kurniawan and Babel 2003b).

In recent years, biosorption has emerged as a promising technique for the removal of heavy metals from aqueous environment especially when adsorbents are derived from plant material. However, agricultural by products vary greatly in their ability to remove metals from solution. Biosorption is a fast and reversible reaction of the heavy metals with non-living biomaterials called biomass. The biomass has the ability to bioadsorb heavy metal ions and can be used as low-cost and environmentally friendly absorbent. Structurally, these materials are composed of cellulose, hemicellulose, and lignin. The presence of these three biological polymers make them rich in hydroxyl and phenolic groups, and these groups can be used to remove metal ions from aqueous solutions (Osman et al. 2010). Laszlo and Dintzis (1994) and Osman et al. (2010) reported that lignocellulosics have ion exchange capacities and general sorptive characteristics, which are derived from their structure and constituent polymers, i.e., extractives, cellulose, hemicelluloses, pectin, lignin, and protein.

Most biosorption studies have focused on untreated plant wastes (Anwar et al. 2010; Babarinde et al. 2006; Hasan et al. 2008). However, pretreatment of plant wastes with basic solutions (sodium hydroxide, calcium hydroxide, and sodium carbonate), mineral, and/or acid solutions (hydrochloric acid, nitric acid, sulfuric acid, and citric acid) removes soluble organic compounds and increases efficiency of metal adsorption (Tarley et al. 2004; Kumar and Bandyopadhyay 2006; Chen et al. 2007; Suradi et al. 2009; Tan and Xiao 2009). The pretreatment of plant material can remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity or surface area which in general, enhances metal adsorption capacities (Chen et al. 2007; Suradi et al. 2009). The objective of this work was to study the adsorption of cadmium (Cd), chromium (Cr), and lead (Pb) from aqueous solutions by chemically treated and untreated ground banana stalks, corn cob, and sunflower achene.

Materials and methods

Preparation of agricultural biosorbents

Locally available agricultural waste materials, i.e., corn cob, sunflower achene head, and banana stalk, were collected, washed thoroughly with tap water, and then rinsed with deionized distilled water. Then the samples were sundried and oven dried at 70 °C. The dried samples were milled to 250 μm. The milled materials were treated with 0.5 M sodium hydroxide (NaOH) for 24 h to activate the surface groups, and then the treated material was divided into three parts. One part was kept without further treatment while the second and third parts were treated with either 1 M sulfuric acid (H_2SO_4) or 1 M nitric acid (HNO_3) for 4 h at room temperature. Subsequently, the samples were rinsed with distilled water several times and dried at 70 °C to a constant weight.

Batch sorption experiments

Batch sorption experiments were carried out in polyethylene centrifuge tubes to study the effect of contact time and initial metal concentrations on metal adsorption. The effect of contact time was studied by equilibrating 1 g of modified and unmodified material of all three sorbents separately with 50 mL of aqueous solution containing 50 mg/L of each of Pb, Cd, Cr, Ni, and Cu. The suspension was shaken constantly on a mechanical shaker at 175 rpm at room temperature for periods of 10, 20, 40, 60, 90, 120, 150, and 180 min. The equilibrated suspensions were filtered and the filtrates were collected separately. In another set of experiments, the effect of initial metal ion concentration on adsorption was evaluated. As previously, 1 g of all the treated and untreated sorbents was equilibrated with 10, 15, 20, 25, and 30 μg mL^{-1} solutions of Cd, Cr, and Pb for 90 min. The equilibrated solutions were filtered and the filtrate was collected separately. The filtrates were analyzed for Pb, Cd, Cr, Ni, and Cu concentrations using an atomic absorption spectrometer with a graphite furnace (Perkin Elmer AAnalyst 800). Each data point was obtained from individual filtrates separately for each experiment.

The amount of metal ion uptake (biosorption capacity) per gram of the biomass q (mg/g) was calculated as follows:

$$q = \frac{(C_i - C_f) \,.\, V}{m_s}$$

where C_i is the initial metal concentration (μg mL^{-1}) of equilibrating solution, C_f is the final concentration (μg L^{-1}) of the solution, V is the volume of the solution (mL), and m_s is the mass of sorbent (g).

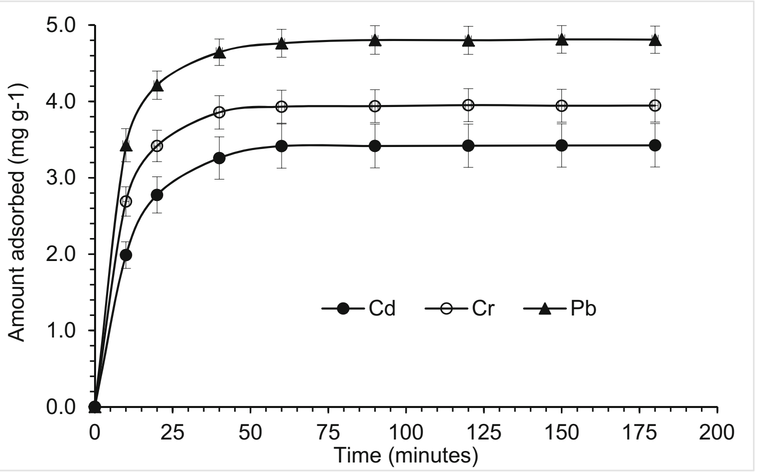

Fig. 1 Effect of contact time on Cd, Cr, and Pb adsorption by agricultural waste materials (average of corn cob, sunflower head, and banana stalk)

In other batch experiments, the metal sorption parameters of maximum sorption capacity and binding strength were determined. One gram of each modified and unmodified biosorbent material was equilibrated with 50 mL of aqueous solution of varying Pb, Cd, Cr, and Cu concentration (0, 50, 100, 200, 300, and 400 μg mL^{-1}) by shaking at 175 rpm at room temperature for 3 h. As described above, the suspensions were filtered and filtrates were analyzed for Pb, Cd, Cr, and Cu concentrations using atomic absorption spectrometry. A mass balance technique was used to calculate the amount of metal sorbed by the biosorbent, and metal sorption parameters were calculated using the Langmuir model.

Results and discussion

Effect of contact time and initial metal concentration

Results of batch experiment conducted to determine the effect of contact time on adsorption of Cd, Cr, and Pb are presented in Fig. 1 (average of modified and unmodified corn cob, sunflower achene, and banana stalk). All three metals had similar adsorption trends; a rapid increase in sorption (81 % of Cd, 84 % of Cr, and 86 % of Pb equilibrium) was observed during the initial phase (20 min), when the active biosorption sites were more available and the metal ions could interact easily with these sites (Tan and Xiao 2009). This rapid initial metal

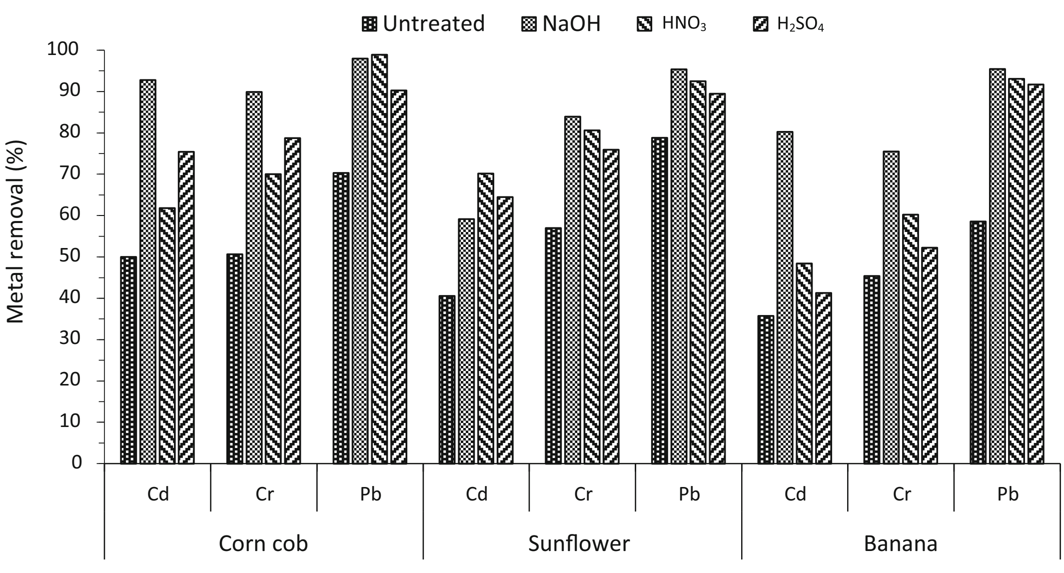

Fig. 2 Metal removal percentage of agricultural by product sorbents from aqueous solution

sorption rate has great practical significance in column and continuous processing where the contact time between the metal solution and the sorbent is generally short. The high initial sorption phase was then followed by a gradual increase to approach equilibrium in about 60 min. Similarly, Noeline et al. (2005) also a reported 60-min time for Pb adsorption equilibrium from an aqueous solution (10 mg L^{-1}) by polymerized banana stem, and Serencam et al. (2013) also reported a 60-min equilibrium time for Cd from 50 mg L^{-1} Cd solution with *Morus alba* L. pomace. In contrast, Tan and Xiao (2009) attained a quicker Cd adsorption equilibrium (in 30 min) when ground wheat stems were exposed to 22.5 mg L^{-1} Cd solution. Although, Cd, Cr, and Pb were equilibrated at the same contact time (60 min), the higher sorption of Pb ions at each was most probably due to ion size—smaller sized ions are heavily hydrated and make the ion larger than less hydrated ions like Pb. This process enhances their sorption by reactive sites as the heavily hydrated ions migrate slowly in aqueous solutions (Chen et al. 2010).

More metal was absorbed as the initial concentration of metals in solution was increased. The increase in metal adsorption capacity with increasing initial metal concentrations may be due to a higher probability of collision between metal ions and adsorbent particles (Tijani et al. 2011). The variation in the extent of adsorption may also be due to the fact that initially all sites on the surfaces of adsorbent were vacant and the solute concentration gradient was relatively high. Although high initial concentration leads to an increase in the affinity of the metal ions toward the active sites, at low concentration, adsorption sites took up the available metal ions more quickly (Saifuddin et al. 2005).

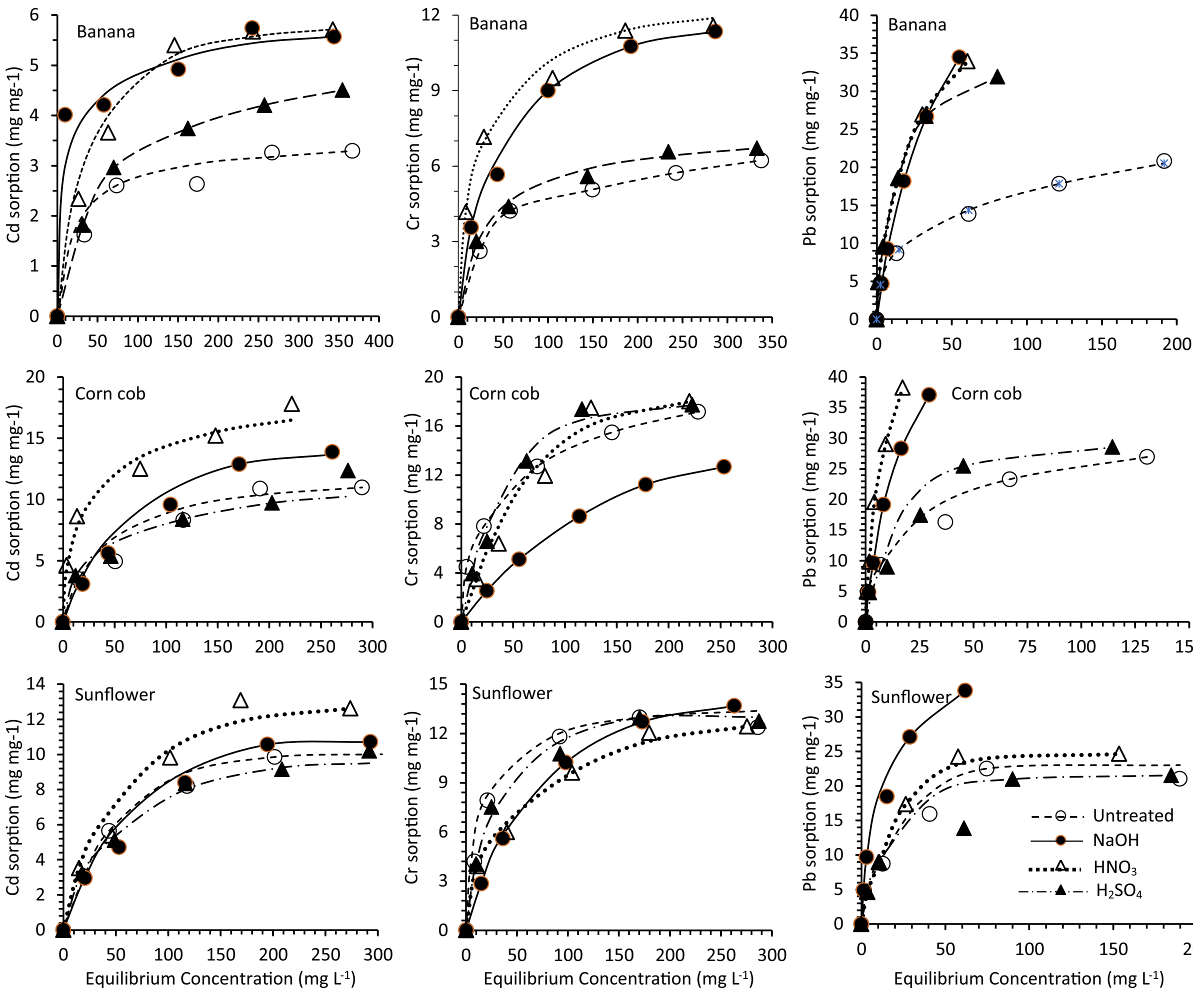

Fig. 3 Langmuir isotherm plot for Cd, Cr, and Pb removal using untreated and treated agricultural biomasses at 25 °C

Effect of chemical pretreatment on metal sorption

The Cd, Cr, and Pb removal capacity of chemically treated and untreated corn cob, sunflower achene head, and banana stalk was evaluated by conducting batch experiments using 50 mL of 50.0 mg L^{-1} metal solution, and the results are presented in Fig. 2. All three treated and untreated materials varied in their ability to remove heavy metal ions from solution. In general, chemical treatment improved the metal removal capacity of adsorbents. This increase was most likely due to the hydrolysis of hemicellulose with base or acid releasing monomeric sugars and soluble oligomers from the cell wall matrix into the hydrolysate. This process increases porosity and chelating properties of plant materials and hence enhances metal sorption capacity and efficiency (Gaballah et al. 1997; Chen et al. 2007). Treated materials of corn cob and sunflower achene removed relatively more Cd and Cr than those of banana stalk, whereas Pb removal was almost the same. Wartelle and Marshall (2000) reported that materials having more lignin may block or allow little penetration of metal ions to reactive sites.

More Cd and Cr were removed by materials treated with NaOH alone than by those treated with H_2SO_4 and HNO_3. Pretreatment with base eliminated residual lignin resulting in the breakdown of fiber bundles which increased the effective surface area and surface charge

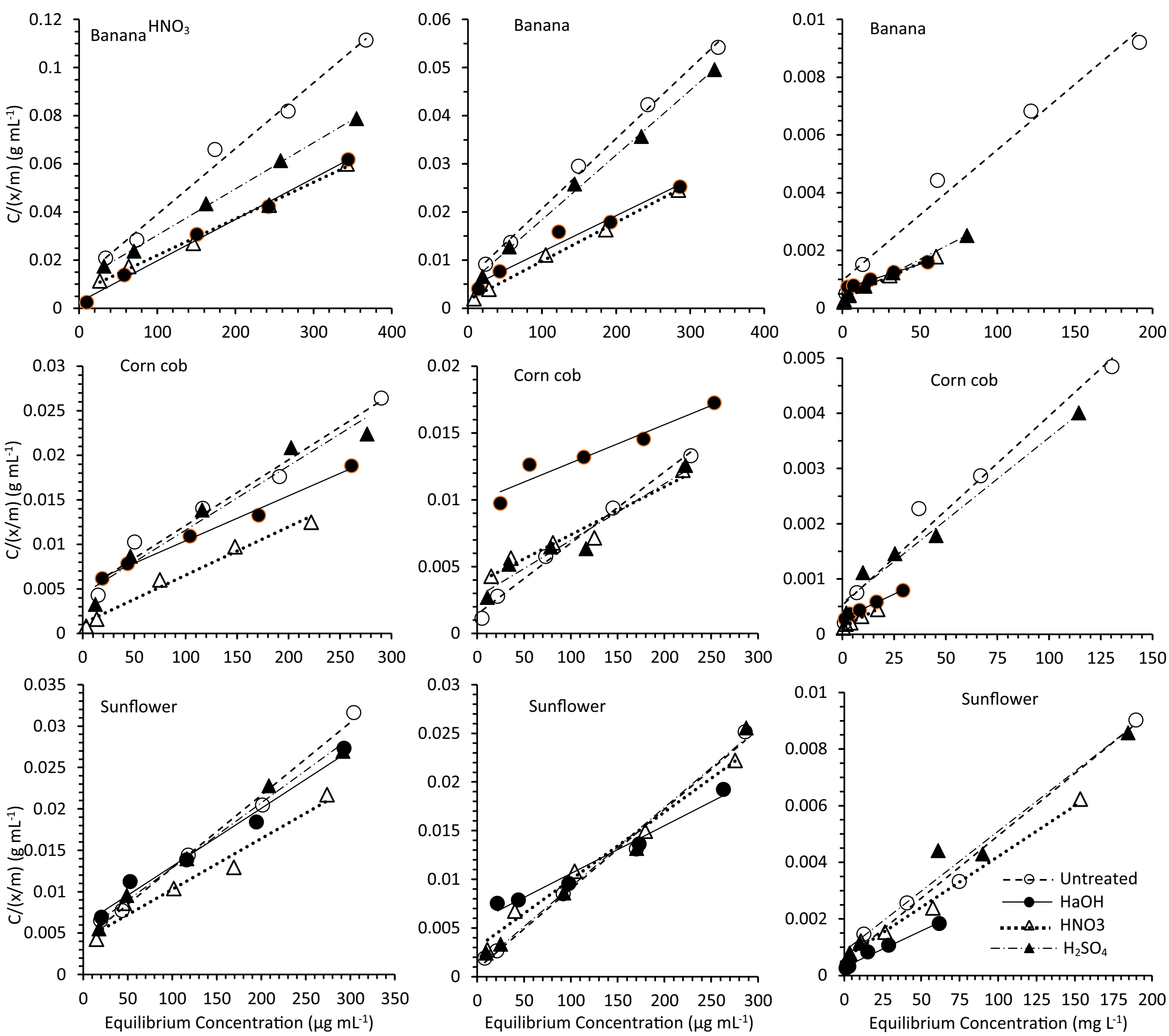

Fig. 4 Linearized Langmuir isotherm for Cd, Cr, and Pb removal by untreated and treated agricultural biomasses at 25 °C

(Suradi et al. 2009). This may be because the base reacts with cementing materials of the fiber, splitting the fibers into finer filaments. In addition, combination with alkaline peroxides enhanced the porosity and pore size of the fiber surface thereby improving physical interlocking and leading to better interfacial bonding between fiber and matrix. Hence, alkaline peroxide enhanced the surface charge, porosity, and pore size of the fiber surface favoring metal ion uptake.

Adsorption isotherms

A classical sorption model, the Langmuir equilibrium isotherm equation, was used to calculate the sorption parameters, i.e., maximum sorption and binding strength from the slope of the line and intercept. A common form of the Langmuir equation is

$$\frac{x}{m} = \frac{KCb}{1+KC}$$

where C is the equilibrium concentration of adsorbate in question, x/m is the weight of adsorbate per unit weight of adsorbent, K is a constant related to the binding strength, and b is the maximum amount of adsorbate that can be adsorbed (i.e., a complete monomolecular layer).

The linear form of the above equation is

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{1}{b}C$$

A plot of $C/x/m$ versus C yields a straight line with slope $1/b$ and intercept $1/Kb$. The Langmuir constant K is obtained by dividing the slope ($1/b$) by the intercept ($1/Kb$).

Langmuir adsorption isotherms for Cd, Cr, and Pb are presented in Figs. 3 and 4 and Table 1. The Langmuir sorption parameters were derived from a linearized form of isotherms (Fig. 4). The regression coefficients (r^2) are high and clearly indicate the goodness of fit for explaining adsorption of Cd, Cr, and Pb (Table 1). The results show that the treatment of the material, either with base or acid, increased the maximum adsorption capacity of Cd, Cr, and Pb for all the tested materials. Pretreatment of lignocellulose can remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity or surface area and chelating efficiency (Gaballah et al. 1997; Chen et al. 2007). Such pretreatment can also

Table 1 The Langmuir parameters for cadmium, chromium, and lead adsorption on chemically treated and untreated materials

Treatments	Cadmium			Chromium			Lead		
	b mg g^{-1}	K L g^{-1}	r^2	b mg g^{-1}	K L g^{-1}	r^2	b mg g^{-1}	K L g^{-1}	r^2
Banana									
Untreated	3.658	0.024	0.99	6.855	0.024	0.97	20.898	0.052	0.97
NaOH	5.815	0.071	0.99	13.349	0.018	1.00	59.391	0.024	1.0
HNO_3	6.738	0.020	0.99	12.408	0.047	1.00	39.909	0.084	0.99
H_2SO_4	5.210	0.017	0.99	7.420	0.028	0.99	36.448	0.068	1.00
Corn cob									
Untreated	13.577	0.016	0.97	18.782	0.038	0.93	29.168	0.069	0.98
NaOH	19.862	0.009	0.99	34.968	0.003	0.94	56.674	0.059	0.97
HNO_3	18.461	0.045	0.99	27.803	0.010	0.95	51.750	0.090	0.98
H_2SO_4	13.891	0.016	0.95	23.667	0.016	0.99	33.393	0.050	0.99
Sunflower									
Untreated	11.404	0.021	0.99	12.206	0.102	0.98	22.644	0.088	0.99
NaOH	14.281	0.011	0.98	20.361	0.009	0.99	39.233	0.085	0.97
HNO_3	16.282	0.015	0.96	14.410	0.023	0.99	27.870	0.060	0.99
H_2SO_4	12.742	0.016	0.99	12.256	0.082	0.99	23.600	0.047	1.00

b maximum adsorption capacity, K binding strength, r^2 regression coefficients increase the number of the functional groups which can enhance the binding capacity of ground plant material (Tan and Xiao 2009). For example, Kumar and Bandyopadhyay (2006) reported that rice husk treated with sodium hydroxide enhanced the adsorption capacity of cadmium. Tarley et al. (2004) found that adsorption of Cd was doubled when rice husk was treated with NaOH. Similar increases in heavy metal adsorption by banana stalk have also been reported by Annadurai et al. (2002).

Treatment of banana, corn cob, and sunflower achene with NaOH greatly increased the maximum adsorption capacity of metal ions while acid-treated materials showed relatively less increase. The increase in maximum adsorption capacity of heavy metals after base treatment might be explained by an increase in the amount of galactouronic acid groups after hydrolysis of *O*-methyl ester groups (Low et al. 2000). Marshall and Johns (1996) observed a 26 % increase in adsorption capacity of soybean hulls after NaOH treatment compared with the untreated control. Similarly, the Pb maximum sorption was also higher when banana stalk and corn cob were treated with NaOH than those given an acid treatment.

The maximum adsorption capacity decreases in the order of Pb > Cr > Cd for all the three adsorbents. The sorption maximum seemed to be inversely proportional to the hydrated ionic radii of the metals, being Pb (4.01 Å) > Cr (4.21 Å) > Cd (4.26 Å) (Lide 1998). The smaller ionic radius of Cd compared to Pb means greater tendency of Cd to be hydrolyzed, leading to reduced sorption (Horsfall and Spiff 2005). This is in agreement with results of Danny et al. (2004) and Lee and Rowell (2004). Hillel (1998) explained that the smaller the ionic radius and the greater the valence, the more closely and strongly the ion is adsorbed. On the other hand, the greater the ion's hydration, the further it is from the adsorbing surface and the weaker its adsorption.

The proportional increase in maximum adsorption capacity due to treatment was higher in banana stalk and corn cob than in sunflower achene. For example, the mean increase in maximum Pb adsorption capacity by banana stalk was 117 % and by corn cob was 62 % while the mean increase in sunflower achene was only 34 %. The smaller increase in maximum sorption with sunflower achene might be associated with its high lignin content. Previously, Wartelle and Marshall (2000) reported that a material having high bulk density, the lignin, can block or restrict penetration of citric acid to reactive sites, leading to lower uptake. Comparison of the present studies with few other adsorbents used in past studies revealed that the maximum adsorption capacity of all the materials was comparable with those reported by Li et al. (2006) but slightly less than those reported by Horsfall Jr and Spiff (2005) and Noeline et al. (2005).

Conclusions

Chemical modification generally improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification and formation of new functional groups that favored metal ion sorption. The rapid metal sorption, >82 % in 20 min, has great practical significance in column and continuous flow processes where the contact time between the metal ion in solution and the sorbent is generally short. The metal sorbents used in this study, banana stalk, corn cob, and sunflower achene, have the potential for removing heavy metal ions from wastewater to prevent water pollution.

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