



Different natural biomasses for lead cation removal

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ABSTRACT

It is believed that some wastes play an important role on the pollution prevention. In this paper, three different natural biomasses were investigated as biosorbent. *Salsola* green plant which grown at Jubail (industrial area) in KSA, it is phyto remediation plant. *Salsola* is metal hyper accumulation plant, it adsorbed (23.5, 25.7 mg lead per gram stem or leaf) from soil. Also it can be reused as ion exchanger for Pb^{2+} from solution. Shrimp shell's used for extraction of chitosan in laboratory with degree of substitution 81%. Chitosan and crosslinked carboxymethyl chitosan were investigated for Pb^{2+} adsorption and compared with crosslinked carboxymethyl corn cob. The adsorption experiments demonstrated that the three biomasses have high adsorption capacity for Pb^{2+} , good reusability and stability for three cycles.

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1. Introduction

Traditional methods for heavy metal removal from contaminated water involve filtration, flocculation, activated charcoal, and ion exchange resins, which are expensive and can result in toxic exposures of the workers involved (Al Duri, 1996; Egawa, Nonaka, & Nakayama, 1990; Kato, Kago, Kusakabe, Morooka, & Egawa, 1990). Therefore, new low cost, effective and environmentally friendly methods need to be developed, to be easily implemented to clean lead or other toxic metals from contaminated area and industrial waste waters (Khalil & Farag, 1998).

Chitosan has undoubtedly been one of the most popular adsorbents for the removal of metal ions from aqueous solution and is widely used in water treatment applications (Babel & Kurniawan, 2003). In spite of its prolific use, the adsorption ability of chitosan has not been realized to a satisfying level. Further chemical modifications of chitosan have been made to improve the capacities for metal ions. Carboxymethylation was prepared and regarded as a simple and effective process to facilitate the adsorption ability of chitosan with heavy metals (Chen & Park, 2003). Carboxymethyl chitosan has many reactive functional groups, amino group, carboxyl group, as well as both primary and secondary hydroxyl groups at the C₃, C₆ positions, respectively. However, carboxymethyl chitosan can dissolve in acidic solution and water, so that it developed to reinforce the adsorption capacity of chitosan by using crosslinker. The crosslinker carboxymethyl chitosan provides the potential for regeneration and reuse after metal adsorption (Hon & Tang, 2000).

Besides carbonization of corn cob at high temperature, an adsorbent can be prepared by chemical treatment using a carboxymethyl process followed by crosslinking (Khan & Wahab, 2006).

Several researchers have shown that biological systems such as phyto remediation which is the application of plants to reduce the toxic metals and other contaminations (Enrst, 1993; Gemel et al., 1997; Heller, Grignon, & Scheidecker, 1973). It is usually described as the use of plant tissues, typically stems and leaves, to adsorb pollutants. The overall benefits of phyto filtration is lower cost for ground water and end of pipe treatment, which is applicable to a broad range of metals, with minimal environmental disturbance. The *Salsola* plant (Roem, et schult) may be a good source for the removal of toxic heavy metal cations. *Salsola* is able to adsorb metal cation such as copper, iron, Zinc and lead cation from soil, it may possess the natural binding sites, necessary to be used as a biomaterial for phyto filtration (Lasat, 2002).

The objective of this study is to determine if the agricultural by products especially corn cob; extracted chitosan and green plant (leaf and stem) can be used to remediate contaminated aqueous solutions, Batch laboratory methods were employed to investigate the potential for lead (II) adsorption by untreated and modified biomass. In addition, desorption experiments were carried out to investigate if the bound lead (II) ions could be recovered from the metal laden biomass.

2. Materials and methods

2.1. Materials

Glutaraldehyde, epichlorohydrin, isopropyl alcohol, ethanol, hydrochloric acid, monochloro acetic acid, sodium hydroxide, lead

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nitrate: were of analytical reagent grade from Aldrich Chemical Co. Fresh shrimp shell's were purchased from local seafood in KSA Company.

Corn cob from local farms and *Salsola baryosma* was grown at Jubail (Industrial area)-KSA. It is Succulent Halophytes plant which has osmotic adjustment due to mineral electrolytes in its tissues. The soil type for this industrial region is a (Dayton–Amity-Concord).

2.2. Pretreatment of *Salsola baryosma*

After cut down, leaves and stems were washed with deionized water and allowed to air dry. Then, the leaf material was separated from stem material prior final drying, which was accomplished in a forced air dryer at 65 °C. Stem materials were cut into 0.3 m sections before grinding. All grinding was accomplished using a Wiley–Mill and the resulting powder was sieved with a 150 mesh screen to achieve uniform particle size.

2.3. Determination of bound lead in *Salsola plant*

About 0.5 g of powdered *Salsola plant* (stems or leaves) accurately weighted in crucible, it was introduced in Muffle for 4 h, at 500–550 °C, then 5 ml of dilute HNO₃ was added to the sample and the volume was completed to 50 ml using measuring flask. The sample was analyzed using a Perkin–Elmer model 3110 atomic absorption spectrometer (Reeve & Barnes, 1994).

2.4. Preparation of chitosan

Chitosan was prepared using chitin which was obtained in our laboratory by modified method (Farag, AL-Afaleq, & Abubshait, 2004). Deacetylation of chitin was carried out and all reaction parameters were optimized as follows. A suspension of 10 g chitin in 500 ml of aqueous sodium hydroxide as deacetylation reagent (50% by weight) was mixed at desired temperature (90–95 °C) under nitrogen purging. After 3–5 h, the solid was filtered off, washed with water and methanol to neutral pH. It was then dried at 85 °C. Deacetylation reaction yield was 81% (using potentiometric titration)(Michiaki, Tomotsugu, & Kazuo, 1999).

2.5. Pretreatment of corn cob

Dry corn cob, which was crushed and separated from its pitch/chaff and sieved to mesh ranges of 100–150 mesh, was used in this study. The corn cob was washed with distilled water in order to reduce the residues content, then dried at 60 °C for at least 12 h, before use in the experiments. The main parts (i.e. woody ring and coarse chaff) of corn cob were used.

Carbon and hydrogen contents were determined by Leibig–Pregle method, nitrogen content was carried out by Dumas–Pregle method (Jekayinfa & Omisakin, 2005). (% carbon 19.73, % hydrogen 15.56, % nitrogen 0.38 and % oxygen 54.98).

2.6. Preparation of carboxymethyl substrates

Carboxymethyl chitosan and carboxymethyl corn cob were prepared according to a modified method (Ramesh, Viswanatha, & Tharanathan, 2004). Ten gram of biomass was dispersed in 100 ml isopropanol using magnetic stirrer (400 rpm) at 20 °C for 30 min. A solution of 15 ml of 10 mol/dm^{−3} sodium hydroxide was added in six equal portions at an interval of 5 min. under agitation. The mixture was stirred for an additional 45 min. Then certain amount of monochloroacetic acid (sodium salt)/isopropanol solution was added to the mixture in four equal portions of interval of 5 min. Then the mixture was stirred for 5 h at 50 °C. The resul-

tant solution was filtered, washed with 80% (V/V) alcohol until the filtrate was neutral, then dried in an oven at 50 °C. Degree of substitution was determined, expressed as m mol COOH/g sample (George, Robert, Reinhardt, & Reid, 1953).

2.7. Crosslinking of carboxymethyl substrates

About 1.0 g of the prepared carboxymethyl chitosan was swelled in 30 ml of distilled water, a certain volume of glutaraldehyde was added with stirring for 5 h at 50 °C, and then the cross-linked product was filtered and washed with distilled water until pH 7 (Sun, Wang, & Wang, 2006).

About 1.0 g of the prepared carboxymethyl corn cob was reacted with certain volume of epichlorohydrin in 12 ml of DMF at 100 °C and stirred for 1 h. Four milli liter of pyridine was added to the solution to accelerate the rate of wetting and the extension of the crosslinking (Morrison & Boyd, 1992). Product was washed with diluted ethanol at 40 °C (ethanol:water = 1:1) to remove pyridine salts and un-reacted epichlorohydrin. The relationship between the dosage of crosslinking agent and adsorption capacity of crosslinked carboxymethyl chitosan and untreated chitosan, for pb²⁺ were studied.

2.8. Chemical modification of *Salsola biomass*

Chemical modification of *Salsola* was achieved by esterification and hydrolyzation (Tiemann et al., 1999). Esterification of the biomass was accomplished by reacting the washed powdered substrate with acidic methanol (0.1 M HCl) for 48 h at 60 °C. The biomass was then washed three times with deionized water and lyophilized. In addition, hydrolyzation of the biomass was achieved by reacting the biomass with 0.1 M sodium hydroxide for 1 h and then washed three times with deionized water and then lyophilized.

2.9. Adsorption experiment

A 0.1 g of treated and untreated biomass under investigation was added to 25 ml of nitrate solution of lead (initial pb²⁺ concentration 0.02 mol/L) with a given pH adjusted with either 0.1 M HCl or 0.1 M NaOH, shaking 24 h at 25 °C, then filtered. The adsorption, capacities of pb²⁺ were obtained from initial and final concentration determined by A Perkin Elmer model 3110 atomic absorption spectrophotometer

2.10. Reusability experiment

All the biomass was dipped into 0.1 mol/L HCl, stirring for 1 h at 25 °C to remove pb(II) and then was treated with 0.1 mol/L NaOH for 8 h. Finally it was filtered and washed with water, ethanol and ether in turn. The obtained materials were used in adsorption experiment, and were repeated four times.

3. Results and discussion

Carboxymethylation is one of the important etherifying derivatization processes resulting in products of potential applications. In the present investigation, there are three different biomasses were studied for their ability to remove pb²⁺ from polluted solutions.

First of them *Salsola baryosma* (metalophytes) green plant. Table 1 shows characterization of *Salsola baryosma* plant.

In order to better understand the metal binding mechanisms of *Salsola* stems or leaves, total Carbohydrates, ash content, carbon%, nitrogen% and sulfur% determinations for the plant tissues were performed(Krolack, 2001; Reeve & Barnes, 1994). The relatively

Table 1Characterization of *Salsola baryosma* plant (Krolack, 2001; Reeve & Barnes, 1994).

Total carbohydrate	36.10 mg/g
Water retention	80.21%
Ash content	29.32%
C%	32.5% (stem) 32.1 (leaves)
N%	0.66% (stem) 0.93 (leaves)
S%	0.38% (stem) 0.21 (leaves)
Pb ²⁺ bound in stems and leaves	23.5; 25.7 milligram/g

Its soil profile, pH 8.05; soil lead accumulation = 0.11 m mol/g.

low percentage of sulfur (0.38% and 0.21% for stems and leaves, respectively), in comparison to the carbon indicates that few sulfur compounds are involved in the adsorption of lead (II) by *Salsola* biomass. However, greater percentages of nitrogen are seen in comparison to the sulfur quantities, which indicate that some nitrogen-containing compounds may be available for lead (II) adsorption. These nitrogen-containing compounds may be part of the plant cellular proteins.

The soil stress factors have great effect on the heavy metal ion accumulation and adsorption around its particle and changed to soluble solution, these factors are acid rains, high temperature, salinity and alkalinity (Chino, 2000; Wang, 2000).

In order to determine the amount of lead (II) that the *Salsola* biomass is capable of adsorbing, batch binding capacity experiments were performed for native, hydrolyzed and esterified *Salsola*. Table 2 shows the binding capacity for the treated and untreated *Salsola* stems and leaves in milligram of pb²⁺ bound per gram of biomass (Kamnev & Van-der Lelie, 2000). *Salsola* leaves were shown to have a statistically significant greater capacity for pb²⁺ binding than the stems, which may be due to differences in the composition and prevalence of chemical functional groups. Additional capacity experiments were performed with esterified *Salsola* stems and leaves to determine the contributions of carboxylic functional groups on the pb²⁺ binding. As seen in Table 2 by blocking the available carboxylic group functional moieties by means of converting them to methyl esters, the capacity for the *salsola* biomasses were decreased, which means that carboxyl groups play a significant role in pb²⁺ binding. Therefore, if carboxyl ligands are involved in the binding of pb²⁺ from aqueous solution, hydrolysis (or saponification) of the available esters on the *Salsola* biomass should produce new carboxyl groups and increase the capacity for lead (II) binding, as observed from the results obtained in Table 2. However, this increase proved not to be statistically significant for the hydrolyzed biomass, which may be due to the low content of cellulosic methyl esters in the *Salsola* plant tissues.

This data demonstrate the differences in the composition of the stems and leaves. Both the esterified and hydrolyzed results are in agreement with other studies on metal binding which have shown that carboxyl groups are involved in metal ion binding by other biomaterials (Wan Ngah & Hanafiah, 2008).

The prepared chitosan has 81% deacetylation (Michiaki et al., 1999). Further chemical modifications of chitosan were made to

Table 2Comparison of capacities for native and chemically modified *Salsola* biomass for lead (II) binding.

Material	Milligram lead bound/gram material
Native <i>Salsola</i> stems	34.3
Hydrolyzed <i>Salsola</i> stems	42.2
Esterified <i>Salsola</i> stems	10.1
Native <i>Salsola</i> leaves	44.2
Hydrolyzed <i>Salsola</i> leaves	52.2
Esterified <i>Salsola</i> leaves	10.8

0.1 g of biomass, pH 6, shaking 24 h, at 25 °C

Table 3Influence of the DS of carboxymethyl chitosan on adsorption capacity for pb²⁺.

m mole COOH/g sample	Adsorption capacity milligram/g sample
0	43.2
0.8	49.1
1.0	53.9
1.2	60.3
1.5	82.0

0.1 g of carboxymethyl chitosan, pH 6, shaking 24 h at 25 °C

improve its capacities for pb²⁺. Carboxymethylation was carried out followed by crosslinking. Table 3 shows the influence of DS of carboxymethyl chitosan on adsorption capacity for pb²⁺. It is observed that the adsorption capacities of pb²⁺ increase with increasing the DS of carboxymethyl chitosan at the range of (0.8–1.5 m mol/g sample) considering the carboxymethyl substituting for hydrogen atom of the –HH₂, the amount of amino group decrease, where as the adsorption capacity of pb²⁺ in nitrate solution increases apparently with an increase of DS.

This phenomenon suggests that the amount of carboxymethyl groups affect the adsorption capacities of pb²⁺ directly and the main adsorption sites of carboxymethyl chitosan for pb²⁺ are on the carboxymethyl group.

Similarly, it is also necessary to investigate the effect of the dosage of crosslinking agent. Table 4 shows that the formation of crosslinking between the amino group and aldehyde group improve the adsorption capacity upto maximum before a decrease

Table 4Relationship between the dosage of crosslinking agent and the adsorption capacity of crosslinked carboxymethyl chitosan for pb²⁺.

Molar ration of CHO/NH ₂	Adsorption capacity milligram/g sample
0.0	80.0
0.29	82.3
0.63	84.1
0.68	82.0
0.72	80.3
1.0	78.0

0.1 g carboxymethyl chitosan, pH 6, shaking 24 h at 25 °C.

Table 5Effect DS of carboxymethyl corn cob on adsorption capacity for pb²⁺ (DS expressed as m mol COOH/g sample).

Sample	m mole COOH/g biomass	Adsorption capacity mg/g sample
Untreated corn cob	–	35.2
Carboxymethyl corn cob	0.86	47.0
Carboxymethyl corn cob	1.11	50.8
Carboxymethyl corn cob	1.31	60.0
Carboxymethyl corn cob	1.68	76.9

0.1 g of carboxymethyl corn cob, pH 6, shaking 24 h at 25 °C.

Table 6Influence of crosslinker dosage on adsorption capacities of crosslinked carboxymethyl corn cob for Pb²⁺ adsorption.

Epichlorohydrin molar ratio	Adsorption capacity milligram/g sample
0.0	76.9
0.3	78.0
0.5	79.3
0.7	80.0
1.0	75.0

0.1 g of cross linked carboxymethyl corn cob, pH 6, shaking 24 h, at 25 °C.

Table 7
Effect of reusability of the three biosorbent under investigation.

Biomass	Adsorbance milligram/g sample					Lead recovery%			
	Zero Cycle	1 Cycle	2 Cycle	3 Cycle	4 Cycle	1 Cycle	2 Cycle	3 Cycle	4 Cycle
Salsola stems (native)	34.3	32.0	30.0	27	22.2	54	49	45	40
Salsola leaves (native)	44.2	41.0	41.0	39	22.3	58	52	48	43
Hydrolyzed Salsola stems	42.2	41.0	40.0	40	33.0	78	75	72	70
Hydrolyzed Salsola leaves	52.2	52.0	50.0	48	42.0	80	78	73	71
Chitosan	80.0	78.9	77.5	76.3	75.0	77	73	70	65
Carboxymethyl chitosan	82.0	80.0	78.2	77.0	76.0	78	72	68	65.2
Crosslinked carboxymethyl chitosan	84.1	84.0	83.0	80.5	77.8	93	88	86	83
Corn cob (untreated)	35.2	30.0	25.0	20.0	20.0	60	58	58	53
Carboxymethyl corn cob	76.2	73.0	70.0	67.0	58.0	75	75	73	70
Crosslinked Carboxymethyl corn cob	80.0	80.0	80.0	78.0	78.0	90	87	85	80

in adsorption capacity occur as the dosage of glutaraldehyde increases. The increase in adsorption capacity at dosage of aldehyde group between 0.29 and 0.63 mol, may be attributed to the low level of crosslinking, which prevent the formation of closely packed chain arrangements without significant decrease in the swelling capacity. As increasing the dosage of crosslinking, an optimum crosslinking network is formed in an aldehyde/amino ratio (0.63 mole aldehyde to 1 mole of amino group) for pb^{2+} adsorption. In addition, it cannot only reduces the opening of polymer network by supplementary linkages between polymer chains, but also the expansion of the polymer network results in a reduction of steric hindrance effect and a significant increase of adsorption capacity for pb^{2+} . Beyond the point of 0.63 mol, the declining swelling and decreasing accessibility of the higher crosslinking polymer are due to a more extensive three dimensional network and an increase in the hydrophobic character, thus resulting in the decrease of adsorption capacity (Sun et al., 2004).

The third biomass was carboxymethyl substrate obtained from corn cob, the carboxymethylation of corn cob resulting DS range is 0.86–1.68 m mole COOH/g , listed in Table 5. The results show that increasing DS has great effect on adsorption capacity for pb^{2+} . Untreated corn cob adsorb 35.2 mg pb^{2+}/g sample which is very low capacity in comparison with treated sample. This explains why they are modified. All agriculture by-products contain cellulose (corn cob contain 37.9% cellulose) (Chang et al., 1998) which is made up of repeating units of D-glucose as a major component of cell walls. The polar hydroxyl groups on the cellulose could be involved in chemical reaction and hence bind heavy metals from solutions. The surface properties of these functional groups on the cellulose could be modified by incorporation of other functional groups, and this also affects the adsorption capacity (Farag, El Jazi, & Al-Faleq, 2002; Gavrilescu, 2004; Igwe, Ogunewe, & Abia, 2005).

The variation of the adsorbed pb^{2+} with crosslinked carboxymethyl corn cob is shown in Table 6. The results show that the increasing in adsorption capacity, this is due to the increasing in the dosage of epichlorohydrin which decrease the enhanced swelling of the biomass. Besides, presumably by lessening inter-polymer distances, so one lead ion is involved in chelation with two carboxylate (possibly adjacent) groups. The mode of sorption can be attributed to two main terms, intrinsic adsorption and coulombic interaction. The coulombic term results from the electrostatic energy of interaction between the carboxylate and lead cations. The charges on both substrates are mostly responsible for the intensity of the interaction. In addition the polar hydroxyl groups on the cellulose could be involved in chemical reaction and hence bind lead cation from solutions.

4. Reusability

The reusability of three different biomasses was investigated in this study. Table 7 shows that the adsorption and recovery of lead

(II) decrease slightly with increasing times of reuse and the adsorption capacity for pb^{2+} is quite higher after reuse for four times, which indicates that the three materials have a good reusability. Recovery ratio was calculated using the following equation:

$$\text{Recovery ratio} = \frac{\text{amount of lead ions desorbed}}{\text{amount of lead ions adsorbed}} \times 100$$

5. Conclusions

Batch laboratory experiments were allowed for the characterization of lead (II) binding by three different biomass the results show that: (1) Salsola green plant is metal hyper accumulation plant and this process is characterized as less disruptive and can be often carried out on site. Also it has shows a remarkable ability for recovery of the bound lead using a more environmentally friendly chemical agent. (2) Prepared chitosan can be used as cation exchanger and the prepared of crosslinked carboxymethyl chitosan, it was found that the adsorption capacity for lead cation greatly increased by increasing the crosslinking dosage to some limit. (3) Native corn cob has good ability for binding lead cation from solution. Carboxyl group incorporation into corn cob increased its capacity for pb^{2+} (II) binding, crosslinking carboxymethyl corn cob shows higher capacity for $\text{pb}(\text{II})$ binding. These data suggest that carboxyl groups are the major ligand involved in lead (II) adsorption by these three biomasses.

Additional reusability was performed and it show that the same efficiency can be achieved for at least three cycles with the same biomass. This innovative study provides a reusable materials derived from green plant, sea food wastes and agriculture wastes are not only biodegradable but also they allow for the environmentally friendly removal and recovery of lead (II) from industrial wastes and polluted waters.

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