



Short Communication

Preparation of cation exchanger from lemon and sorption of divalent heavy metals

Hasan Arslanoglu, H. Soner Altundogan, Fikret Tumen *

Department of Chemical Engineering, Firat University, 23279 Elazig, Turkey

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Abstract

A cation exchanging material was developed from lemon by modifying the pectic–cellulosic substances in the lemon peel by lemon juice having citric acid. For this purpose, chopped lemon removed from seeds and yellow skin was heated in two stages, firstly at 50 °C for 24 h and subsequently at 120 °C for 2 h. The material obtained was ground, repeatedly washed with water and dried. Lemon peel and lemon resin obtained were characterized through physicochemical analyses and FTIR spectroscopy. Heavy metal binding performance of this material was determined by removal tests conducted by using 10 mM solutions of divalent metals. Experimental results show that the resin prepared from lemon is effective especially for Pb and Cu removals. For a lemon resin dosage of 10 g l⁻¹, sorption affinity of divalent metal ions is found to be in an order of Pb > Cu > Ni > Fe > Cd > Zn > Co > Mn. Typically, sorption capacities are about 0.87 and 0.43 mmol g⁻¹ for Pb and Mn, respectively.

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Keywords: Lemon peel; Lemon juice; Cation exchanger; Cross-link; Heavy metal removal**1. Introduction**

The contamination of water reservoirs by the toxic heavy metals has become a worldwide environmental problem that has to be urgently controlled. Increasing public awareness and sensitivity related to the environmental issues and stricter regulations on the discharge of heavy metals make it necessary to develop efficient technologies for their removal. The methods for the removal of heavy metals from wastewaters are based on chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption techniques (Patterson, 1985). Chemical precipitation is the most commonly used method for the removal of heavy metals from wastewaters. The main alternative techniques that promise for heavy metal removal are adsorption and

ion exchange processes. In recent years, intensive studies have been performed to find low-cost and effective sorption materials for heavy metal removal (Babel and Kurniawan, 2003; Bailey et al., 1999; Pollard et al., 1992). In this context, agricultural residues and agroindustrial by-products mainly consisted of lignocellulosic substances have been evaluated for sorption of heavy metals (Crini, 2005). In some studies, such materials have been converted into active carbons and/or modified products to enhance their sorption capability. A part of those studies have been documented in review articles (Babel and Kurniawan, 2003; Bailey et al., 1999; Crini, 2005; Pollard et al., 1992).

Low-cost cation exchange resins can be prepared from agricultural residues by incorporation of acidic groups on to the complex polysaccharide matrix (Marshall et al., 1999). With this purpose, chemical modification of pectic and lignocellulosic materials via cross-linking has been extensively studied (Dronnet et al., 1998a,b; Laszlo and Dintzis, 1994; Marshall et al., 2000, 2001; Wing, 1997). Mostly, citric acid has been used as a modification agent

* Corresponding author. Tel.: +90 424 2370000/5523; fax: +90 424 2415526.

E-mail address: ftumen@firat.edu.tr (F. Tumen).

in order to attach free carboxyl groups on to the hydroxyl of polysaccharide matrix of cellulosic waste materials (Marshall et al., 2000; Wartelle and Marshall, 2000) or starch (Wing, 1996). It has been reported that an estimated production cost for citric acid-modified soybean hull is \$1.17/kg versus typical retail costs \$4–40/kg for commercial, petroleum-based cation-exchange resins when purchased in bulk quantities (Marshall et al., 2001).

The majority of commercial polymers and ion-exchange resins are derived from petroleum-based raw materials using processing chemistry that is not always safe and environmentally friendly. Today, there is a growing interest in developing natural low-cost alternatives to synthetic polymers. Polysaccharides can be used for this purpose.

Consequently, the increasing number of publications on adsorption of toxic compounds by these natural polymers shows that there is a recent interest in the synthesis of new adsorbent materials containing polysaccharides (Crini, 2005).

Lemon peel principally consists of cellulose, hemicellulose and pectin substances, while lemon juice contains significant amount of citric acid (Kefford and Chandler, 1970). It means that the lemon provides a ready source of alcoholic and polyacid groups in its different parts, which may be sufficient for the preparation of an ion exchanging resin.

The main objective of this study was to investigate the feasibility of obtaining a cation exchanging material from lemon peel by modifying with lemon juice as a source of citric acid. Then, the binding of different heavy metal ions was determined by using the material obtained from lemon.

2. Methods

2.1. Preparation of resin

Lemon, grown in the Mediterranean region of Turkey, was purchased from local market. The yellow coloured outer thin film of lemon was removed by grating and the lemons were chopped into small pieces less than 10 mm. Seeds were picked out. The material was placed on a glass tray and heated in an oven at 50 °C for 12 h. Resulting material was finally heated at 120 °C for 2 h. The brown-black material obtained was ground in a coffee mill and sieved to $-150\ \mu\text{m}$. In order to remove citric acid unreacted and other soluble substances, material was subjected to washing. To do this, the powdered product was slurried in distilled water with a water/solid ratio of 20 and agitated for 30 min. The mixture was filtered and same amount of water was added. The washing was repeated until the washing water does not give Pb-citrate precipitate with a tester solution prepared from $\text{Pb}(\text{NO}_3)_2$. The final product was dried at 105 °C for 24 h, cooled in a dessicator and stored in tightly capped jars during the experimental study. This material was nominated as lemon resin (LR).

Separately, a portion of lemon peel was obtained. It was processed at the same condition with LR. This material

was labelled as lemon peel (LP), was used in parallel experiments in order to provide a comparison.

2.2. Preparation of stock metal solutions

Stock solutions (250 ml) of metals were prepared in the concentration of 0.25 M by dissolving appropriate amount of metal salts ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{Pb}(\text{NO}_3)_2$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). In order to prevent precipitation of metals by hydrolysis, 3–4 drops of concentrated appropriate acid was added to the stock solutions.

2.3. Metal removal capacity

Lemon peel (LP) and lemon resin (LR) samples were evaluated for metal ion sorption by a method (Marshall et al., 1999) applied for soybean hulls modified with citric acid. Working solutions in the concentration of 10 mM were prepared by diluting appropriate volume of 0.25 M stock metal solutions with buffer solution of 0.07 M sodium acetate–0.03 M acetic acid (pH 4.8). One gram of material was added to 100 ml of metal solution and the mixture was agitated for 24 h at $25 \pm 1\ ^\circ\text{C}$ at speed of $200\ \text{min}^{-1}$ in a shaking incubator (Selecta Rotabit). The pH of suspensions was measured (Mettler Delta 350 pH meter) at the beginning and at the end of the contact period. Filtrates were analyzed for determining the metal content.

The experiments were regularly performed in duplicate and the maximum deviation was found to be $\pm 5\%$.

2.4. Analytical methods

FTIR spectroscopy was used to identify the chemical groups present in lemon peel and lemon resin. Spectra of lemon peel and lemon resin were recorded in a Fourier transform infrared spectrometer (ATI Unicam Matson 1000) with the sample prepared as KBr discs.

For characterization, water contacted with samples at the conditions of metal binding study (at $10\ \text{g l}^{-1}$ solid concentration, for 24 h at 25 °C) was subjected to pH and conductivity measurements.

Solubility in water was determined by weighing after drying at 105 °C of the residue of 1 g sample agitated together with 100 ml of water at 25 °C for a period of 24 h. For the solubility in 0.25 M HCl, the same procedure was followed by using 0.25 M HCl solution instead of water. Solubility values were calculated from the weight differences of dried washing residues and original samples and expressed as percentage.

Swelling capacities (SC) of samples were measured by bed volume technique (Kuniak and Marchessault, 1972). SC values were calculated from the volume difference of swollen and original samples and expressed as ml volume per gram of dry matter (ml g^{-1}).

Water retention capacities (WRC) for lemon peel and lemon resin were determined by measuring of

water-saturated weight of samples by using centrifugation method (MacConnel et al., 1974). It was calculated from the difference of the weight difference of wet and dry samples. The WRC values were expressed as weight of water absorbed per unit weight of dry sample (g g^{-1}).

Ash content of samples were determined by weighing the residues after igniting at 500 °C for 6 h and then at 900 °C for 1 h.

Chemical oxygen demand (COD), which is a measure of pollution potential originated from an organic adsorbent or ion exchanger itself, was determined. For this purpose, 1 g of resin sample was contacted with 100 ml of distilled water by shaking for 24 h at 25 °C. COD analyses of the filtrates were performed by using dichromate method (APHA, 1989) and results were expressed as mg O_2 per gram of dry matter (mg g^{-1}).

Cation exchange capacity was determined by measuring the total number of milliequivalents of exchangeable hydrogen in the material (ASTM, 1989).

The acidity of lemon juice was determined by titration the aliquot of the juice with 0.1 N NaOH solution.

Filtrates obtained from heavy metal sorption study were analyzed using flame Atomic Absorption Spectrophotometry (Perkin Elmer, PE 370) for metal content. The amounts of metal ions sorbed on material were determined from the measured bulk concentrations, using the following equation,

$$q = \frac{V}{M}(C_0 - C) \quad (1)$$

where q is amount of metal ions sorbed (mg g^{-1} or mmol g^{-1}), V is volume of solution (liter), M is amount of sorbent used (g), C_0 and C are initial and final metal ion concentrations (mg l^{-1} or mmol l^{-1}), respectively.

3. Results and discussion

In order to characterize the lemon used in the study, one kg of lemon was partitioned and various parts of lemon were weighed. Acidity, density and dry matter content of lemon juice were determined. The results are given in Table 1.

Lemon (10 kg) was converted into a cation exchanger resin in a yield of 6.88%. Some characteristics of lemon peel and resin obtained are summarized in Table 2.

Table 1
Some properties of lemon and lemon juice used in the study

Parts of lemon	%
Peel	27.8
Internal pomace	17.7
Juice ^a	42.4
Grated yellow skin ^b	9.5
Seed ^b	2.6
Total	100

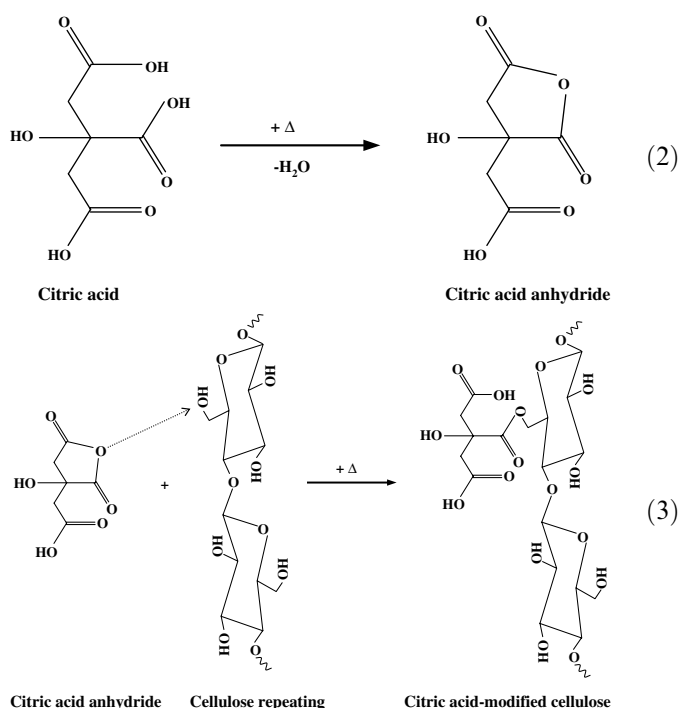
^a Density of juice: 1.06 g/cm^3 . Dry matter of juice: 9.65%. Acidity of juice: 4.12% (in citric acid basis).

^b Discarded.

Table 2
Characteristics of lemon peel and lemon resin

Parameter	Values	
	Lemon peel	Lemon resin
pH	4.40	3.60
Conductivity ($\mu\text{S cm}^{-1}$)	410	325
Specific gravity (g cm^{-3})	0.585	0.670
Ash (%)	5.15	4.26
Solubility in water (%)	42.4	2.4
Solubility in 0.25 M HCl (%)	55.7	8.5
Cation exchange capacity (mmol g^{-1})	0.67	1.79
Swelling capacity ($\text{cm}^3 \text{g}^{-1}$)	10.70	2.95
Water retention capacity (g g^{-1})	9.18	2.41
Chemical oxygen demand ($\text{mg O}_2 \text{g}^{-1}$)	495	42.5

It is evident that cellulose and pectins in polysaccharide structure have metal binding properties (Dronnet et al., 1998a,b; Kartel et al., 1999). It has been stated that the metal sorption affinity of pectins could be stemmed from the formation of pectates that are compounds formed due to ions binding with pectin polymeric framework via hydroxyl groups of polysaccharide matrix and/or carboxylic groups of galacturonic acid (Kartel et al., 1999). This may explain the significant copper binding capability of untreated lemon peel. Increasing the cation exchanging capacity of lemon peel from 0.67 to 1.79 mmol g^{-1} confirms the hypothesis that extra carboxyl groups are attached to the cellulose molecules by esterification with citric acid. As a consequence of incorporation of carboxyl groups on to the complex polysaccharide matrix, new sorbing sites are provided. Following equations (Marshall and Wartelle, 2006) shows the possible mechanism:



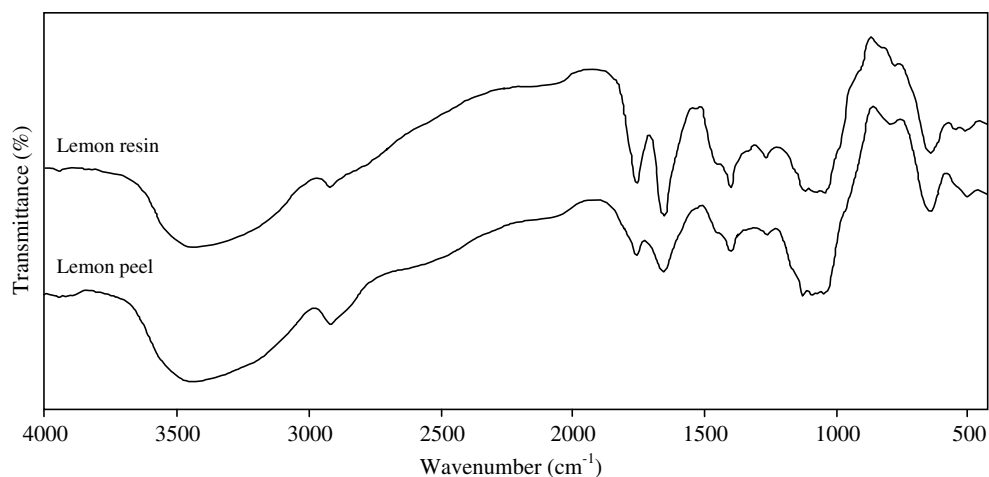


Fig. 1. FTIR spectra of lemon peel and lemon resin samples.

Fig. 1 shows the FTIR spectra of lemon peel and lemon resin. The FTIR spectra exhibits characteristic cellulose peak in the finger print region of $1000\text{--}1200\text{ cm}^{-1}$ (Chakravarty et al., 2007), which shows the main skeleton is cellulose. Bands around 1650 and 1750 cm^{-1} are indicative of free and esterified carboxyl groups which may be useful in identifying pectins (Gnanasambandam and Proctor, 1999) present in LP and LR. The broad peak between 3200 and 3600 cm^{-1} is indicative of the existence of hydroxyl groups of macromolecular association (cellulose, pectin, etc.). Compared to the intensity of the characteristic ester peak at 1750 cm^{-1} , visible increase for LR may confirm the reaction (Eq. (3)) between alcohol groups of cellulose in LP and citric acid in lemon juice. Moreover, the peak that appears at around 1650 cm^{-1} is due to CO stretching vibration of a

carboxylic acid and strengthening of this peak, in the case of lemon resin, may be indicative for increasing number of carboxyl groups on cellulose or pectin chains.

Solubilization of organic matter in the solution having metals during removal process is not desirable because this causes an increase in COD of the water. Comparison of solubility and COD test results of lemon peel and lemon resin show that the resin is more water-insoluble due to the cross-linking occurred between pectic–cellulosic substances and citric acid. Washings applied during resin preparation are another reason of removal of soluble materials. About 3.5-fold decreased swelling capacity (SC) value of LR shows that resin is more stable compared to LP and, hence, it may be used in columnar applications. Also, water retention capacity of LR is found to be one-third of that of

Table 3

pH and concentration values obtained in metal binding tests (experimental conditions: 1 g LP or LR; 100 ml metal solution (prepared in buffer); initial metal ion conc., 10 mM; contact time, 24 h; shaking speed, 200 min^{-1})

Metals	pH _i	pH _f	Concentrations				% Removal
			C _i (mM)	C _f (mM)	C _i (mg l ⁻¹)	C _f (mg l ⁻¹)	
<i>Lemon peel</i>							
Cd	4.73	4.67	10	8.26	1124.0	927.9	17.45
Co	4.80	4.71	10	7.71	589.3	454.8	22.83
Cu	4.79	4.75	10	7.12	635.4	452.5	28.79
Fe	4.77	4.73	10	7.62	558.5	425.7	23.78
Mn	4.80	4.73	10	9.07	549.4	498.4	9.28
Ni	4.78	4.72	10	8.61	587.1	505.7	13.86
Pb	4.73	4.69	10	5.89	2071.9	1221.0	41.07
Zn	4.77	4.70	10	7.98	653.7	521.4	20.24
<i>Lemon resin</i>							
Cd	4.38	4.26	10	2.61	1124.0	293.1	73.92
Co	4.43	4.39	10	4.15	589.3	244.5	58.51
Cu	4.45	4.40	10	1.75	635.4	110.9	82.54
Fe	4.47	4.41	10	2.59	558.5	144.9	74.06
Mn	4.43	4.37	10	5.73	549.4	314.8	42.71
Ni	4.39	4.33	10	2.04	587.1	119.8	79.60
Pb	4.42	4.38	10	1.33	2071.9	275.8	86.69
Zn	4.42	4.29	10	3.75	653.7	244.8	62.55

LP. Significant high value of specific gravity of LR compared to that of LP may show that the material turned into a compact structure. All these findings reveal that material gains a stabilization probably due to an esterification (represented in Eqs. (2) and (3)) occurring between alcohol groups of cellulosic substances in the lemon peel and carboxyl groups of the citric acid in the lemon juice.

Divalent heavy metal binding capacity of the resin prepared from lemon peel and lemon juice were examined by means of an equilibration test conducted in the buffer solution of 0.07 M sodium acetate–0.03 M acetic acid (pH 4.8) for 24 h at the initial heavy metal concentration and sorbent dosage of 10 mM and 10 g l⁻¹, respectively. Initial and final values of pH and metal concentration of the solutions are given in Table 3 and calculated metal binding capacities are shown as histogram in Fig. 2. For a comparison, results obtained at the same conditions by using LP are included.

As seen from Table 3, although the ideal pH of the buffer system of 0.07 M sodium acetate–0.03 M acetic acid can be calculated as about 4.8, measured initial pH values varied in the range of 4.38–4.47 due to the acidic character of metal stock solutions. In addition, when pH_f values are compared to corresponding pH_i values, significant lower values measured in pH_f may be due to the exchange of metal ions with protons in the resin body. Increased acidity may also be stemmed from the ionization of carboxyl groups in the resin. However, the similar results were obtained from the tests using untreated lemon peel. Thus, it can be stated that the pH decrease may be originated from ion exchange in a significant extent.

The uptake magnitudes of divalent metals on lemon peel and lemon resin are compared in Fig. 2. The metal ions sorption affinity with respect to the values calculated in the basis of mmol g⁻¹ is in the order of Pb > Cu > Fe > Co > Zn > Cd > Ni > Mn for lemon peel and that of

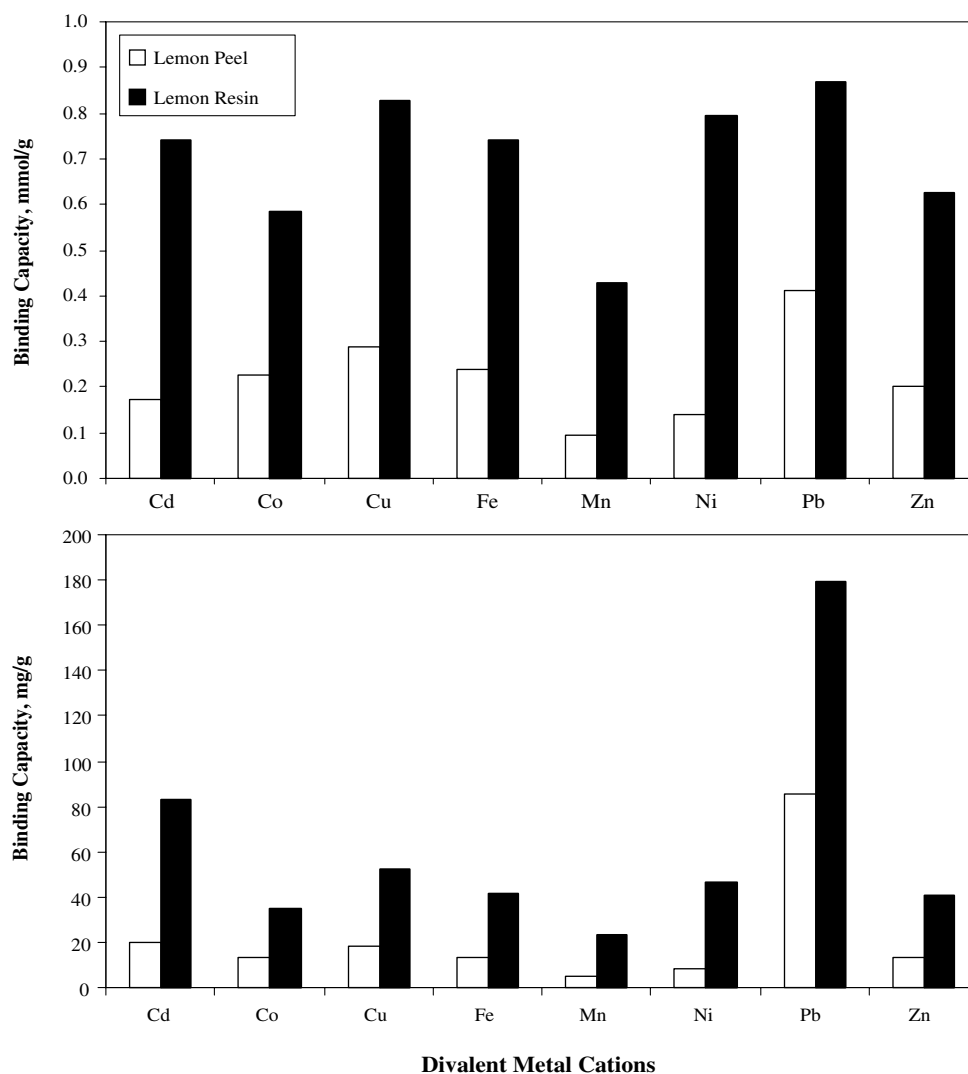


Fig. 2. Metal binding capacities of lemon peel and lemon resin (experimental conditions: 1 g LP or LR; 100 ml metal solution (prepared in buffer); initial metal ion conc., 10 mM; contact time, 24 h; shaking speed, 200 min⁻¹).

Pb > Cu > Ni > Fe > Cd > Zn > Co > Mn for lemon resin. When the sorption capacity is considered in mg-metal/g-resin, for example, lead and mangan binding capacities are about 180 and 23 mg g⁻¹, respectively. Corresponding values calculated as mmol g⁻¹ for lead and mangan are 0.87 and 0.43, respectively. As it is seen, a greater percentage of Pb²⁺ or Cu²⁺ were sorbed than Mn²⁺ under the same conditions of pH, initial metal concentration and sorbent dosage. Burns et al. (1999) have stated that higher first hydrolysis constant lowers the degree of solvation of metal ions. pK₁ values for the metal ions in question are Pb²⁺: 7.7; Cu²⁺: 7.9; Zn²⁺: 9.0; Fe²⁺: 9.5; Co²⁺: 9.6; Ni²⁺: 9.9; Cd²⁺: 10.1; Mn²⁺: 10.6 (Baes and Mesmer, 1976; Burgess, 1978). The affinity sequence observed in this study is in agreement to some extent with the order of first equilibrium hydrolysis constants, so Pb²⁺ or Cu²⁺ present a better approach to the sorbent surface than Mn²⁺ ions. Some deviations may be due to the particular affinity of surface functional groups or different anions present in solution.

The copper sorption capacity of lemon resin was found as 0.83 mmol g⁻¹ which is consistent with the observation in the literature for the citric acid modified cellulosic materials. In a study carried out by using the citric acid-modified agricultural by-products obtained starting from base extracted agricultural by-products, copper uptake from a 20 mM copper solution prepared in the same buffer solution has been reported to be in the range of 0.31–1.44 mmol g⁻¹ (Table 4) (Wartelle and Marshall, 2000). However, some more amount of citric acid has been used in resin preparation in mentioned study. In fact, it has been stated that the citric acid used is in the concentration of 0.6 M and in the solution/material ratio of 7 in the studies dealing with citric acid modification (Marshall et al., 2000, 2001; Vaughan et al., 2001; Wafwoyo et al., 1999; Wartelle and Marshall, 2000). Also, the use of more concentrated metal solution in sorption tests may be another reason of higher sorption capacity of their resin due to the saturation. However, particle size of sorbent can affect the adsorption capacity. In present study, the citric acid con-

centration of juice is 0.23 M and the amount of juice is limited with its juice content. Despite these limitations, the resin obtained from lemon was shown to be effective metal ion adsorbent for possible use. In case of emergency, it could be easily prepared and used.

4. Conclusions

This introductory study shows that lemon can be converted into a stable cation exchanger material by cross-linking the pectic and cellulosic substances with citric acid which are all available in lemon and the resin obtained can be used effectively in the treatment of heavy metal ions from aqueous solution.

When comparing to the corresponding values found for lemon peel, resin gains stability. For instance, COD value of water contacted with resin implicated that the resin did not release substantial amount of soluble organics into the solution. Also, low swelling capacity value revealed that the resin might be used as columnar sorbent.

Standard metal binding tests carried out by using lemon resin showed that sorption affinity of divalent metal ions was in the order of Pb > Cu > Ni > Fe > Cd > Zn > Co > Mn for lemon resin. The sorption capacities were also found as about 0.87 and 0.43 mmol g⁻¹ (or about 180 and 23 mg g⁻¹) for Pb and Mn, respectively.

Further investigations on a more detailed heavy metal sorption analysis of the resin prepared from lemon are in progress.

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Table 4

Copper ion uptake for citric acid modified agricultural by-products (Wartelle and Marshall, 2000)

Agricultural by-product	Copper ion uptake mmol Cu ²⁺ /g
Sugarcane bagasse	1.27
Peanut shells	0.83
Macadamia nut hulls	1.12
Rice hulls	0.76
Cottonseed hulls	0.98
Corn cob	0.99
Soybean hulls	1.44
Almond shells	0.80
Almond hulls	1.31
Pecan shells	0.39
English walnut shells	0.31
Black walnut shells	0.34

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