

# Copper biosorption from aqueous solutions by sour orange residue

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## Abstract

In this study, copper uptake by sour orange residue (SOR) was investigated. Equilibrium isotherms and kinetics were obtained and the effects of solution pH, temperature, and particle size were studied in batch experiments. Equilibrium was well described by Langmuir and Freundlich isotherms and kinetics was found to be best-fit pseudo-second order equations. Maximum uptake was observed at pH 5. With an increase in temperature from 20 to 50 °C, copper removal decreased about 20%. Additional chemical treatment of the biosorbent by NaOH, increased the biosorption capacity. It was found that increase in biosorbent particle size had no significant effects on the final equilibrium concentration, but decreased biosorption rate.

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## 1. Introduction

Contamination of environmental by heavy metal is a serious problem and this has led to the development of new and improved methods for treating wastewaters. The conventional methods used to remove heavy metals from wastewaters are precipitation, coagulation, reduction and membrane processes, ion exchange. However, industrial application of such processes is often restricted because of technical and or economic constraints. Adsorption is an effective technique for removal of heavy metal. Therefore, numerous approaches have been studied for the development of cheaper and effective metal adsorbent such as microbial biomass and agricultural by-products [1,2]. Some of these by-products are carrot residue [3], apple residue [4], olive mill residue [5], and wheat shell [6]. An important step to the development of biosorption processes is the selection of optimal physicochemical conditions such as medium pH, temperature and biomass concentration. The study of process kinetics and equilibrium is another fundamental step, giving important information about the uptake mechanism [7].

Sour orange (*Citrus aurantium*) is one of the citrus that are abundant in north and south of Iran and sour orange residue

(SOR) is a by-product of fruit industries that is mainly used as animal feed.

SOR, like other citrus fruit residue, is composed of peel and pulp (the fraction screened from the juice). The peel is the major part of the SOR, which is comprised of the flavedo (exterior yellow peel) and the albedo (interior white peel). Dominant components of these fractions are respectively pectin, cellulose, hemicellulose, lipid, some nitrogen compound and almost 3% ash content [8].

Pectic substances are the predominant type of polysaccharide identified for the cell walls of SOR [9]. Due to the carboxyl functions of galacturonic acid, pectic substances are known to strongly bind metal cations in aqueous solution [10].

The aim of this work was to study adsorption capacity of SOR for removal of Cu(II) from the solution and investigate effects of contact time, pH, temperature, particle size and biomass treatment on the biosorption efficiency. Reusability of biosorbent was also studied.

## 2. Materials and methods

### 2.1. Biosorbent preparation

The SOR biomass was obtained from a fruit-processing factory near Shiraz (Iran). After washing with deionized water and

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drying at 70 °C in a convection oven the residues were ground and sieved into different fractions.

## 2.2. Chemical treatment of SOR

Biosorbent was treated with NaOH solution to enhance the capacity of metal uptake. For this reason, 200 g of dried SOR were treated in 1000 ml NaOH (0.1 M) solution for 24 h. After decantation and filtration, treated biomass was washed with deionized water until the solution reached a pH value of 7.0.

## 2.3. Copper solution preparation

An aqueous stock solution of CuSO<sub>4</sub> in a concentration of 6350 mg l<sup>-1</sup> of Cu(II) was used in all experimental runs. Calculated quantities of this stock solution were measured and used for further experimental solution preparation. The pH of the solution was adjusted with H<sub>2</sub>SO<sub>4</sub> and NaOH solutions. Deionized water was used for all experiments and all of materials used were of analytical grade and were obtained from Merck.

## 2.4. Analysis of Cu(II) ions

The concentration of unadsorbed Cu(II) ions in the sample supernatant was determined spectrophotometrically. The coloured complex of Cu(II) ions with cuprizone solution was read at 600 nm [11].

## 2.5. FTIR spectroscopy

FTIR spectroscopy was used to identify the chemical groups present in the biosorbent. Spectra of the biosorbent before and after Cu(II) binding were recorded in a Fourier transform infrared spectrometer (Bruker, Tensor 27) with the samples prepared as KBr discs.

## 2.6. Determination of pH<sub>pzc</sub>

The surface charge of biomass is a function of pH. The pH with which the charge of the solid surface is zero is referred to as the zero point of charge (pH<sub>pzc</sub>). The determination of the pH<sub>pzc</sub> of the samples was carried out using a procedure similar as described previously by Rivera et al.: 50 ml of 0.01 M NaCl solutions were placed in a closed Erlenmeyer flasks. The pH of each solution in each flask was adjusted to values of 2, 4, 6, 8, 10 and 12 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then, 0.15 g of SOR sample was added and the final pH measured after 48 h under agitation at room temperature. The pH<sub>pzc</sub> is the point where the curve pH<sub>final</sub> versus pH<sub>initial</sub> crosses the line equal to pH<sub>final</sub> [12].

## 2.7. Desorption procedure

The desorption of the adsorbed Cu(II) ions from the biosorbents was studied in a batch system. 0.2 g metal loaded biomass was added to flask containing 100 ml of desorbing agent (0.1 N HCL) and stirred at 190 rpm at 30 °C. After shaking for 60 min,

the solution was centrifuged and the supernatant was analyzed for Cu(II) ion desorbed. In order to determine the reusability of the biomass after biosorption process, the biomass were taken out from the solution and washed with deionized water. Consecutive biosorption–desorption cycles were repeated four times by using the same biosorbents. Desorption ratio was calculated from the following equation:

$$\text{Desorption ratio} = \frac{\text{amount of Cu(II) ions desorbed}}{\text{amount of Cu(II) ions biosorbed}}$$

## 2.8. Experimental run

### 2.8.1. Kinetics studies

Metal uptake rate is important for designing biosorption process. Batch kinetic experiments were carried out at a constant temperature (25 °C), using 500-ml Erlenmeyer flasks. The experiments were conducted with two different particle sizes (0.71–1 mm and 0.15–0.35 mm) at the initial metal concentration of 150 mg l<sup>-1</sup> and biomass dosage of 10 g l<sup>-1</sup>. The mixtures were agitated at 300 rpm. The samples were taken at predetermined time intervals from the mixture and immediately centrifuged at 10,000 rpm for 5 min to remove suspended particles. The supernatant was analyzed for the residual metal ion concentration.

### 2.8.2. Biosorption isotherms

A number of batch experiments were conducted at constant temperature (28 °C) using 250-ml Erlenmeyer flasks. Varying amounts of dried SOR (4–20 g l<sup>-1</sup>) were added to each flask consisted of a total volume of 100 ml copper ion solution with an initial concentration of 300 mg l<sup>-1</sup>. The initial pH value of 4.5 was used for all experiments. All flasks were then sealed to minimize evaporation, and shaken at 150 rpm on a rotary shaker for 24 h, which is more than ample time for biosorption equilibrium. The amount of metal adsorbed was determined by using the following equation:

$$q = \frac{(C - C_0)V}{m}$$

where  $q$  is metal uptake (mg g<sup>-1</sup>) and  $C_0$  and  $C$  are the concentrations of the metal ions before and after biosorption (mg l<sup>-1</sup>),  $V$  the volume of the aqueous phase (l), and  $m$  the amount of the biosorbent (g).

## 3. Results and discussion

### 3.1. Effect of pH and pH<sub>pzc</sub> on biosorption

The uptake of Cu(II) ion by SOR biomass was strongly affected by pH in the range of 2–6 as seen in Fig. 1. The effect of pH can be explained in terms of pH<sub>pzc</sub> of the adsorbent and species of Cu(II) formed in the solution. The pH with which the charge of the solid surface is zero is referred to as the zero point of charge (pH<sub>pzc</sub>). Above pH<sub>pzc</sub> the surface charge of the adsorbent is negative. The SOR displays a zero point charge at pH<sub>pzc</sub> 5 (Fig. 2). Perusal of the literature on Cu(II) speciation

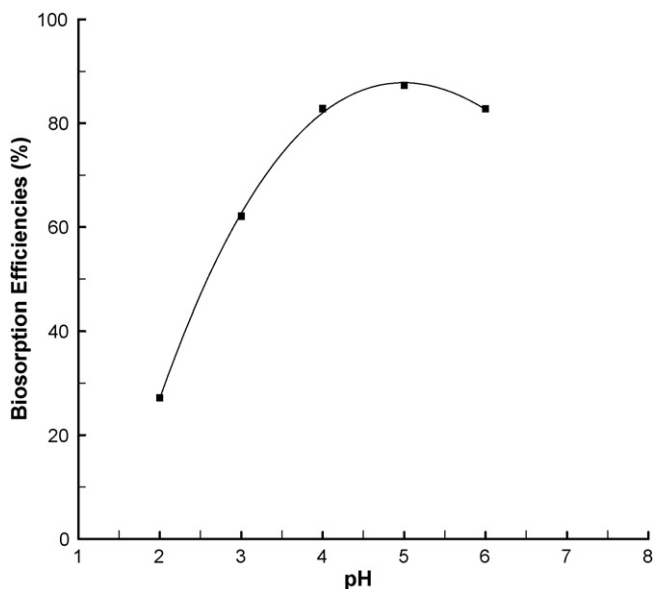


Fig. 1. Effect of solution pH on Cu(II) biosorption by SOR ( $C_0 = 100 \text{ mg l}^{-1}$ , biomass concentration  $5 \text{ g l}^{-1}$ ).

diagram shows that the dominant Cu(II) species at  $\text{pH} > 6.0$  is  $\text{Cu}(\text{OH})_2$  and at  $\text{pH} < 6.0$  is  $\text{Cu}^{2+}$  and  $\text{Cu}(\text{OH})^+$  [13].

At a pH value of two, the amount of Cu(II) uptake was small. There was an increase in copper uptake with increasing pH 2–5. The highest biosorption efficiencies were observed between pH 4.5 and 5.5. These observations can be explained by the facts that at lower pH values the surface charge of the biomass is positive and cations adsorption is not favorable also hydrogen ions compete strongly with metal ions for the active sites, so biosorption was small. When the pH was increased, electrostatic repulsion between cations and surface sites and the competing effect of hydrogen ions decreased and consequently the metal uptake was increased. At a pH value greater than 5.5 precipitation of copper

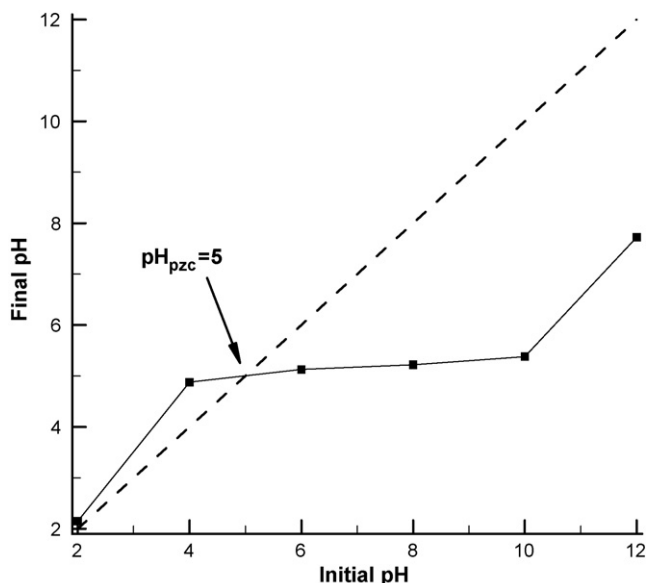


Fig. 2. Determination of pH zero point of charge ( $\text{pH}_{\text{pzc}}$ ).

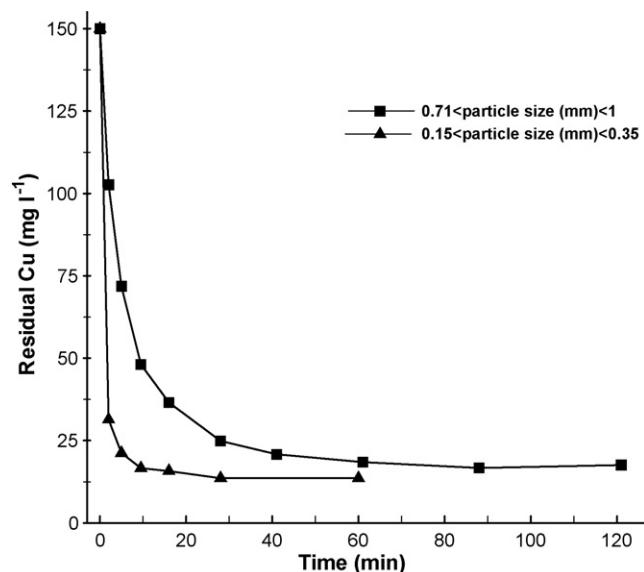


Fig. 3. Effect of contact time on Cu(II) removal with different particle size ( $C_0 = 150 \text{ mg l}^{-1}$ , biomass concentration  $10 \text{ g l}^{-1}$ ).

was observed. Similar pH effects on copper biosorption have been reported for wheat shell [6].

### 3.2. Biosorption kinetics

Fig. 3 shows the copper concentration profiles versus agitation time using dried SOR with two different particle sizes at initial pH values of 4.6 and initial copper concentration of  $150 \text{ mg l}^{-1}$ . It can be seen that biosorption consisted of two phases: a primary rapid phase and a second slow phase, which is more apparent for small particle size diameter (0.15–0.35 mm).

Equilibrium times were reached after 20 min for 0.15–0.35 mm size and 80 min for the 0.7–1.0 mm size. The agitation speed was enough fast (300 rpm) to overcome the film diffusion resistance, so it seems that intraparticle diffusion could be the major difference in equilibrium time. Although the difference in particle size affected the kinetic of biosorption, the effects of it on final concentration and biosorption efficiencies were small.

The kinetics of Cu(II) biosorption on SOR were analyzed using pseudo-second order Eq. (1)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1)$$

where  $q_t$  and  $q_e$  are biosorption capacity at time  $t$  and equilibrium, respectively ( $\text{mg g}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the rate constant of pseudo-second order equation.

The plot of  $(t/q_t)$  and  $t$  for both different particle sizes were shown in Fig. 4. The linear plots indicate the applicability of this kinetic model for Cu(II) uptake. Values of  $k_2$  obtained from the plot were  $0.252 \text{ g mg}^{-1} \text{ min}^{-1}$ , for the 0.15–0.35 mm size and  $0.0228 \text{ g mg}^{-1} \text{ min}^{-1}$ , for the 0.7–1.0 mm size. Values of  $q_e$  for both sizes were calculated as  $13.72 \text{ mg g}^{-1}$ .

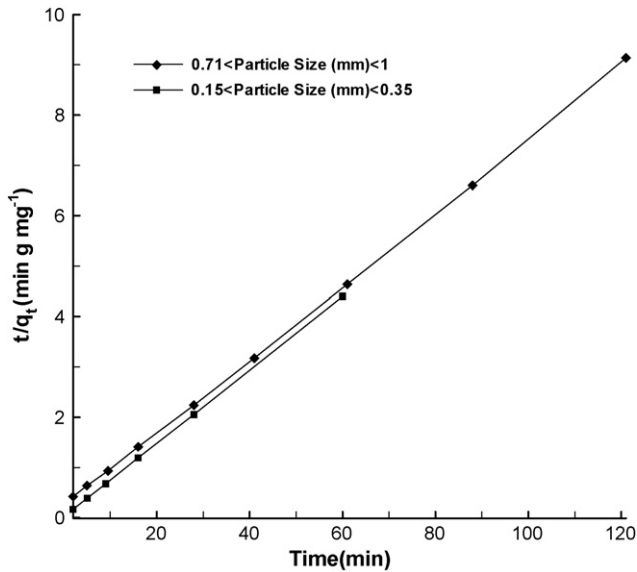


Fig. 4. Plots of  $t/q_t$  vs. time ( $t$ ) for the sorption kinetic of Cu(II) on SOR of different particle size ( $C_0 = 150 \text{ mg l}^{-1}$ , biomass concentration  $10 \text{ g l}^{-1}$ ).

### 3.3. Biosorption isotherms

Both Langmuir and Freundlich models were used to describe biosorption isotherm. The Langmuir equation has the form:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where  $q_e$  is the amount of metal adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg l}^{-1}$ ),  $b$  is a

constant related to the energy of biosorption ( $\text{l mg}^{-1}$ ), and  $q_m$  is the amount of metal per unit weight of adsorbent to form a complete monolayer on the surface. The constants  $b$  and  $q_m$  are the parameters of the Langmuir equation and can be determined from a linearized form of the above equation

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

The Freundlich model has the form:

$$q_e = k C_e^{1/n} \quad (4)$$

where  $k$  and  $n$  are empirically constants and were determined from a linearized form of Freundlich equation:

$$\ln(q_e) = \ln(k) + \frac{1}{n} C_e \quad (5)$$

Fig. 5(a) and (b) shows the applicability of these models for copper biosorption for natural and NaOH-treated SOR. Models parameters and correlation coefficient values ( $r^2$ ) are given in Table 1. As can be seen from this table the maximum uptake capacity of treated SOR is significantly higher than untreated SOR. A comparison of biosorption capacities ( $q_m$ ) of untreated SOR and some other biosorbents reported in literature are listed in Table 2.

### 3.4. Effect of the temperature

The effect of the temperature on the efficiency of biosorption by SOR biomass was studied considering temperature range  $20\text{--}50^\circ\text{C}$ . The experiments were done with a biomass concen-

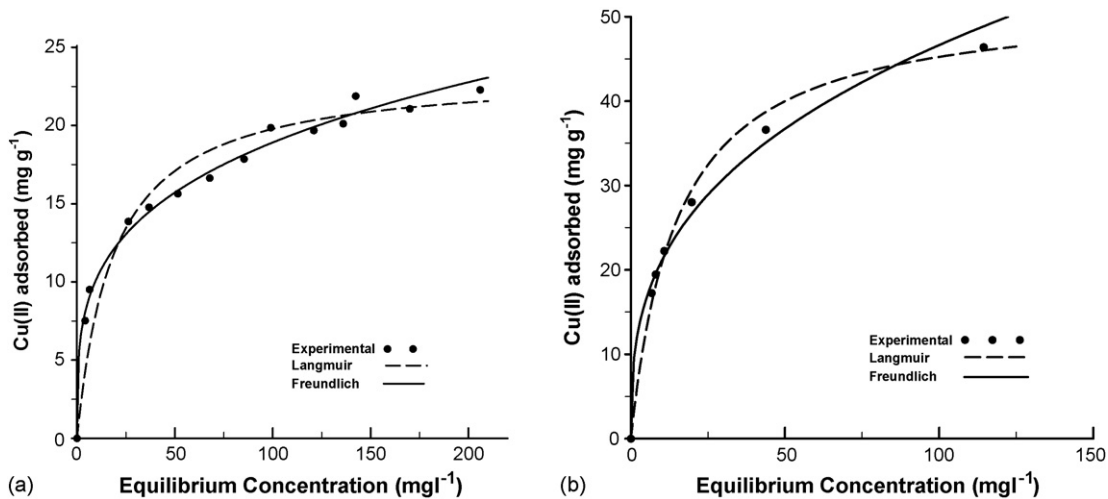


Fig. 5. Copper biosorption isotherms (a) untreated SOR and (b) NaOH-treated SOR.

Table 1  
Langmuir and Freundlich model parameters for treated and untreated biomass

	Langmuir isotherm			Freundlich isotherm		
	$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{l mg}^{-1}$ )	$r^2$	$k$	$n$	$r^2$
NaOH treated biomass	52.08	0.066	0.99	9.52	2.90	0.98
Untreated biomass	23.47	0.054	0.98	5.52	3.74	0.98

Table 2  
Copper biosorption capacities of some agriculture by-products reported in literature

Adsorbent	$q_{\max}$ (mg g <sup>-1</sup> )	Reference
Dehydrated wheat bran	51.51	[15]
Soybean hulls	38.7	[1]
Carrot residue	32.74	[3]
Sour orange residue	21.7	This study
Sugar beet pulp	21	[10]
Leaves of <i>M. truncata</i>	20	[16]
Cork oak	20	[17]
Papaya wood	19.88	[18]
Cottonseed hulls	19.1	[1]
Olive mill residue	13.5	[5]
Tree fern	11.7	[1]
Apple wastes	10.8	[1]
Pine bark	9.47	[19]
Wheat shell	8.26	[6]
Banana peel	4.75	[20]
Oil-palm fibers	1.98	[1]
Sawdust	1.79	[21]

tration of 7 g l<sup>-1</sup> and metal concentration of 63 mg l<sup>-1</sup> of Cu(II) solution. The resulting isotherms can be observed in Fig. 6. The results indicate that there was a negative effect on the biosorption efficiency for copper uptake as the temperature was increased. In order to estimate the heat of biosorption ( $\Delta H$ ) a new set of experiments at three levels of temperature were carried out and Langmuir parameters were also calculated. Since  $b$  is an equilibrium constant, its dependence with temperature can be used to estimate enthalpy changes of biosorption.

$$\ln b = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

The plot of  $\ln b$  versus  $1/T$  is a straight line from which and with universal gas constant  $R$  (1.987 cal mol<sup>-1</sup> K<sup>-1</sup>) the value

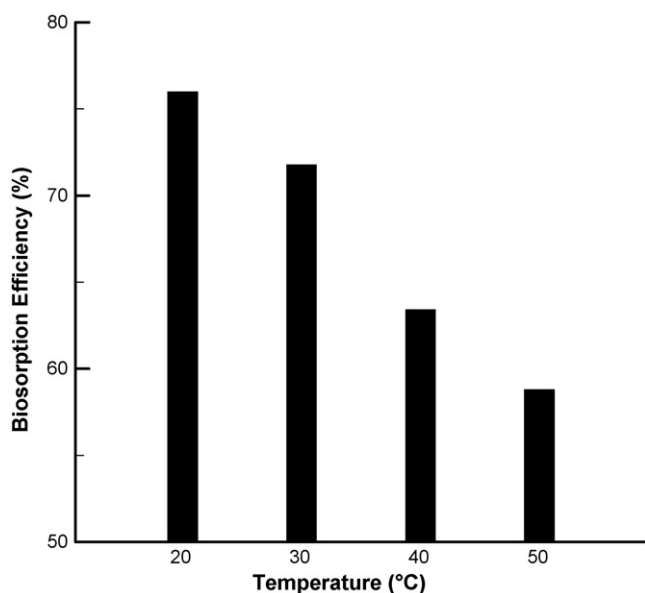


Fig. 6. The effect of the temperature on the biosorption efficiencies ( $C_0 = 63$  mg l<sup>-1</sup>, biomass concentration 7 g l<sup>-1</sup>).

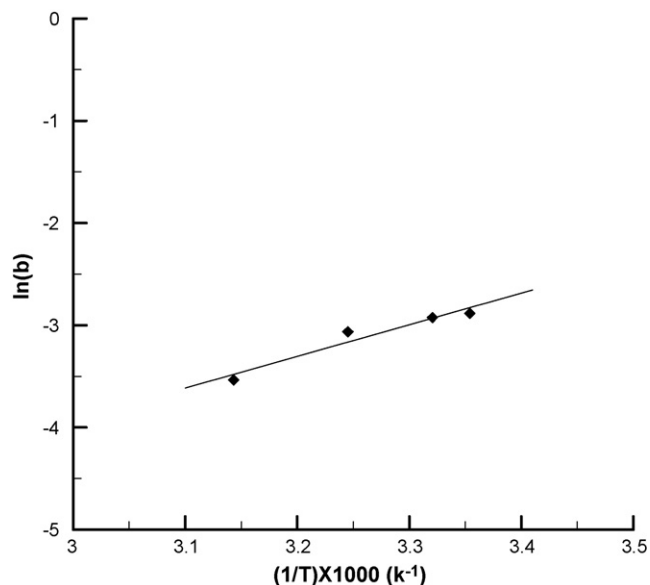


Fig. 7. The determination of biosorption heat using  $b$  (Langmuir parameter) at different temperature and initial pH 4.5.

of  $\Delta H$  was found to be  $-6.149$  kcal mol<sup>-1</sup>, which indicated the exothermic reaction Fig. 7.

The magnitude of  $\Delta H$  may give an idea about the type of sorption. Two main types of adsorption are physical and chemical. The enthalpy for physical adsorption is usually no more than 1 kcal mol<sup>-1</sup> and the enthalpy for chemical adsorption is more than 5 kcal mol<sup>-1</sup> [14]. So, it seems that biosorption of Cu(II) on SOR is almost a chemical process.

### 3.5. FTIR analysis

Fig. 8(a) and (b) shows FTIR spectra of the biomass before and after metal ions biosorption. As it could be seen from FTIR spectra, many functional groups were presented on the biomass surface. Different adsorption mechanisms including complexation, ion exchange, and electrostatic attraction may be involved in the biosorption process. Looking at the spectra, it shows band shifting and possible involvement of hydroxyl groups around the broad peak 3423 cm<sup>-1</sup>. The peak at 2925.88 cm<sup>-1</sup> is due to CH

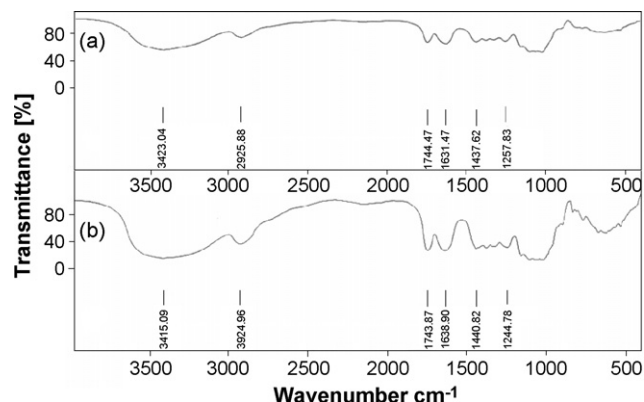


Fig. 8. FTIR analysis of SOR (a) before Cu binding and (b) after Cu binding.

stretching vibrations of CH, CH<sub>2</sub>, and CH<sub>3</sub> groups. Very little change was observed in the free carboxyl band 1744 cm<sup>-1</sup>, but an increase in the asymmetric C=O band at 1631 cm<sup>-1</sup> indicates some carboxyl binding. Shifting of the symmetric C=O band was also seen, but this shift is less than instrument resolution (4 cm<sup>-1</sup>) and cannot be discussed reliably. Apart from this the major visible change is the increase in the C–O carboxyl band 1257–1244 cm<sup>-1</sup>. Changes in this band usually result from complexation of the carboxyl oxygen. From these spectra it appears that carboxyl and hydroxyl groups are involved in Cu binding to the SOR.

### 3.6. Desorption and reuse

The Cu(II) ions adsorbed onto biosorbents were eluted with 0.1 M HCl. More than 99% of the adsorbed Cu(II) ions was desorbed from the biosorbents. In order to examine the reusability of the biomass, biosorption–desorption cycles were repeated four times by using the same preparations. After the first cycle the biosorption capacity decreased 14% and remained constant for all consecutive cycles. These results showed that sour orange residue can be repeatedly used in biosorption process without detectable losses in their adsorption capacities.

## 4. Conclusions

The removal of copper ions from aquatic systems is carried out using sour orange residues. The selected biomass exhibited high sorption capacity. The copper uptake performance of SOR was strongly affected by pH. The biosorption efficiencies were decreased with increasing in temperature. Effects of particle size on biosorption efficiencies were small, but rate of biosorption decreased with increasing the particles size. Sorption kinetic was found to be best-fit pseudo-second order equation. The selected biomass exhibited high sorption capacity and its capacity, and it was found that it is favorable adsorbent for copper removal from waste. The interactions between Cu(II) ions and functional groups on the cell wall surface of the biosorbent cells were confirmed by FTIR analysis and the spectra showed that carboxyl and hydroxyl groups are involved in Cu binding to the SOR.

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