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Removal of heavy metals from their aqueous solutions through adsorption onto natural polymers

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ABSTRACT

Commercial sodium alginate was converted into water insoluble material through a very simple acidification treatment with alcoholic HCl solution. The so-obtained acidified sodium alginate (ASA) was found to exhibit complete water insolubility and to have a carboxyl content of 465 mequi./100 g sample. The ASA was used to remove Zn (II) ions from their aqueous solutions and different factors affecting the adsorption of Zn (II) ions onto ASA, like, pH, adsorbent dose, agitation time, and adsorbate concentration were extensively studied. Adsorption of Zn (II) ions onto ASA was found to be pH-dependent and maximum adsorption was obtained at pH 6.

1. Introduction

The contamination of water from toxic compounds, like heavy metals and dyes remains a severe environmental and public problem. Heavy metal ions and dyes are often found in the environment as a result of increasing industrial use. They are common contaminants in wastewater and known to be toxic and carcinogenic.

Strict legislation on the discharge of these toxic products makes it then necessary to develop various efficient technologies for the removal of pollutants from wastewater. Different technologies and processes are currently used to remove such pollutants from the wastewater. Biological treatments (Gonçalves, da Costa, Leite, & Sant'Anna, 2007; Taştan, Ertuğrul, & Dönmez, 2010; Viggi et al., 2010), membrane processes (Bessbousse, Rhlalou, Verchère, & Lebrun, 2008; Mbareck, Nguyen, Alaoui, & Barillier, 2009; Zou et al., 2009), advanced oxidation processes (Bradu et al., 2010; El-Ashtoukhy & Amin, 2010; El-Desoky, Ghoneim, El-Sheikh, & Zidan, 2010; Osugi et al., 2009), chemical and electrochemical techniques (Belkacem, Khodir, & Abdelkrim, 2008; Raghu & Basha, 2007), and adsorption procedures are the most widely used techniques for removing metal and dyes from industrial effluents.

Adsorption is a well-known equilibrium separation process, in which the adsorbent may be of mineral, organic or biological origin. Activated carbons (Amin, 2009; Kadirvelu, Thamaraiselvi, & Namasivayam, 2001), zeolites (Sohrabnezhad & Pourahmad, 2010; Wang, Li, Wang, Sun, & Huang, 2009), clays (Anirudhan, Bringle, & Rijith, 2010; Potgieter, Potgieter-Vermaak, & Kalibantonga, 2006), silica beads (de la Rosa, Gardea-Torresdey, Peralta-Videa, Herrera, & Contreras, 2003; Huang, Liao, & Shi, 2010), industrial by-products (Abdel-Halim, Abou-Okeil, & Hashem, 2006; Hashem, Abdel-Halim, El-Tahlawy, & Hebeish, 2005; Hashem, Abdel-Halim, Maauof, Ramadan, & Abo-Okeil, 2007), agricultural wastes (Demirbas, 2008; Hashem, Sokkar, Abdel-Halim, & Gamal, 2005; Sud, Mahajan, & Kaur, 2008), biomass (Chu & Chen, 2002; Lesmana, Febriana, Soetaredjo, Sunarso, & Ismadji, 2009; Pengthamkeerati, Satapanajaru, Chatsatapattayakul, Chairattanamanokorn, & Sananwai, 2010), and polymeric materials (Liu, Ma, Xu, & Shao, 2010; Uğuzdoğan, Denkbaş, Öztürk, Tuncel, & Kabasakal, 2009) are examples for different adsorbents. Recently numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as algenic acid (Jeon, Park, & Yoo, 2002; Jeon, Nah, & Hwang, 2007), starch and its derivatives (Hashem, Abdel-Halim, & Sokker, 2007; Renault, Morin-Crini, Gimbert, Badot, & Crini, 2008), chitosan (Fujiwara, Ramesh, Maki, Hasegawa, & Ueda, 2007; Singh, Sharma, Tripathi, & Sanghi, 2009) and cyclodextrin (Ozmen & Yilmaz, 2007) deserve particular attention. These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards heavy metal ions, resulting from the presence of reactive chemical groups in polymer chains. Moreover, it is well known that polysaccharides which are abun-

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dant, renewable and biodegradable resources have a capacity to associate by physical and chemical interactions with a wide variety of molecules. Hence adsorption onto polysaccharide derivatives can be a low-cost procedure of choice in water decontamination. Among the industrially attractive polysaccharide biopolymers, alginate is known to have high complex formation ability with various heavy metals (Aravindhan, Fathima, Rao, & Nair, 2007; Ngomsik et al., 2009).

Sodium alginate is soluble in water forming viscous solution but its hydrogen form (alginic acid) is approximately water insoluble. Therefore, the present work aims at preparing a low-cost biopolymer adsorbent through acidification of commercial sodium alginate. The work examines the utilization of the so-obtained acidified sodium alginate (ASA) for the removal of Zn (II) ions from their aqueous solutions under equilibrium conditions, taking into consideration the factors affecting the adsorption process and to what extent the adsorption data obey Langmuir and Freundlich adsorption isotherms.

2. Experimental

2.1. Materials

Sodium alginate was supplied by Sisco Research Laboratories, Mumbai, India. Hydrochloric acid, ethanol, EDTA and zinc acetate were all of laboratory grade reagents.

2.2. Acidification of sodium alginate

Ten ml of concentrated HCl was added to 200 ml ethanol/water mixture 50/50 (v/v). The alcoholic HCl solution was stirred vigorously at room temperature and 20 g of powdered sodium alginate was added very slowly during the vigorous stirring. The system was kept under stirring for 4 h and at the end of the reaction time, the ASA was filtered then washed thoroughly with ethanol/water mixture 50/50 (v/v) until the filtrate became free from chloride ions. The ASA was finally washed twice with absolute alcohol and air dried overnight. To examine the water insolubility of ASA, one gram of the prepared sample was weighed accurately, stirred in 1000 ml distilled water overnight. After filtering and drying, the sample was found to weigh 1 g.

2.3. Determination of carboxyl content

The carboxyl content of ASA was determined according to a reported method (Mattisson & Legendre, 1952).

2.4. Adsorption studies

ASA was ground and sieved to a particle size of 200–400 μm. A stock solution of Zn (II) ions was prepared by dissolving accurate weight of zinc acetate in definite volume of distilled water. Proper concentrations of the adsorbate were prepared from the stock solution through proper dilution. The pH of the adsorbate was adjusted during the dilution step using diluted sulfuric acid or sodium bicarbonate. The batch adsorption experiments were performed on a temperature controlled shaking water bath (shaking rate 200 rpm) using 100 ml-Erlemeyer flasks. At the end of a predetermined time interval, the adsorbent was removed by filtration and the residual Zn (II) was estimated in the filtrate via direct titration against standardized EDTA solution (Vogel, 1961). The effect of initial pH (3–6), sample dose (1–5 g/l), agitation time (5–60 min), and Zn (II) initial concentration (50–1200 mg/l) on the adsorption process, as well as to what extent the adsorption data obey Langmuir and Freundlich adsorption isotherms were investigated.

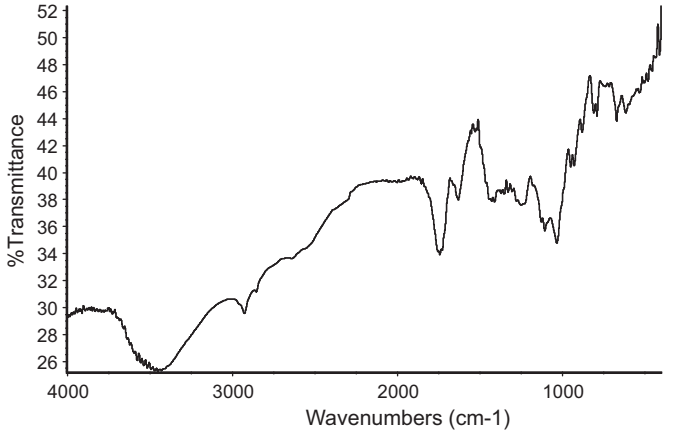
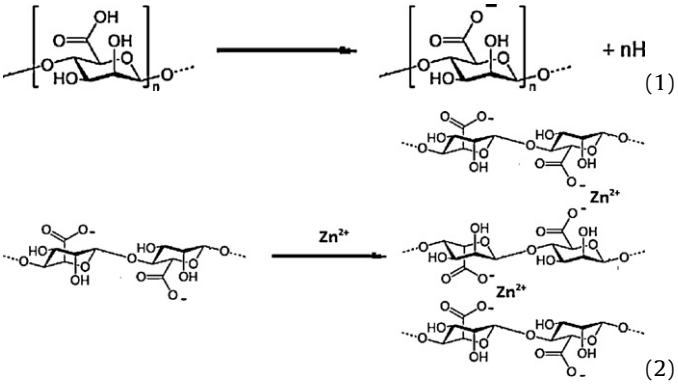


Fig. 1. IR spectrum of acidified sodium alginate (ASA) before metal removal.

3. Results and discussion

3.1. IR spectroscopy

Zn (II) ions replace protons in ASA by an ion exchange mechanism as shown below:



Inspection of the IR-spectra of ASA before metal removal (Fig. 1) and after metal removal (Fig. 2) also supports the suggested mechanism. Both spectra show close resemblance to each other around 3430 cm^{-1} (alcoholic –OH). On the other hand, the spectra are non-superimposable in the finger print region (1600–650 cm^{-1}). Thus, the strong carbonyl group absorption at 1740.93 cm^{-1} in the spectrum of I due to the –COOH group appeared only as a band of weak intensity in the spectrum of II. Moreover, the IR spectrum of II

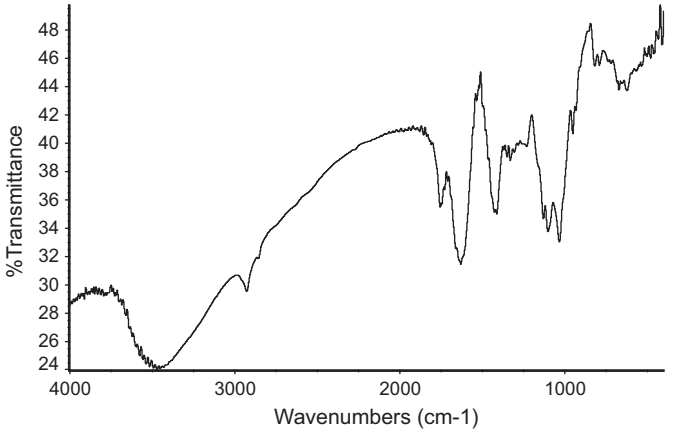


Fig. 2. IR spectrum of acidified sodium alginate (ASA) after metal removal.

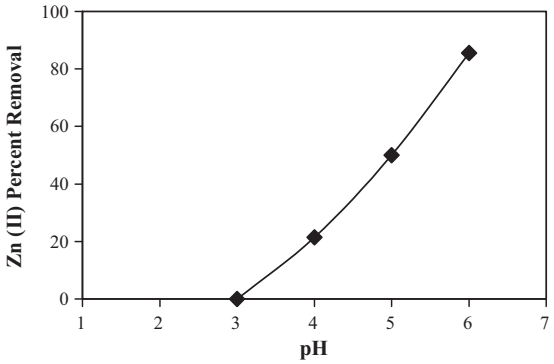


Fig. 3. Effect of pH on Zn (II) adsorption onto ASA. Adsorbent dose, 1 g/l; agitation speed, 200 rpm; agitation time, 120 min; 30 °C; [Zn (II)], 300 mg/l.

revealed the presence of the expected two bands due to the carboxylate anion at 1627.97 cm^{-1} (asymmetric stretching vibration, strong) and at 1400 cm^{-1} (symmetric stretching vibration, weak). This indicates that protons of the –COOH groups and not of the –OH groups are involved in the suggested ion exchange mechanism.

3.2. Effect of pH

Initial pH is one of the most important factors that affect the adsorption process. It affects not only the surface charge of the adsorbent, but also the ionization degree of the adsorbate. To investigate the role of pH in Zn (II) removal efficiency, the initial pH of the adsorbate solution was varied in the range of 3–6. The adsorption study could not be carried out experimentally at pH values higher than 6 due to the solubility of ASA as well as the precipitation of zinc hydroxide in this pH range.

Fig. 3 shows the percent of Zn (II) removal as a function of pH. It can be seen that the percent Zn (II) removal is maximum (85.5%) at pH 6. At pH values less than 6 the percent removal decreases continuously until it vanishes (0%) at pH 3.

The first stage of ion exchange is deprotonation of the carboxylic group which is represented by Eq. (1), while Eq. (2) represents the attachment of the metal cation to the reactive carboxylate anion. The zero percent removal at pH 3 can be attributed to the fact that at pH ≤ 3, the high concentration of H^+ in the adsorption medium shifts the equilibrium in Eq. (1) to the left direction. This means that the carboxyl groups do not ionize and the ion exchange sites on ASA surface are still protonated. Under such conditions the metal ions do not exchange and remain in the solution. As the pH value increases from 3 to 6, the deprotonation equilibrium in Eq. (1) is shifted to right and as a result, the adsorption capacity increases according to Eq. (2) until it reaches its maximum value at pH 6.

3.3. Effect of adsorbent dose

The dependence of Zn (II) removal on adsorbent dose was investigated by varying the amount of ASA from 1 to 5 g/l, while keeping other parameters (pH, agitation speed and time, temperature and adsorbate concentration) constant.

Fig. 4 shows the dependence of Zn (II) removal extent on the adsorbent dose. It is clear from the figure that the extent of Zn (II) removal increases by increasing ASA dose. This can be explained based on the fact that the higher the adsorbent dose in the adsorbate solution, the greater the availability of exchangeable sites for Zn (II) ions (Eq. (2)).

3.4. Effect of agitation time

Time taken for the adsorption process to attain thermodynamic equilibrium is very important in characterization and prediction of

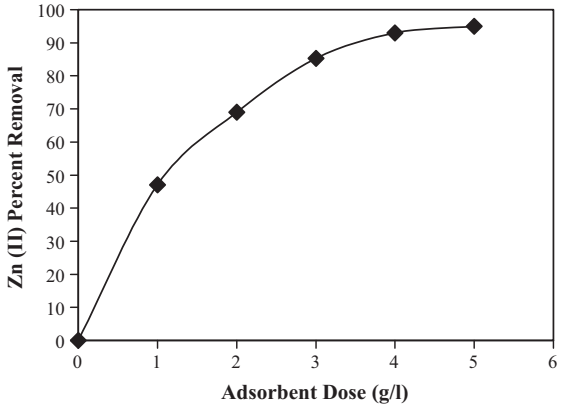


Fig. 4. Effect of adsorbent dose on Zn (II) adsorption onto ASA. Agitation speed, 200 rpm; agitation time, 120 min; 30 °C; [Zn (II)], 700 mg/l; pH 6.

both the efficiency and the feasibility of an adsorbent for its use in water pollution control. The effect of agitation time was studied for two adsorbate concentrations (200 mg/l and 400 mg/l). Fig. 5 shows that the percent Zn (II) removal increases sharply with increasing agitation time up to 10 min. and then it increases very slowly and becomes nearly constant after 40 min.. The constant percent removal after 40 min. means that thermodynamic equilibrium is attained at that extent. It is clear from Fig. 5 that the lower the adsorbate concentration, the higher the percent Zn (II) removal and this is a benefit because industrial wastewater is actually a very diluted solution of different pollutants. The curves obtained are single and smooth indicating the formation of a monolayer of Zn (II) ions on the adsorbent surface.

3.5. Adsorption isotherms

The relation between Zn (II) initial concentration and its extent of removal from aqueous solutions was studied at various Zn (II) concentrations and at fixed adsorbent dose. Fig. 6 shows the adsorption isotherm of Zn (II) onto ASA at 30 °C and pH 6. Adsorption data for a wide range of adsorbate concentrations is the most commonly described by adsorption isotherms, such as Langmuir or Freundlich isotherms, which relate adsorption density, q_e (adsorbate uptake per unit weight of the adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase (C_e).

According to Langmuir (1918), maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. The linear form of Langmuir isotherm is given

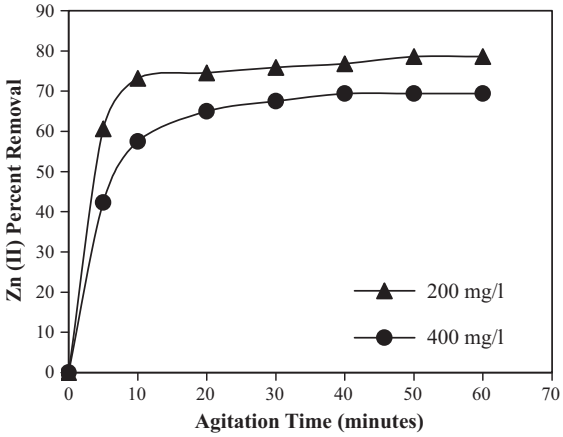


Fig. 5. Effect of agitation time on Zn (II) adsorption onto ASA. Adsorbent dose, 1 g/l; agitation speed, 200 rpm; 30 °C; pH 6.

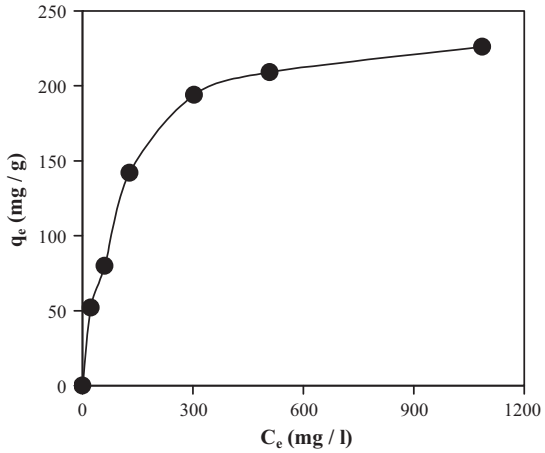


Fig. 6. Equilibrium adsorption isotherm of Zn (II) onto ASA. Adsorbent dose, 2 g/l; agitation time, 120 min; agitation speed, 200 rpm; 30 °C; pH 6.

by the following equation:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max} \times b}\right) + \left(\frac{C_e}{Q_{max}}\right)$$

where C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the amount of metal adsorbed at equilibrium (mg/g), and Q_{max} (mg/g) and b (l/mg) are the Langmuir constants related to the adsorption capacity and energy, respectively.

The adsorption process was found to obey Langmuir adsorption isotherm, thus on plotting C_e versus C_e/q_e (Fig. 7) a straight line with correlation coefficient (R^2) of 0.9933 was obtained. The values of Langmuir constants for ASA, Q_{max} and b were calculated and found to equal 303 mg/g and 6.25×10^{-3} l/mg, respectively.

The essential characteristics of Langmuir can be expressed in terms of a dimensionless equilibrium parameter, R_L, which describes the type of isotherm (Hall, Eagleton, Acrivos, & Vermevlem, 1966) and is defined by:

$$R_L = \frac{1}{1 + b \times C_0}$$

where b (l/mg) is the Langmuir constant and C_0 (mg/l) is the initial concentration of Zn (II) solution. The parameter R_L shows the shape of isotherm according to Table 1. The values of R_L for different Zn (II) initial concentrations are listed in Table 2. As it is clear from

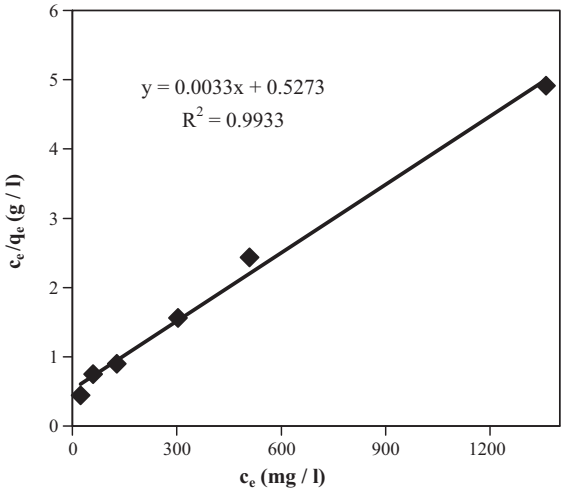


Fig. 7. Langmuir adsorption isotherm of Zn (II) onto ASA.

Table 1
Effect of separation factor, R_L on isotherm shape.

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 2
R_L values based on Langmuir equation for Zn (II) adsorbed on ASA.

Zn (II) concentration (mg/l)	R_L value
50	0.7619
100	0.6153
200	0.4444
400	0.2857
600	0.2105
1200	0.1142

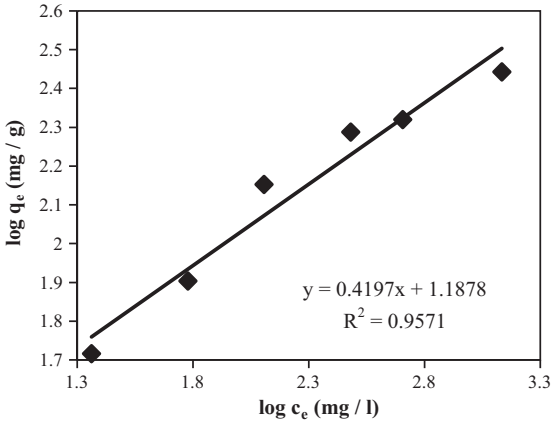


Fig. 8. Freundlich adsorption isotherm of Zn (II) onto ASA.

Table 2, all R_L values range between 0 and 1, indicating the favorable adsorption of Zn (II) onto ASA.

Moreover, the adsorption process was also found to obey Freundlich adsorption isotherm (Freudlich, 1907), thus on plotting $\log C_e$ against $\log q_e$ (Fig. 8) a straight line with a correlation coefficient (R^2) of 0.9571 was obtained. Freunlich isotherm is represented by the equation:

$$\log q_e = \log K_F + \frac{1}{n \times \log C_e}$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium adsorbate concentration (mg/l), and K_F and n are Freundlich constants, related to capacity of adsorbent and favorability of the adsorption, respectively. The values of Freundlich constants for ASA, K_F and n were calculated and found to equal 15.41 and 2.3826, respectively. As shown from the results, the value of n is 2.3826 (i.e. $0 < n < 10$) showing that the adsorption of Zn (II) onto ASA is favorable.

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