

Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash

E. Pehlivan^{a,*}, S. Cetin^a, B.H. Yanik^b

^a Department of Chemical Engineering, Selcuk University Campus, 42071 Konya, Turkey

^b Konya Sugar Factory, Konya, Turkey

Received 12 August 2005; received in revised form 16 November 2005; accepted 16 November 2005

Available online 20 December 2005

Abstract

In the present work, the abilities of native sugar beet pulp (SBP) and fly ash (FA) to remove copper (Cu^{2+}) and zinc (Zn^{2+}) ions from aqueous solutions were compared. The SBP and FA, an industrial by-product and solid waste of sugar industry, were used for the removal of copper and zinc from aqueous water. Batch adsorption experiments were performed in order to evaluate the removal efficiency of SBP and lignite-based FA. The effect of various operating variables, i.e. initial pH, adsorbent dose, initial metal ion concentration, and time on adsorption of copper and zinc onto the SBP and FA, has been studied. The sorption process was relatively fast and equilibrium was reached after about 60 min of contact. As much as 60–97% removal of copper and zinc for SBP and FA are possible in about 60 min, respectively, under the batch test conditions. Uptake showed a pH-dependent profile. The overall uptake for the SBP is at a maximum at pH 5.5 and gives up to 30.9 mg g^{-1} for copper and at pH 6.0 and gives 35.6 mg g^{-1} for zinc for SBP, which seems to be removed exclusively by ion exchange and physical sorption. Maximum adsorption of copper and zinc occurred 7.0 and 7.84 mg g^{-1} at a pH value of 5.0 and 4.0 for FA, respectively. A dose of 8 g l^{-1} of SBP and 8 g l^{-1} FA were sufficient for the optimum removal of both the metal ions. The sorption data were represented by the Freundlich for SBP and the Langmuir and Freundlich for FA. The sorption data were better represented by the Langmuir isotherm than by the Freundlich one for FA in the adsorption of zinc ion, suggesting that the monolayer sorption, mainly due to ion exchange. The presence of low ionic strength or low concentration of Na and Cl ions does not have a significant effect on the adsorption of these metals by SBP and FA. The SBP and FA are shown to be effective metal adsorbents for these two metals.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Sugar beet pulp; Fly ash; Copper and zinc; Sorption isotherms

1. Introduction

During recent years, interest has been primarily focused on heavy metals due to their known toxicity as they are discharged in small quantities by numerous activities into the environment. Metals can be distinguished from other toxic pollutants, since they are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders [1–3]. In the present work, an attempt has been made to develop an inexpensive adsorbent system for the removal of copper and zinc from wastewater using sugar beet pulp (SBP) and fly ash (FA) which are the basic

wastes from the sugar factory in Konya city. The sugar industry is one of the most important agro-based industries in Turkey and has tonnes of FA occurs as the result of burning young lignites for obtaining energy. The FA, an industrial solid waste generated from the burning of lignite in sugar industry, causes a great disposal problem.

The wastewaters of metal cleaning and plating baths, pulp, paperboard mills, wood pulp production and fertilizer industry, etc., contain high level of toxic metal ion and in order to avoid, water pollution treatment is needed before disposal. Conventional methods for removing metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolytic processes, membrane separation, activated carbon [4,5], ion-exchange [1–3], reverse osmosis, ultra filtration, biological systems [6,7], and adsorption [8]. Adsorption involves the use of natural materials that form complexes with metal ions using their ligand or functional groups. Processes for metal

* Corresponding author. Present address: Department of Chemical Engineering, Selcuk University, Konya 42079, Turkey. Tel.: +90 332 2232127; fax: +90 332 2410635.

E-mail address: erolpehlivan@yahoo.com (E. Pehlivan).

removal like adsorption have been suggested as being cheaper and more effective than the other technologies [9–11]. Numerous by-products of agro-industrial production have been studied for potential use as inexpensive biosorbents [12–14]. Agricultural by-products, such as onion skins [15,16], palm kernel husk, modified cellulosic materials [17], corn cobs [18], sunflower stalks [19], pine bark [20], apple wastes [21], etc., have received attention in these type of applications. The sorption of metals by these kinds of materials might be attributed to their proteins, carbohydrates, and phenolic compounds that have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions. Many examples are available in the literature concerning the direct or activated use of these materials as adsorbents [12–23].

The FA was obtained from Konya Factory. FA, the inorganic residue from the combustion of powdered coal has, for many years, been considered a waste material, the production of which has continued to increase, hence, the motivation to look for possible industrial applications. The removal efficiencies of heavy metal ions using FAs as adsorbents varied, according to the characteristics of the FA and the status of adsorption experiments. The effects of FA characteristics on adsorption behavior, especially its carbon and pH increase tendency, have not been investigated in detail. FA has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance and easy availability. FA has potential use in wastewater treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, and its physical properties, such as porosity, particle size distribution, and surface area. Some investigations have reported that alkaline FAs could serve as a stabilizer or binding reagent for fixing heavy metals present in hazardous wastes [24–26]. FAs can also serve as adsorbents for wastewater treatment [27,28].

Biosorption is an alternative technology to remove toxic metals from aqueous solutions. Biomass can be used to bind and accumulate metal ions by different mechanisms, such as physical adsorption, ion exchange, complexation, and surface micro-precipitation. One of these low-cost sorbents particularly suited to biosorption is SBP, which exhibits a large capacity to bind metals [29,30]. The use of SBP as natural sorbent for the decontamination of industrial effluents contaminated with toxic metals may be a way to enhance its value. The SBP used in this work is a by-product of the sugar industry and is mainly used as animal feed. This material is very cheap (US\$ 100 per metric ton) and its production reaches 14×10^6 tonnes of dry matter each year in Konya city. SBP is a natural polysaccharide and is composed of 20% cellulosic and more than 40% of pectic substances. The pectic substances are complex hetero-polysaccharides containing galacturonic acid, arabinose, galactose, and rhamnose as the major sugar constituents [29]. Chemically, pectins appear as polyuronides, i.e. straight chains of a few hundred molecules of α -D-galacturonic acid linked by 1–4-glycosidic bounds. Pectins are not pure polyuronides; however, the polysaccharide also contains 1–2 linked α -L-rhamnose molecules (1–4%). Pectic substances contain polygalacturonic acids which carry carboxyl functions and they are known to strongly bind metal cations in aqueous solution and consequently exhibit good capacities

to retain metal ions. Rhamnose residues are covalently bound to L-arabinose and *o*-galactose molecules (10–15%). In most pectin, some of the galacturonic acids are methyl esterified [31,32].

The present study was undertaken to evaluate the effectiveness of FA and SBP in the removal of copper and zinc by adsorption. For each single metal, batch experiments were designed for the sorption process and batch kinetics and isotherm studies were conducted to determine the adsorption capacity of sorbents. The effect of contact time, pH, sorbent dosage, and initial concentration of adsorbate on adsorption were studied. Both Langmuir and Freundlich sorption isotherms were applied to the experimental results.

2. Materials and methods

All chemicals and reagents used were of analytical grade and were obtained from Merck, Germany. Stock solutions of copper and zinc were prepared from analytical reagent grade copper sulphate, copper nitrate, and zinc nitrate in deionised water, respectively. The pH measurements were performed with Jenway 3010 Model pH meter. A thermo-stated shaker (Gallenkamp Incubator) of Orbital model was used for adsorption experiments. The concentrations of metal ions were determined by atomic absorption spectrometer Unicam 929 Model Atomic Absorption Spectrometer (AAS). Solutions of 0.1 M NaOH and 0.1 M HNO₃ or 0.1 M HCl were used for pH adjustment. Constant ionic strength 0.1 M NaCl was used in all experiments. All working solutions were prepared by diluting the stock solutions with deionised water.

2.1. Adsorbent development

SBP, a solid by-product and FA, a solid waste material of the sugar industry, were collected from Konya Sugar Factory, Turkey. The SBP and FA were dried and then sieved to find its particle size distribution.

2.2. Adsorption studies

SBP for these experiments was obtained from the sugar mill. The wet SBP was dried overnight at 70 °C in a convection oven, ground in a ball mill, and sieved into different fractions (100–150 μ m). In order to eliminate soluble components, such as tannins, resins, reducing sugars, and coloring agents, the SBP was successively washed with 1.0 M HCl and distilled deionised water until a constant pH was achieved. The ionic strength in solution was adjusted with NaCl. The batch tests for the determination of the effect of initial metal concentration were conducted for the equilibrium time mixing at a constant speed of 200 rpm after adjusting the pH to the optimum value for maximum adsorption. Various initial metal concentrations were prepared by serial dilution of 1000 ppm of standard solution of metals. The pH in solution was adjusted with 0.1 M HCl and 0.1 M NaOH to cover a pH range from 2 to 7. The test tubes were then sealed with caps and placed on the thermostatic shaker. The test tubes were removed after 24 h shaking and centrifuged

for 5 min at 3000 rpm. The supernatant was analyzed using AAS for residual metal content.

The FA used herein was obtained from burning of young brown coal at the sugar factory. The bulk FA was dried and sieved into different fractions (100–150 μm). The FA was baked at 500 $^{\circ}\text{C}$ for 2 h to remove the carbon residue. Then the adsorption studies have been completed described above.

The effect of contact time (0–300 min), concentration (1×10^{-4} to 1×10^{-3} M), solution pH (3.0–7.0), adsorbent dose (0.1–1.0 g) for SBF and contact time (0–240 min), concentration (1×10^{-4} to 1×10^{-3} M), solution pH (3.0–8.0), adsorbent dose (0.025–0.300 g) for FA were studied at room temperature. Isotherms were obtained by adsorbing different concentrations of metal ions. After prescribed contact times, the solutions were filtered and the concentrations of metal ions were determined by atomic spectrometry. Average values of three replicates were taken for each determination. The effect of interfering ion sodium chloride has also been studied on the adsorption of two metal ions on the sorbents. The ionic strength for all adsorption experiments in this study was 0.1 M.

3. Results and discussion

3.1. Effect of contact time

The effect of time on the adsorption of metal ions by the SBP and FA were studied by taking 0.1 g sorbent with 20.0 ml of 0.001 M metal salt solution in different stoppered flasks. The flasks were shaken for different time intervals in a temperature-controlled shaker. Fig. 1a and b shows the effect of contact time on adsorption of copper and zinc using both sorbents. The results show that the percentage of metal ion adsorption by the both sorbents increased with increasing time of equilibration and it reached the plateau value at about 60 min for copper and zinc metal ions for both metal ions.

3.2. Effect of pH on adsorption

pH in solution has been identified as the most important variable governing metal adsorption on sorbents. This is partly due to the fact that hydrogen ions themselves are strongly competing adsorbate and the solution pH influences the ionization of surface functional groups. These experimental results indicate that the binding of copper and zinc is pH-dependent. The decrease in copper removal capacity SBF at pH >6.3 may be caused by hydrolysis accompanying by precipitation of metal hydroxides. The experiments were carried out at pH values below pH 7 where metal hydroxide chemical precipitation occurs, which has been estimated as pH >6.3 for $\text{Cu}(\text{OH})_2(\text{s})$.

SBP is composed mainly of cellulose (20–30%), pectin (26–40%), pentosan(24%), protein(5%), and lignin (10%), all of them with the capacity to bind metal cations due to carboxylic and phenolic groups. The metal ions are mainly fixed on these acid sites. At pH values higher than 3–4, carboxyl groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced. At low pH, the surface of SBP would also be surrounded by hydronium

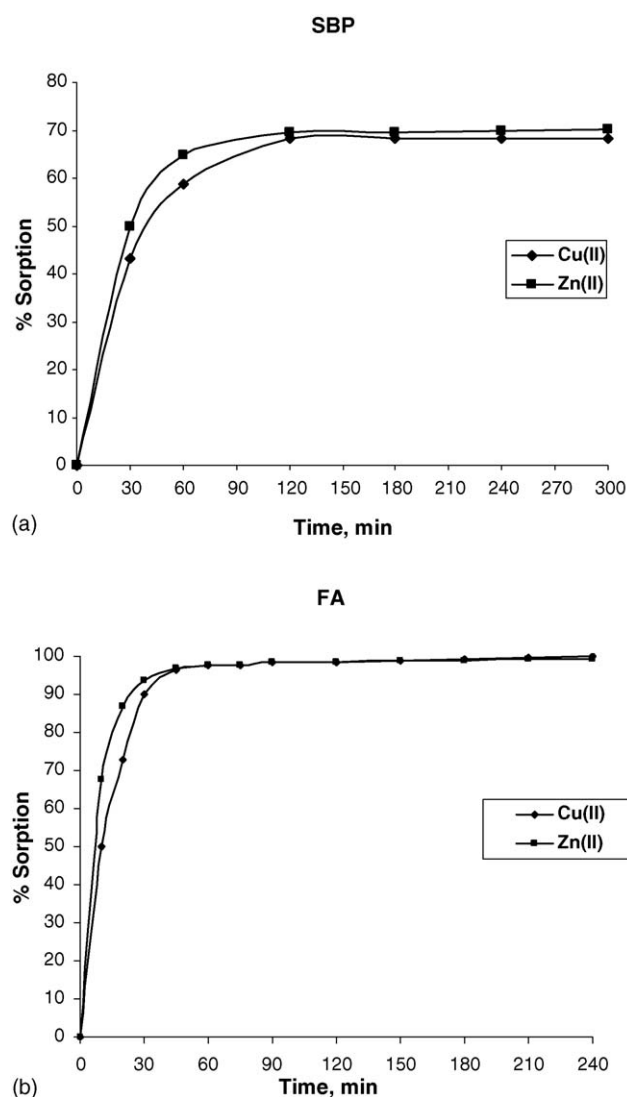


Fig. 1. (a) Effect of contact time on the sorption of copper and zinc by SBP (adsorption conditions: initial concentration of metal ions, 1×10^{-3} M; amount of adsorbent, 0.4 g; volume of adsorption medium, 50 ml; temperature, 25 ± 1 $^{\circ}\text{C}$; stirring rate, 200 rpm; pH 5.5–6.0). (b) Effect of contact time on the sorption of copper and zinc by FA (adsorption conditions: initial concentration of metal ions, 1×10^{-3} M; amount of adsorbent, 0.2 g; volume of adsorption medium, 25 ml; temperature, 25 ± 1 $^{\circ}\text{C}$; stirring rate, 200 rpm; pH 4.0–5.0).

ions which decrease the metal ion interaction with binding sites of the sorbent by greater repulsive forces. The smaller sorption values observed at pH values 3.0–4.0 have been attributed to the competition between the sodium ion and the metal ions released. As expected, the sorption increases with pH. As the pH increased, the overall surface on the SBP became negative and the metal sorption is improved due to the lower competition between the sodium ions and metal ions. The plots showing the effect of pH on the adsorption of two metal ions are shown in Fig. 2a. The adsorption equilibrium is rapidly achieved and only 60 min contacting time is considered enough to achieve equilibrium conditions.

Batch adsorption experiments are conducted to evaluate how carbon and mineral fraction of FAs contributes to surface adsorption. Since FA contains abundant alkaline materials, such as CaO

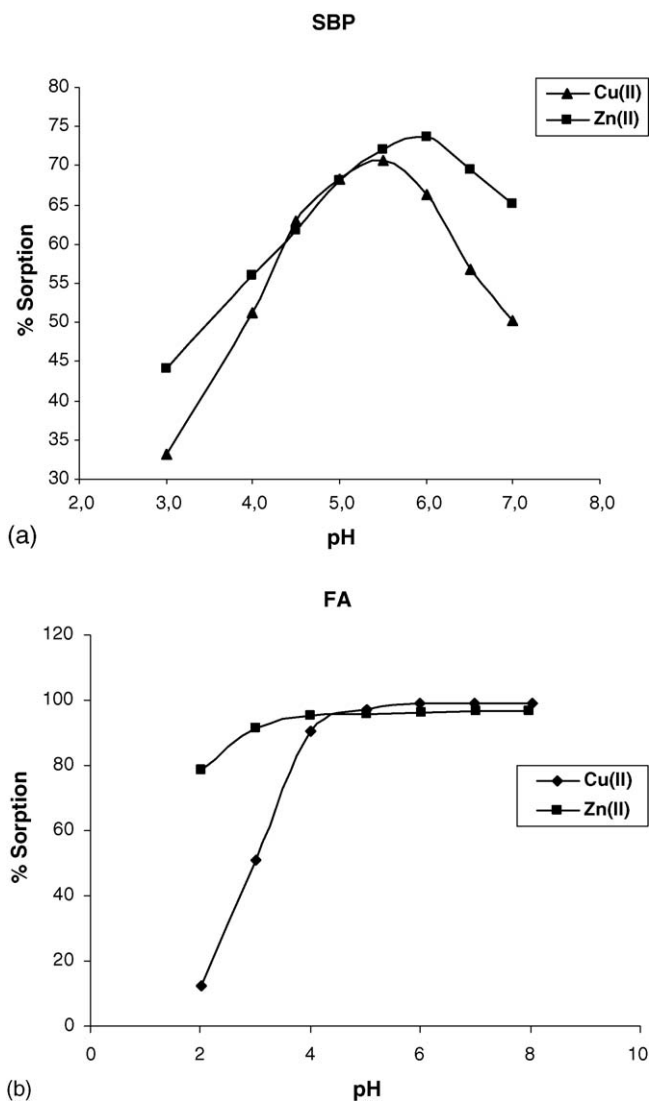


Fig. 2. (a) Effect of pH on the sorption of copper and zinc by SPA (adsorption conditions: initial concentration of metal ions, 1×10^{-3} M; amount of adsorbent, 0.4 g; volume of adsorption medium, 50 ml; temperature, 25 ± 1 °C; stirring rate, 200 rpm). (b) Effect of pH on the sorption of copper and zinc by FA (adsorption conditions: initial concentration of metal ions, 1×10^{-3} M; amount of adsorbent, 0.2 g; volume of adsorption medium, 25 ml; temperature, 25 ± 1 °C; stirring rate, 200 rpm).

and MgO, the hydroxide ion ($\sim\text{OH}$) is liberated, raising pH during adsorption. In such cases, Cu(II) may then form an insoluble product of $\text{Cu}(\text{OH})_2(\text{s})$. The Zn and Cu removal capacity exhibited by the FA depends on the pH of the initial metal solution, decreasing with decreasing pH. As shown in Fig. 2b, the maximum adsorption of copper and zinc was found to occur at pH 4.0–8.0. This may be attributed to the surface charge development of FA and the concentration distribution of metal ions which both are pH-dependent. All experiments were carried out in the pH range of 2.0–8.0 where chemical precipitation is avoided, so that metal removal could be related to the adsorption process. It was evident from the plots that the maximum uptake of copper and zinc occurred at pH 5.5 and 6.0, respectively, for SBP and at pH 5.0 and 4.0, respectively, for FA and the other sorption experiments were performed at these pH values. The

pH of the solution was measured before and after the adsorption with SBF and slightly change was noticed in the pH. Due to the alkaline nature of FA, the pH increases as the FA is added into the solution. When the above occurs, the copper and zinc ions are expected to precipitate out of the solution under higher pH conditions. To elucidate the effect of such a pH increase on copper and zinc removal with FA, experiments were performed with pH control. The FA particles exhibit a pH_{zpc} of 7.0. This indicates that at pH lower than 7.0, the FA surface is positively charged and the opposite is true at pH higher than 7.0 [33]. Therefore, under the pH conditions at adsorption equilibrium, i.e. pH 7.0–7.5 for both Zn^{2+} and Cu^{2+} solutions, the surface of the FA is negatively charged. According to the simple species diagrams which were constructed by Leyva-Ramos et al. [34] for Zn^{2+} and Cu^{2+} , respectively, all the species occurring at pH values of 7.0 and below carry a positive charge either as Zn^{2+} , $\text{Zn}(\text{OH})^+$, Cu^{2+} , or $\text{Cu}(\text{OH})^+$. In this case adsorption occurs by electrostatic attraction. The increase in adsorption with increase of pH may also be explained on the basis of aqua complex formation of the oxides present in the FA and its subsequent acid–base dissociation at the solid–solution interface [24]. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This allows the silica surface to act as a weak acid. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charged.

3.3. Effect of SBP and FA dosage on adsorption

The effect of the SBF dose on the removal of copper and zinc is shown in Fig. 3a. The adsorption increased from 60.0 to 66.0% with increase in adsorbent dose from 0.1 to 1.0 g in the case of copper and then became almost constant. The increase in adsorption was found to be from 60 to 70% in the case of zinc for a similar increase in adsorbent dose. The results indicate that a dose of 8 g l^{-1} of adsorbent is sufficient for the optimum removal of both the metal ions. Fig. 3b illustrates the effect of the FA amount that is added to the solution keeping the copper and zinc concentrations constant. It is observed that as the dose of FA increases, amount of copper and zinc increases gradually. For instance, the removal of copper and zinc by FA increases from 25.8 to 100.0% and 80.9 to 99.7%, respectively, by increasing the FA dosage from 0.025 to 0.300 g under equilibrium conditions and a dose of 8 g l^{-1} of adsorbent is sufficient for the optimum removal of both the metal ions. This may be attributed to the higher percentage of FA and consequently greater surface area or FA constituents available for the adsorption of copper and zinc absorbable aqueous ionic species.

3.4. Adsorption studies

3.4.1. Effect of initial metal concentration on adsorption

The initial metal concentration provides an important driving force; hence a higher initial concentration of metal ions will increase the sorption rate. The effect of changing the initial concentration of copper and zinc ions on adsorption, while keeping the dosage of SBP and FA constant at room temperature and equilibrium pH values is illustrated in Fig. 4a and b. These plots

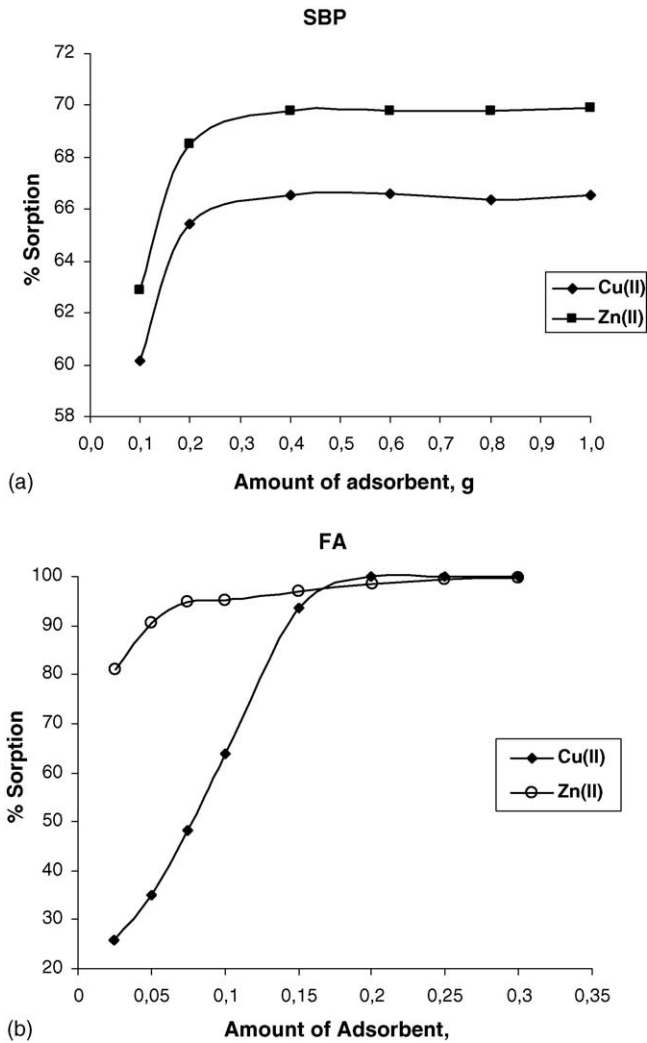


Fig. 3. (a) Effect of amount of adsorbent on the sorption of copper and zinc by SBP (adsorption conditions: initial concentration of metal ions, 1×10^{-3} M; volume of adsorption medium, 50 ml; temperature, $25 \pm 1^\circ\text{C}$; stirring rate, 200 rpm; pH 5.5–6.0). (b) Effect of amount of adsorbent on the sorption of copper and zinc by FA (adsorption conditions: initial concentration of metal ions, 1×10^{-3} M; volume of adsorption medium, 25 ml; temperature, $25 \pm 1^\circ\text{C}$; stirring rate, 200 rpm; pH 4.0–5.0).

showed that the total metal ion adsorbed increased sharply in the beginning and then slowly towards the end of the run. For the different initial concentrations, adsorption equilibrium was rapidly achieved. As shown in Fig. 4a, with the increase of the initial concentration of copper and zinc from 2×10^{-3} to 20×10^{-3} M, the percentage removal for the SBP increases from 55.0 to 62.0 for copper and 63.0 to 71.0 for zinc. For SBP, sorption increased with increasing initial metal concentration, the extent of the increase depending on the metal cation. At low metal concentrations, steep isotherms were obtained which are highly desirable as they indicate high affinity of the sorbent for the given sorbed species [29]. For FA, initial concentrations of copper and zinc change from 2×10^{-3} to 20×10^{-3} M, the percentage removal increases from 78.9 to 97.8 for copper and 97.7 to 99.0 for zinc. The chemical constituents of FA affect its adsorptive properties towards metal cation. Therefore, an attempt was made to estab-

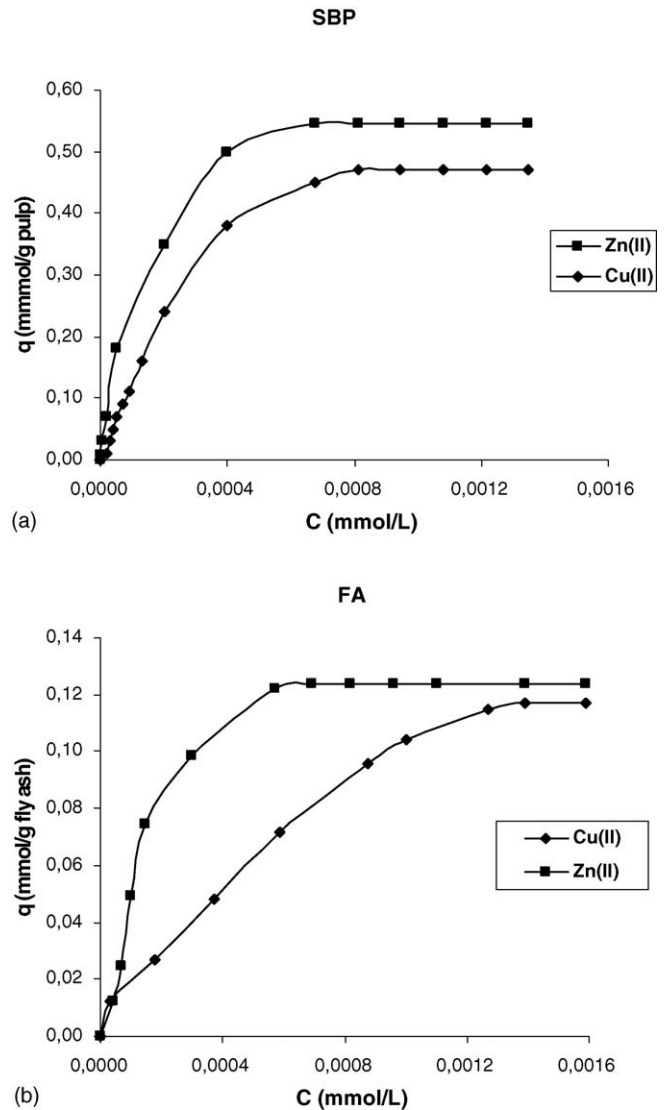


Fig. 4. (a) Effect of initial concentration on the sorption of copper and zinc by SBP (adsorption conditions: initial concentration of metals, $2\text{--}20 \times 10^{-3}$ M; amount of adsorbent, 0.4 g; volume of adsorption medium, 50 ml; temperature, $25 \pm 1^\circ\text{C}$; stirring rate, 200 rpm; pH 5.5–6.0). (b) Effect of initial concentration on the sorption of copper and zinc by FA (adsorption conditions: initial concentration of metals, $2\text{--}20 \times 10^{-3}$ M; amount of adsorbent, 0.2 g; volume of adsorption medium, 25 ml; temperature, $25 \pm 1^\circ\text{C}$; stirring rate, 200 rpm; pH 4.0–5.0).

lish a relationship between the adsorption capacity of the FA and its major chemical constituents, such as mineral oxides (calcium, aluminum, and silica oxides) and carbon. As assumed herein, the FA is a dual adsorbent that means it adsorbs by both mineral and carbon. Copper and zinc removal by FA was achieved through the competitive adsorption between carbon and mineral.

3.4.2. Adsorption isotherms

Equilibrium data are basic requirements for the design of adsorption systems and adsorption models are used for the mathematical description of the adsorption equilibrium of the metal ion on to the adsorbent. The results obtained on the adsorption of copper and zinc were analyzed by the well-known models given

Table 1
Parameters of Langmuir and Freundlich isotherms for sorption of copper and zinc on SBP and FA

	Freundlich isotherm			Langmuir isotherm		
	k	n	R^2	Q_0^a	b^b	R^2
SBP						
Cu(II)	4.04	0.99	0.99	0.0024	104.13	0.60
Zn(II)	6.23	0.99	0.99	0.0027	60.22	0.74
FA						
Cu(II)	5.15	1.71	0.99	0.1800	1121.59	0.92
Zn(II)	701.13	0.94	0.92	0.1700	5011.50	0.99

^a mmol g⁻¹ adsorbent.

^b l mmol⁻¹.

by Langmuir and Freundlich [1,2]. For the sorption isotherms, initial metal ion concentration was varied while the pH of solution and adsorbent weight in each sample held constant. The sorption isotherms were realized with SBP and copper at pH 5.5 and zinc at pH 6.0. The experimental results were used for the calibration of parameters of the Freundlich adsorption isotherm and are presented in Table 1. The modeling of these results by the Langmuir and Freundlich equations gave the coefficients presented in Table 1. The corresponding correlation coefficients are, respectively, between the ranges 0.60 and 0.99. The Freundlich theory was found to represent better than the Langmuir approach. The Freundlich model is valid for a multilayer sorption model on a surface containing a finite number of sites with mutual interactions between sorbed metal cations. Freundlich isotherm was generated by plotting q versus C_e .

Freundlich equation:

$$q = K_f C_e^n \quad (1)$$

where n is the Freundlich constant, K_f the adsorption coefficient, q the weight adsorbed per unit weight of adsorbent, and C_e is the equilibrium metal concentration in fluid. Taking logs and rearranging equation (1):

$$\log q = \log K_f + n \log C_e \quad (2)$$

The plot of $\log q$ against C_e for the adsorption data of copper and zinc shows that the data are fitting very well to the Freundlich model. The Freundlich equation predicts that the metal ion concentration on the sorbent will increase as long as there is an increase in the metal ion concentration while experimental results showed a plateau indicating a limiting value of the sorption. The coefficients K_f and n can be estimated from the slopes. As shown in Fig. 4a, curved isotherms were found according to the Freundlich's sorption model, suggesting that it was not applicable over the entire solute concentration range. Linear regions were observed on each isotherm but did not correspond to the same range of data according to the metal cation. The electrostatic interactions, which would only occur with the more weakly bound cations, would contribute to the sorption of copper and zinc explaining their higher affinity for pectins inside cell walls. Hydroxyl functions close to carboxyl functions would participate in the complexation of such highly bound cations and allow

the participation of less than two carboxyl functions to hold one divalent cation.

The Langmuir isotherm has been used by various workers for the sorption of variety of compounds. The Langmuir isotherm is given by the following equation:

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (3)$$

where C_e is the equilibrium concentration (mg l⁻¹), q_e the amount of adsorbed material at equilibrium (mg g⁻¹), b the "affinity" parameter or Langmuir constant (l mmol⁻¹), and Q_0 is the "capacity" parameter (mmol g⁻¹) [1]. The Langmuir isotherm parameter was determined by least-squares fit of the sorption data in Fig. 4a and b. Q_0 and b were determined from the slope and intercept of the Langmuir plot and are presented in Table 1. The Langmuir isotherm equation provided an excellent fit to the equilibrium sorption data, giving correlation coefficients of 0.99 on the FA for zinc ion but Freundlich isotherm equation was applicable for copper ion adsorption on the FA. The essential feature of the Langmuir equation can be given in terms of a dimensionless. The values of constants indicate favorable conditions for adsorption. Langmuir model was more applicable than the Freundlich model, since the correlation coefficients for the former were higher for the adsorption of zinc ion on the FA. Langmuir-type model presupposes homogeneity of the sorbing surface and no interactions, involving uniform energies of sorption on the surface and no transmigration of metal cations in the plane of the surface. The difference in adsorption capacities of two sorbents is believed to be largely due to the physical-chemical properties of them or the chemistry of the metal containing solutions.

3.5. Effect of sodium chloride concentration

The effect of sodium chloride concentration on metal uptake worked with 0.1 M NaCl concentration. The electrostatic attraction at low ionic strength appears to play a negligible role in the removal of copper and zinc for both adsorbents. The results indicate that, up to 0.1 M NaCl, there was no significant decrease in the removal of copper or zinc. However, increasing the ionic strength over 0.1 M results in a decrease in metal ions removal about 22% for copper and about 25% for zinc for SBP and 25% for copper and about 30% for zinc for FA. Metal uptake is sensitive to changes in the concentration of the supporting electrolyte if electrostatic attraction is the significant mechanism for metal removal. It can be seen that an increase of chloride concentration may results in a decrease of the free copper and zinc species and an increase in the formation of chloro-complexes. The general tendency was adsorption decreasing with increasing ionic strength of the solution.

3.6. Desorption studies

The reversibility of the process was also investigated. The desorption of copper and zinc which were previously deposited

on the SBP and FA back into the deionised water was observed only in acidic pH values during 1-day study period and was generally rather low.

4. Conclusions

The results obtained with the FA were also compared with results obtained with the SBP. These sorbents, compared to others, have several advantages. They are cheap raw material or waste products from Konya Sugar Factory. The FA can be used as an adsorbent for copper and zinc solutions. Metal retention using the FA decreases when the pH of the initial solution decreases. Metal sorption is pH-dependent and maximum sorption for both metals was found to lie between 5.5 and 6.0 for SBP and 5.0 and 4.0 for FA. Metal adsorption is very quick at the different concentrations studied under the experimental conditions used. When ionic strength increases, the maximum adsorption capacity diminishes for the SBP and FA. The removal of the two metal ions takes place by a partial diffusion mechanism. The adsorption data for the SBP fit very well to the Freundlich model and for the FA fit to the Langmuir model for zinc and Freundlich model for copper. The amount of copper and zinc adsorbed by the SBP and FA increased with the increase in concentration. The extent of adsorption for both metals increased along with an increase of the SBP and FA dosage. The SBP could be extensively used in its raw form without recycling due to its very low cost. It was confirmed that the native SBP is dominated by negatively charged sites that are largely carboxylate groups with some weaker acidic groups.

Acknowledgement

We express our thanks to the Selcuk University Scientific Research Foundation, which has financed the project (2003/028), a part of which is presented in this study.

References

- [1] F. Gode, E. Pehlivan, J. Hazard. Mater. B100 (2003) 231.
- [2] F. Gode, E. Pehlivan, J. Hazard. Mater. B119 (2005) 175.
- [3] F. Gode, E. Pehlivan, Fuel Process. Technol. 86 (2005) 875.
- [4] C.-J. Lin, J.-E. Chang, Chemosphere 44 (2001) 1185.
- [5] F.A. Lopez, C. Perez, E. Sainz, M. Alonso, J. Chem. Technol. Biotechnol. 62 (1995) 200.
- [6] L. Zhang, J. Zhou, D. Zhou, Y. Tang, J. Membr. Sci. 162 (1999) 103.
- [7] H. Leinonen, J. Lehto, React. Funct. Polym. 43 (2000) 1.
- [8] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, Water Res. 37 (2003) 4038.
- [9] C. Gabaldon, P. Marzal, A. Seco, J. Chem. Technol. Biotechnol. 66 (1996) 279.
- [10] F.A. Lopez, C. Perez, E. Sainz, M. Alonso, J. Chem. Technol. Biotechnol. 62 (1995) 200.
- [11] S.J. Allen, P.A. Brown, J. Chem. Technol. Biotechnol. 62 (1995) 7.
- [12] J.A. Laszlo, F.R. Dintzis, J. Appl. Polym. Sci. 52 (1994) 531.
- [13] Z. Reddad, C. Gerente, Y. Andres, M.C. Ralet, J.F. Thibault, P.L. Cloirec, Carbohydr. Polym. 49 (2002) 23.
- [14] W.E. Marshall, L.H. Wartelle, D.E. Boler, C.A. Toles, Carbon 9 (2000) 1407.
- [15] P. Kumar, S.S. Dara, J. Polym. Sci. Polym. Chem. Ed. 19 (1981) 397.
- [16] J.A. Omgbu, V.I. Iweanya, J. Chem. Ed. 67 (19) (1990) 800.
- [17] Y.S. Ho, Water Res. 37 (2003) 2323.
- [18] E.T. Hawthorne-Costa, A.A. Winkler Hechenleitner, E.A. Gomez-Pineda, Sep. Sci. Technol. 30 (12) (1995) 2593.
- [19] G. Sun, W. Shi, Ind. Eng. Chem. Res. 37 (1998) 1324.
- [20] S. Al-Asheh, Z. Duvnjak, Sep. Sci. Technol. 33 (9) (1998) 1303.
- [21] L. Sung-Ho, J.-W. Yang, Sep. Sci. Technol. 32 (8) (1997) 1371.
- [22] D.C. Sharma, C.F. Forster, Bioresour. Technol. 47 (1994) 257.
- [23] N.W. Broughton, C.C. Dalton, G.C. Jones, E.L. Williams, Int. Sugar J. 97 (1995) 57/60.
- [24] B. Bayat, Water, Air, Soil Pollut. 136 (2002) 69.
- [25] M. Vincini, F. Carini, S. Silva, Bioresour. Technol. 49 (1994) 213.
- [26] J. Parsa, S.H. Munson-McGee, R. Steiner, J. Environ. Eng. 122 (10) (1996) 935.
- [27] N.J. Sell, J.C. Norman, M.B. Vandembasch, Resour. Conserv. Recov. 10 (1994) 279.
- [28] V.K. Gupta, D. Mohan, S. Sharma, Sep. Sci. Technol. 33 (9) (1998) 1331.
- [29] V.M. Dronnet, C.M.G.C. Renard, M.A.V. Axelos, J.-F. Thibault, Carbohydr. Polym. 34 (1997) 73.
- [30] C. Gerente, P. Couespel Du Mesnil, Y. Andres, J.-F. Thibault, P. Le Cloirec, React. Funct. Polym. 46 (2) (2000) 135.
- [31] C. Garnier, M.A.V. Axelos, J.F. Thibault, Carbohydr. Res. 256 (1994) 71.
- [32] M.T. Kartel, L.A. Kupchik, B.K. Veisov, Chemosphere 38 (11) (1999) 2591.
- [33] B.E. Reed, M.R. Matsumoto, Sep. Sci. Technol. 28 (13–14) (1993) 2179.
- [34] R. Leyva-Ramos, J.R. Rangel-Mendez, J. Mendoza-Barron, L. Fuentes-Rubio, R.M. Guerrero-Coronado, Water Sci. Technol. 35 (7) (1997) 205.