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Biosorption of Chromium from aqueous solution by using *Citrus reticulata*: Equilibrium and kinetic studies

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ABSTRACT

The biosorption of chromium ions from aqueous solution by Citrus reticulata was studied in a batch adsorption system as a function of pH, contact time, chromium ion concentration, and biosorbent dosage and biosorbent size. The biosorption capacities and rates of chromium ions onto Citrus reticulata were evaluated. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. It was determined that the best fitted adsorption isotherm models were obtained. The kinetic experimental data were properly correlated with the second-order kinetic model.

Key words: Biosorption; *Citrus reticulata*; Adsorption isotherms; Kinetic studies

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INTRODUCTION

The effects of heavy - metal ions on human health have received great attention in the last decades. As a consequence, methods to remove metal species from waste waters have been the subject of different researchers, in order to improve the water quality. The removal of toxic metal ions and recovery of valuable ions from mine waste waters, soils and waters have been important in economic and environmental problems [1-4]. Heavy metals and other metal ions exist as contaminants in aqueous waste streams of many industries, such as metal plating, electro plating, mining, ceramic, batteries and pigment manufacturing [5, 6].

Heavy metals such as lead, mercury, arsenic, copper, chromium, zinc and cadmium are highly toxic when adsorbed into the body [7]. Chromium is one of the most important metals often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal waste water treatment plants and not biodegradable and travels through the food chain via bioaccumulation. Therefore, there is significant interest regarding chromium removal from waste waters [8] and its toxicity for humans at levels of 100-500 mg/day [9]. World health organization (WHO) recommended the maximum acceptable concentration of chromium in drinking water as 0.05 mg/L [10].

Conventional methods for removing toxic heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery. However, these technology processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [11-14]. Therefore, there is a need for some alternative technique, which is efficient and cost effective. Biosorption, based on living or non living microorganisms or plants could be such an alternative method of treatment. It can be defined as the ability of biological materials to accumulate heavy metals through metabolically mediated or physico-chemical path ways of uptake which has advantages compared to other processes which include minimal cost of materials, easiness of operation and selectivity over the alkaline metals [15]. Kuyucak indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process [16]. Therefore, low-cost biomass becomes a crucial factor when considering practical application of biosorption.

The present work investigates the potential use of unreacted Citrus reticulata biomass as metal sorbent for chromium from aqueous solution. Citrus reticulata was chosen as a biosorbent because of the relative lack of information about its sorption ability. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, biosorbent dosage and biosorbent size was evaluated. The equilibrium adsorption data were evaluated by Langmuir, Freundlich and Temkin isotherm models. The kinetic experimental data were correlated by first and second order kinetic models.

EXPERIMENTAL SECTION

2.1. Preparation of biosorbent

The *Citrus reticulata* is collected from local areas of Guntur, Andhra Pradesh, India. They washed with deionized water several times to remove dirt particles. Then they are dried and powdered using domestic grinder with size of 75-212 µm, which is used as bio-sorbent without any pretreatment for chromium adsorption.

2.2 Chemical

Analytical grades of $K_2Cr_2O_7$, HCl and NaOH are purchased from Merck (Mumbai, Maharastra, India). Chromium ions are prepared by dissolving its corresponding sulphate salt in distilled water. The pH of solutions is adjusted with 0.1 N HCl and NaOH. All the experiments are repeated five times and the average values have been reported. Also, blank experiments are conducted to ensure that no adsorption is taking place on the walls of the apparatus used.

2.3 Biosorption experiments

Biosorption experiments are performed at room temperature (30 ± 1^0C) in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different chromium concentrations. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g *Citrus reticulata* powder, equilibrium was reached and the reaction mixture is centrifuged for 5 min. The metal content in the supernatant is determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with 0.45 µm filter paper. The amount of metal adsorbed by Citrus reticulata powder is calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = \left(C_0 - C_f\right)\frac{V}{M} \tag{1}$$

Where q is the metal uptake (mg/g); C_0 and C_f the initial and final metal concentrations in the solution (mg/L), respectively; V the solution volume (mL); M is the mass of biosorbent (g).The pH of the solution was adjusted by using 0.1N HCl and 0.1N NaOH.

The Langmuir [17] sorption model was chosen for the estimation of maximum chromium sorption by the biosorbent.

The Langmuir isotherm can be expressed as

$$q = \frac{Q_{\max} b C_{eq}}{1 + b C_{eq}} \tag{2}$$

Where Q_{max} indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant b (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}C_{eq}} \quad (3)$$

The Freundlich [18] model is represented by the equation:

$$q = KC_{eq}^{\frac{1}{n}} \quad (4)$$

Where K (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and 1/n is the Freundlich exponent related to adsorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows:

$$\ln q = \ln K + \frac{1}{n}\ln C_{eq} \quad (5)$$

2.4. Biosorption Kinetics

The kinetic studies were carried out by conducting batch biosorption experiments with different initial chromium concentrations. Samples were taken at different time periods and analyzed for their chromium concentration.

RESULTS AND DISCUSSION

3.1. The effect of contact time

The data obtained from the biosorption of chromium ions on the *Citrus reticulata showed* that a contact time of 30 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and un -adsorbed chromium concentrations at the end of 30 min are given as the equilibrium values (q_e , mg/g;C_{eq} mg/L), respectively (Fig. 1) and the other adsorption experiments were conducted at this contact time of 30 min (pH 6).

3.2. Effect of pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions [20–24].*Citrus reticulata* presents a high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it very liable to the influence of the pH. As shown in Fig. 2, the uptake of chromium increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in literature for different biomass systems [25–27]. At pH values lower than 2.0, chromium removal was inhibited possibly as a result of the competition between hydrogen and chromium ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in *Citrus reticulata* would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface. In this study, these chromium cations at around pH 6 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for chromium adsorption was found as 6 and the other adsorption experiments were performed at this pH value.

3.3. Effect of metal ion concentration

Fig. 3 shows the effect of metal ion concentration on the adsorption of chromium by *Citrus reticulata* .The data shows that the metal uptake increases and the percentage adsorption of chromium decreases with increase in metal ion concentration. This increase (5.35–12.54 mg/g) is a result of increase in the driving force, i.e. concentration gradient. However, the percentage adsorption of chromium ions on *Citrus reticulata* was decreased from 76.29 to 45.93%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of chromium displays an opposite trend. At lower concentrations, all chromium ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher chromium ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

3.4. Effect of adsorbent size

The effect of different adsorbent particle sizes on percentage removal of chromium is investigated and showed in Fig. 4 It reveals that the adsorption of chromium on *Citrus reticulata* decrease from 76.29 to 52.64% with the increased particle size from 75 to 212 µm at an initial concentration of 20 mg/L. The smallest size obtained was 75µm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

3.5. Effect of adsorbent dosage

Fig. 5 shows the effect of adsorbent dosage on the % removed at equilibrium conditions. It was observed that the amount of chromium adsorbed varied with varying adsorbent dosage. The amount of chromium adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 g. The percentage chromium removal was increased from 78.29 to 90.61% for an increase in adsorbent dosage from 0.1 to 0.5 g at initial concentration of 20 mg/L. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for chromium removal using Azadirachta indica as adsorbent [28].

4. Biosorption equilibrium

The equilibrium biosorption of chromium on the *Citrus reticulata* as a function of the initial concentration of chromium is shown in Fig. 6-7. There was a gradual increase of adsorption for chromium ions until equilibrium was attained. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich isotherm constants are given in Table 1.

It is found that the adsorption of chromium on the *Citrus reticulata* was correlated well with the Langmuir equation compared to Freundlich equation under the concentration range studied. Examination of the Freundlich data shows that this isotherm was not modeled as well across the concentration range studied.

5. Kinetics of adsorption

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig.8 shows the plot between amount adsorbed, q_e (mg/g) versus time, t (min) for an initial concentration of 20 mg/L. The adsorption rate within the first 5 min was observed to be very high and there after the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 30 min based on the initial metal concentration. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first- and pseudo-second-order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows:

5.1. The pseudo-first-order equation

The pseudo-first-order equation of Lagergren [29] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first-order sorption (min^{-1}). After integration and applying boundary conditions, q_t =0 to q_t = q_t at t = 0 to t = t; the integrated form of Eq. (7) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{8}$$

The pseudo-first-order rate constant k_1 can be obtained from the slope of plot between log(q_e-q) versus time, t (Fig.8). The calculated k_1 values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient value R_1^2 found 0.9689, which shows that this model cannot be applied to predict the adsorption kinetic model.

5.2. The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [30]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (9)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k is the rate constant of pseudo-second-order sorption (g/(mg min)). For the boundary conditions q_t =0 to q_t = q_t at t = 0 to t = t; the integrated form of Eq. (9) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (10)$$

where t is the contact time (min), q_e (mg/g) and q_1 (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. Eq. (10) does not have the problem of assigning as effective q_e. If pseudo-second-order kinetics is applicable, the plot of t/q_t against t of Eq. (10) should give a linear relationship, from which q_e and *k* can be determined from the slope and intercept of the plot (Fig. 9) and there is no need to know any parameter beforehand. The pseudo-second-order rate constant k_2, the calculated q_e value and the corresponding linear regression correlation coefficient value R_2^2 are given in Table 2. At an initial chromium concentration of 20 mg/L, the linear regression correlation coefficient R_2^2 value was higher. The higher R_2^2 value confirms that the adsorption data were well represented by pseudo-second order kinetic model.

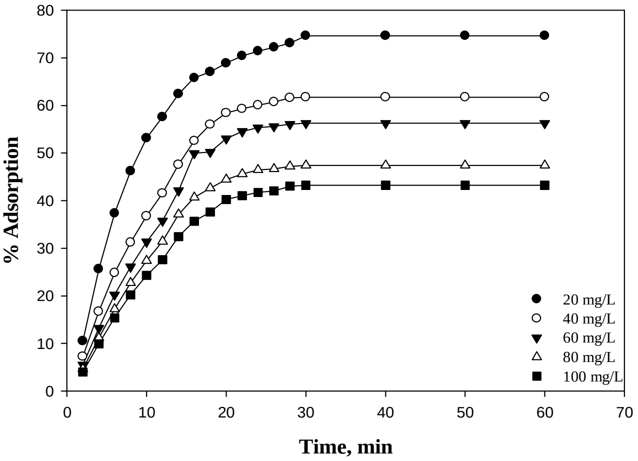

Fig.1. Effect of contact time on adsorption of chromium by *C. reticulata* for 0.1 g/30 mL of adsorbent concentration.

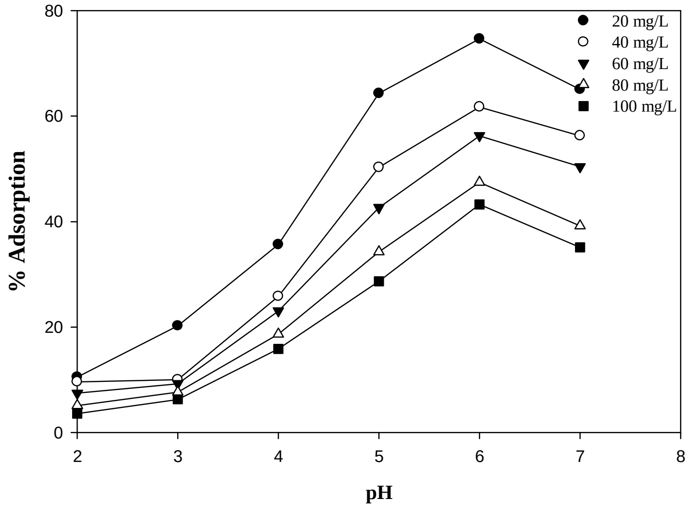

Fig.2. Effect of pH on chromium adsorption by *C. reticulata* for 0.1 g/30 mL of adsorbent concentration.

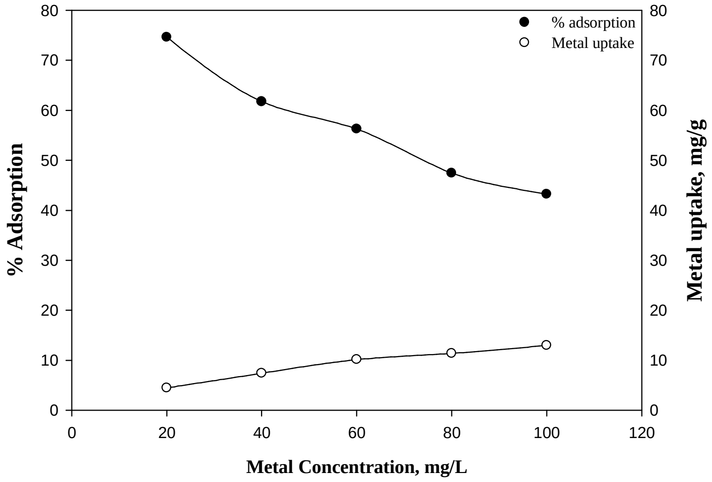

Fig.3. Effect of metal concentration on the adsorption of chromium by *C. reticulata* at 0.1 g/30 mL of adsorbent concentration.

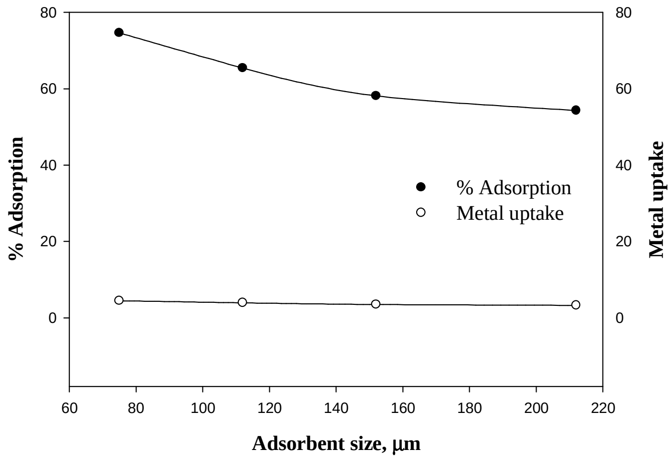

Fig.4. Effect of *C. reticulata* particle size on adsorption of chromium for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

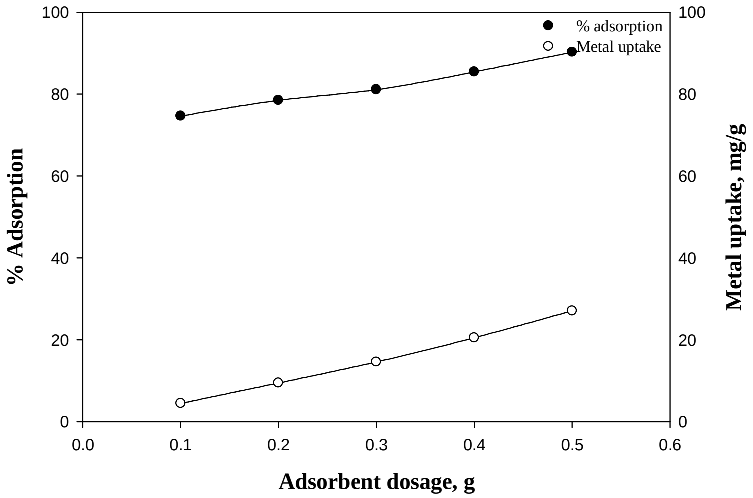

Fig. 5. Effect of *C. reticulata* dosage on adsorption of chromium for 20 mg/L of metal concentration.

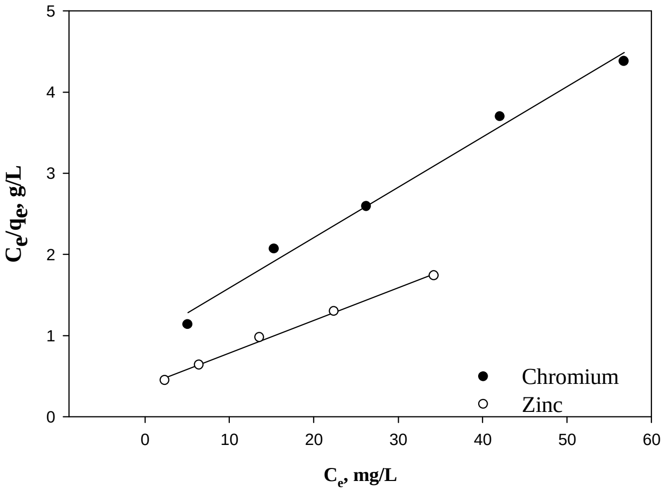

Fig.6 Langmuir adsorption isotherm at 0.1 g/30 mL of adsorbent concentration.

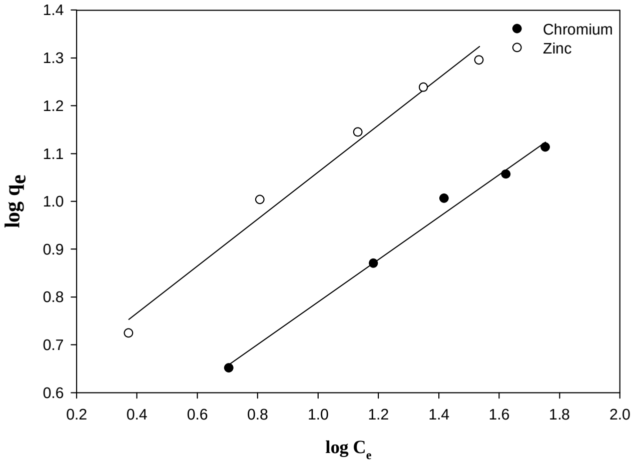

Fig.7 Freundlich adsorption isotherm at 0.1 g/30 mL of adsorbent concentration.

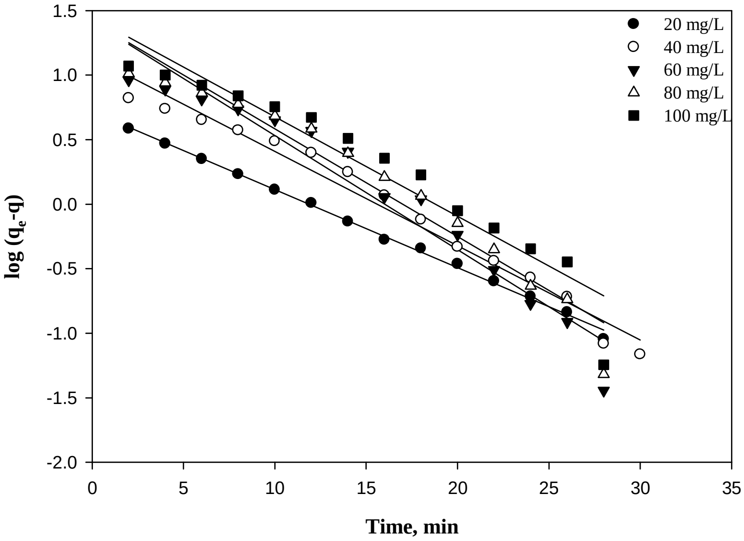

Fig.8 Pseudo-first-order adsorption of chromium by *Citrus reticulata* for 0.1 g/30 mL of adsorbent concentration.

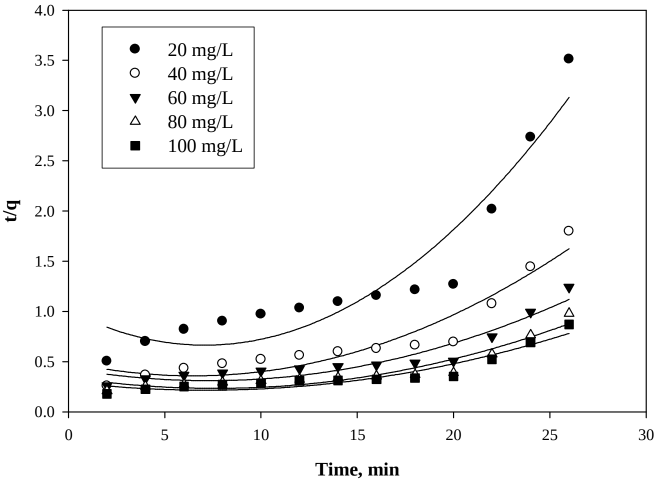

Fig.9 Pseudo-second-order adsorption of chromium by *Citrus reticulata* for 0.1 g/30 mL of adsorbent concentration.

Table 1 Langmuir, Freundlich isotherm constants and correlation coefficients

Metal ion	**Freundlich isotherm**			**Langmuir isotherm**		
	K_f(mg/g)	**n**	**R^2**	**b (l/mg)**	**Q_{max}(mg/g)**	**R^2**
Chromium	1.7676	0.4914	0.9839	1.0318	15.6	0.9893

Table 2 Maximum adsorption capacities for chromium adsorption to different adsorbents

Adsorbent material	**Adsorption Capacity (mg/g)**	**pH**	**Reference**
Na-Mont morillonite	3.61	5	[31]
Crushed concrete fines	33	5.5	[32]
Coir	8.6	5.5	[33]
Barley straw	5.3	5.5	[33]
Peat	11.71	5.5	[33]
Coniferous bark	7.4	5.5	[33]
Sil/PE1/GA$_{0.5}$	32.79	5–6	[34]
Fontinalis antipyretica	14.7	5.0	[35]
Activated carbon	31.11	4.5	[10]
Streptoverticillium cinnamoneum	21.3	5.5	[06]
Aspergillus niger 405	4.70	5.0	[36]
Penicillium digitatum	9.7	5.5	[37]
Streptomyces noursei	1.6	5.8	[38]
Mucor rouxii (live)	4.89	5.0	[39]
Mucor rouxii (NaOH pretreated)	5.63	5.0	[39]
Mucor rouxii (Na_2CO_3 pretreated)	3.26	5.0	[39]
Mucor rouxii (NaHCO3 pretreated)	6.28	5.0	[39]
Pseudomonas syringae	8.0	n.a	[40]
Rhizopus arrhizus	13.5	6–7	[41]
Citrobacter strain MCMB-181	23.62	6.5	[42]
Sargassum sp.	24.35	4.5	[43]
Animal bones	11.55	5.0	[44]
Botrytis cinerea biomass	12.98	5–6	[45]
Citrus reticulata	15.60	6	Present study

CONCLUSION

The present study shows that the *Citrus reticulata* was an effective biosorbent for the adsorption of chromium ions from aqueous solution. The effect of process parameters like pH, metal ion concentration, adsorbent dosage and adsorbent size on process equilibrium was studied. The uptake of chromium ions by *Citrus reticulata* was increased by increasing the metal ion concentration and the adsorbent dosage and decreased by increasing the adsorbent size. The uptake was also increased by increasing pH up to 6. The adsorption isotherms could be well fitted by the Langmuir equation followed by Freundlich isotherm. The biosorption process could be best described by the second-order equation.

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