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BIOSORPTION OF TOXIC HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS BY LOW-COST WASTE BIOMATERIAL

NILISHA P. ITANKAR[a] and YOGESH B. PATIL[*]

Symbiosis Institute of Research and Innovation (SIRI), Symbiosis International University (SIU),
Lavale, PUNE – 412115 (M.S.) INDIA
[a]Symbiosis Institute of Technology (SIT), Symbiosis International University (SIU),
Near Lupin Research Park, Lavale, PUNE – 412115 (M.S.) INDIA

ABSTRACT

Chromium metal has unique properties and therefore finds large number of applications in industries like chrome-plating, steel and alloy, leather tanning and ammunition factories. These industries consequently, discharge large quantities of hexavalent chromium (Cr^{6+}) containing effluents. Since chromium is toxic to all life forms, its removal from effluents is the key. Conventional processes used are highly energy-intensive and economically unattractive. Biosorption, a technically feasible and economical process has gained immense creditability in the recent years. The present study explores the possibility of using biosorption process for the removal of Cr^{6+} from aqueous solutions using low-cost biomaterial viz. saw dust (SD). Optimum parameters for maximum biosorption of Cr^{6+} (10 mg/L) were as follows: pH 1-4, contact time 60 min and biomass quantity of 1 g/10 mL. Biosorption conformed to the Langmuir and Freundlich adsorption isotherms ($R^2 = > 0.97$). It was found that the equilibrium sorption capacity of the sorbent increased with increasing initial concentration of Cr^{6+} from 5 to 300 mg/L. Overall, the study showed that SD has immense potential as "biomaterial" for its use in the removal/recovery of hexavalent chromium from aqueous industrial solutions.

Key words: Biomaterial, Biosorption, Hexavalent chromium, Low-cost biomass, Saw dust.

INTRODUCTION

Industrial effluents can broadly be classified as wastes rich in organic matter on one hand; and wastes rich in inorganic matter on the other. Heavy metals form a significant part of the latter type of wastes. One such known heavy metal is chromium. It exists in environment both as trivalent and hexavalent forms. It is known that hexavalent chromium is 500 times more toxic than the trivalent form[1]. Chromium is industrially indispensable metal

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[*] Author for correspondence; E-mail: head_respub@siu.edu.in

because of its some unique properties of corrosion resistance, hardness and colour and therefore finds large number of applications in modern industries like chrome-plating, steel and alloy manufacturing, paints manufacturing, leather tanning, textiles and ammunition factories[2]. In addition, chromium finds application as a cost-effective biocide in the water recirculated in cooling towers. Many of these industries use hexavalent chromium (Cr^{6+}) either in chromate or dichromate forms. These industries consequently, discharge large quantities of Cr^{6+} containing effluents. Cr^{6+} is a known mutagen and carcinogen[3]. Therefore, the prevalent water pollution control laws in most countries requires it's complete removal from waste streams before discharge. The Indian Statutory Limits of Cr^{6+} for industrial effluents discharge in inland surface waters is 0.1 mg/L[4].

Several conventional processes are employed to cleanse chromate-bearing effluents. These techniques include like reverse osmosis, adsorption onto ion-exchange resins and reduction followed by chemical precipitation[5]. The latter process is used most widely. It involves treatment of the effluent with reagents like sodium bisulfate to form chromous sulfate. Then it is followed by its precipitation as chromium hydroxide with sodium hydroxide or lime. However, the mentioned process is highly energy-intensive, consumes large quantities of chemicals and hence is not economically attractive. It is therefore imperative to seek for new practical and economic alternate treatment methods. Use of biological treatment methods is one such effective alternative. Under the purview of biological methods, use of either live (active) or dead (passive) biomass could be employed. Significant work has been carried out on microbial reduction of chromium[6]. However, live biomass is subject to the toxicity and could only be used when chromium concentration is very low. Therefore, biosorption (passive biomass), a technically feasible and economical process has gained immense creditability in the recent years[7,8]. Moreover, chromium being a non-renewable and finite natural resource, the argument is not limited only to their removal from the effluents, but also extends to finding an efficient and economical ways of recovery/recycling[9,10]. There are several reports of using various biosorbents for chromium removal[11]. The researchers in the present study explores the possibility of using (bio) sorption process for the removal of Cr^{6+} from aqueous solutions using low-cost waste SD biomaterial.

EXPERIMENTAL

Biomaterials

The biomaterial employed in the present study was SD. It was obtained from Sawmill located in Pune city. SD sample was collected in polythene bag and transported to the laboratory and washed several times with tap water followed by distilled water (DW) to remove the dirt and other contaminants, if any, present on the sample. After washing, the samples were subjected to oven for drying at 50-60°C for 2-3 days till the constant weight was obtained. Later, the dried biomass was ground using electric mixer and sieved so as to get uniform particle size of ≤ 500 µm (0.5 mm). Conventional sorbent like activated charcoal were used as reference materials.

Batch equilibrium studies using sawdust

Batch equilibrium studies were conducted using SD. Use of preconditioned SD was avoided in the present studies. Experiments were performed as per the method prescribed by key research papers[12,13]. Sorbent (0.2 g) was contacted with 10 mL of 10 mg/L Cr^{6+} of desired pH (4.0) in a set of 25 mL capacity conical flasks. The flasks were agitated on rotary orbital shaker at 30°C for 1 h, unless otherwise stated. Contents of the flasks were filtered and analysed for residual Cr^{6+}. All experiments were performed in duplicates and repeated twice to confirm the results. Appropriate controls were run simultaneously.

In order to evaluate the influence of pH on biosorption of Cr^{6+}, powdered unconditioned SD biomass was contacted with Cr^{6+} solution of different pH ranging from 2 to 10 prior to sorption. Cr^{6+} loading capacity (µmol Cr^{6+} bound per gram weight of biomass) was determined by contacting 0.2 g SD biomass several times with fresh batches of 10 mL of 10 mg/L Cr^{6+} solution till saturation was achieved. For optimum biosorbent, Cr^{6+} was contacted with varying amounts of biomass powder (0.1-5% w/v). Rate of Cr^{6+} uptake was studied by contacting the biosorbent for a period ranging between 0-5 h.

Glassware, chemical and analyses

All the chemicals used in the present study were of analytical grade. Glassware used were of borosilicate material. Stock solution of Cr^{6+} (1000 mg/L) was prepared in glass DW (10-15 µS) using potassium dichromate ($K_2Cr_2O_7$). Required concentrations of Cr^{6+} solutions for experimental purpose were prepared from the stock solution. pH of the solutions were adjusted using 0.1-1 M of HCl and/or NaOH. Reagents prepared for analytical purpose were stored under refrigerated conditions (8-10°C). Cr^{6+} from the solutions was analysed by 1,5-diphenylcarbazide (DPC) method at maximum wavelength (λ_{max}) of 540 nm according to the method prescribed in Standard Methods[14]. pH was determined using digital pH meter (Systronics, India).

Batch sorption isotherm models

Cr^{6+}solutions of varying concentrations (5-300 mg/L) were used to study the effect of initial Cr^{6+} concentration on it adsorption. The amount of Cr^{6+} sorbed at equilibrium, Q (μmol/g), which represents the Cr^{6+} uptake, was calculated from the difference in Cr^{6+} concentration in the aqueous phase before and after adsorption, according to the following equation:

$$Q = V (C_i - C_f)/1000\ m \qquad ...(1)$$

Where, Q is the Cr^{6+} uptake (μmol per gram biomass); V is the volume of Cr^{6+} solution (ml); C_i is the initial concentration (mg/L); C_f is the final concentration (mg/L); m is the mass of biosorbent (g).

To examine the relationship between sorbed and aqueous concentration at equilibrium, sorption isotherm models viz. Freundlich[15] and Langmuir[16] were used for fitting the data.

$$\ln Q = \ln K + (1/n)C_{eq} \qquad \text{Freundlich eq.} \qquad ...(2)$$

$$C_{eq}/Q = 1/bQ_{max} + C_{eq}/Q_{max} \qquad \text{Langmuir eq.} \qquad ...(3)$$

Where, C_{eq} is the liquid phase concentration of Cr^{6+}; b is the Langmuir constant; K is the constant; 1/n is the intensity of adsorption and Q is the specific metal uptake; Q_{max} is the maximum Cr^{6+} uptake.

RESULTS AND DISCUSSION

Impact of pH on Cr^{6+} sorption

Influence of pH on the biosorption of Cr^{6+} ions using SD, a low-cost biomaterial was conducted in the range of 1.0 to 10.0. It was observed that the maximum sorption of Cr^{6+} ions was observed in the pH range of 1.0 to 4.0 (98%). Biosorption of Cr^{6+} decreased with increase in pH value up to 10 (Fig. 1).

In acidic conditions, the biosorbent is positively charged due to protonation and dichromate ion exists as oxyanion leading to an electrostatic attraction between them[17]. Sharp decrease in biosorption above pH 4 may be due to occupation of the adsorption sites by oxyanionic species like $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, etc., which hinders the approach of such ions further toward the sorbent surface[8]. Results attribute that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biomaterial[18]. Cr^{6+} containing industrial wastewaters generally have acidic pH. Obviously, no pH adjustments would be required prior to biosorption, thereby reducing the cost of Cr^{6+} biosorption process.

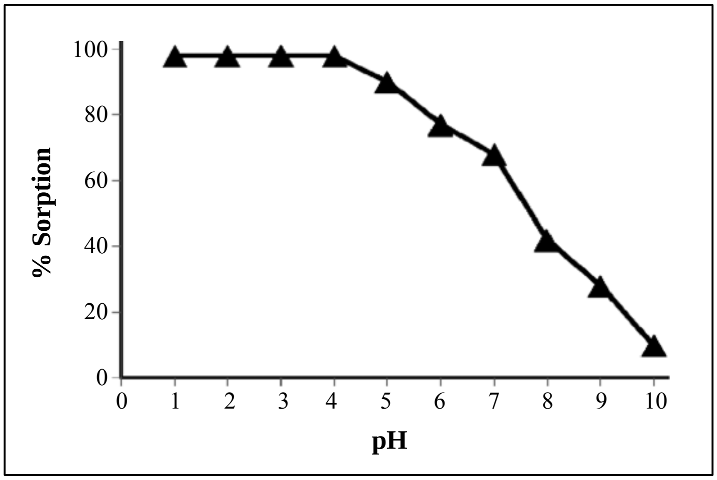

Fig. 1: Influence of pH on Cr^{6+} biosorption by SD

Impact of contact time

The impact of contact time on Cr^{6+} biosorption was studied at optimum pH of 4. 10 mL of Cr^{6+} solution having concentration 10 mg/L was contacted with 0.2 g of SD biomass for the period upto 300 min. The time intervals chosen to study the effect of contact time were 0, 5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 150, 180, 240 and 300 min. Periodically the flask content were removed by filtration and the filtrate were analysed for Cr^{6+} concentration. Curve in the Fig. 2 representing the kinetics of Cr^{6+} sorption showed that rate of Cr^{6+} uptake was maximum in the first 30-40 mins with over 70% of biosorption. Later, the sorption rate slowed down until it reached a plateau after 60 min, indicating equilibration of the system. Maximum sorption of Cr^{6+} observed at 60 min was 83% (Fig. 2).

The process of (bio)sorption is essentially a surface interaction and is characterised by rapid uptake of ions by biomass surfaces. Rapidity of the process makes it a good candidate for use in effluent treatment on a large scale. Kinetics of sorption showed that rate of Cr^{6+} uptake was more in the first 30-40 mins with over 70% of biosorption. Later, the sorption rate slowed down until it reached a plateau after 60 min, indicating equilibration of the system. Maximum sorption of Cr^{6+} (upto 85%) was observed at 60 min (Fig. 2). The rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy.

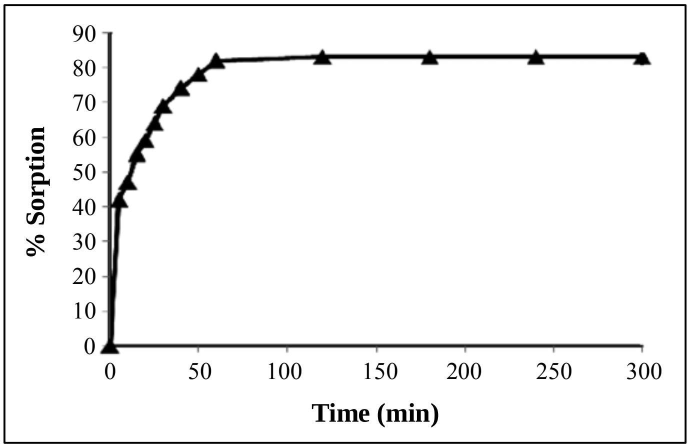

Fig. 2: Influence of contact time on Cr^{6+} biosorption by SD

Impact of biomaterial quantity

The influence of biomass quantity on Cr^{6+} biosorption was studied at optimum pH of 4, room temperature (30 ± 2°C) and contact time of 60 min. Amount of biomass varied from 0.01 to 2 g keeping the volume of Cr^{6+} solution constant i.e. 10 mL. The results indicate that as the biomass quantity increased the % biosorption of Cr^{6+} also increased. Maximum uptake (~95%) was observed at 1 g of SD biomass (Fig. 3).

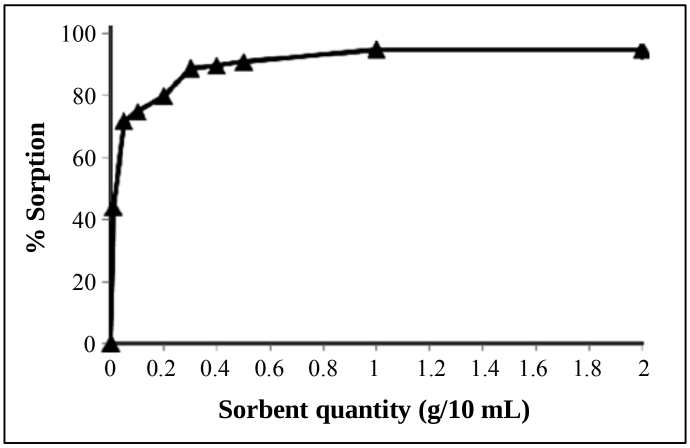

Fig. 3: Influence of biomaterial quantity on Cr^{6+} biosorption by SD

For the cost-effective treatment of industrial wastewaters for Cr^{6+} removal, it is necessary to know the biomass quantity (i.e. solid-to-liquid ratio) required. In our experiments, it was found that as the biomass quantity increased the percentage biosorption of Cr^{6+} also increased. This is due to availability of more biosorbent as well as greater availability of surface area[19]. More quantity of biosorbent results in increasing of surface area and biosorption regions which causes removal of more chromium. However, as the concentration of biomass was further increased the Cr^{6+} sorption did not increase but remained constant. No specific Cr^{6+} uptake at increased biomass loading is attributable to the interference between binding sites at higher quantities[20].

Adsorption isotherm models

The effect of initial concentration provides an important driving force to overcome all mass transfer resistance of target ion between the aqueous and solid phases. The biosorption of Cr^{6+} was carried out at different initial Cr^{6+} concentrations ranging from 5 to 300 mg/L at pH 4.0 using 1 g/10 mL of SD biomass.

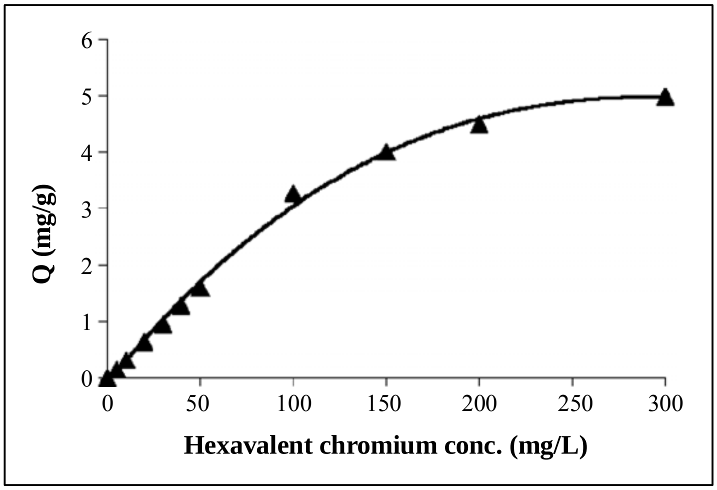

Fig. 4: Influence of initial Cr^{6+} concentration on biosorption by SD

Fig. 4 depicts the Cr^{6+} uptake by SD biomass. It could be seen that the equilibrium sorption capacity of the sorbent increased with increasing initial concentration of Cr^{6+} from 5 to 300 mg/L. This was due to the increase in the number of ions competing for the available binding sites in the biomass. The uptake of Cr^{6+} by the sorbent reached to a plateau at 300 mg/L. There was a significant increase in the specific uptake of Cr^{6+} upto 300 mg/L. Later the specific uptake of Cr^{6+} decreased with increased concentration. This might be due to the saturation of binding sites, which clearly showed that Cr^{6+} uptake by SD biomass was a chemically equilibrated and saturable phenomenon. To examine the relationship between sorption, isotherm models are widely employed for fitting the experimental data. Langmuir and Freundlich models were used to describe the equilibrium between the Cr^{6+} sorbed on SD biomass and Cr^{6+} ions in the solution. Fig. 5 and 6 shows that Cr^{6+} uptake values could be well fitted to the Langmuir and Freundlich isotherm models with regression value of > 0.97.

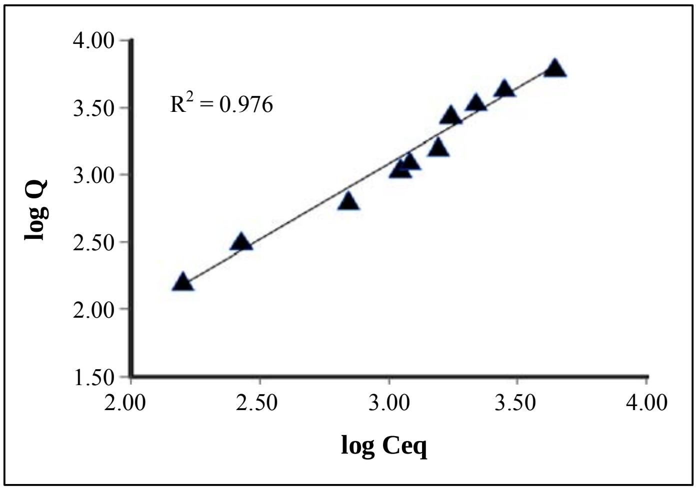

Fig. 5: Freundlich isotherm model for Cr^{6+} biosorption onto SD

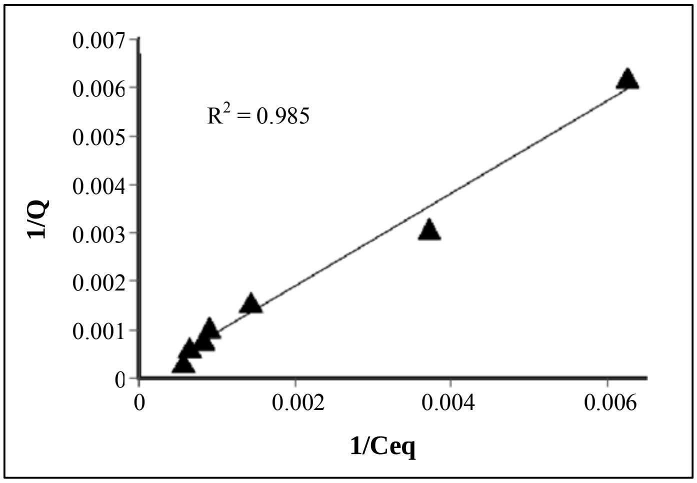

Fig. 6: Langmuir isotherm model for Cr^{6+} biosorption onto SD

Despite the complexity of the adsorption process, which can include several mechanisms, adsorption isotherms have been used widely to characterise uptake of the target compound and they appear to be of use for projected industrial applications[21]. Hence, it was decided to fit the available Cr^{6+} sorption data with two most widely accepted adsorption models, viz. Freundlich and Langmuir. Linear transformation of the adsorption data using

Freundlich and Langmuir models ($R^2 = >0.97$) allowed computation of the Cr^{6+} adsorption capacities. Experimental data obtained in the studies were found to obey basic principles underlying these models, that is, heterogeneous surface adsorption and monolayer adsorption at constant adsorption energy, respectively[15,16]. Further studies on loading capacity, adsorption and desorption and scale up studies for chromium removal and recovery is under progress.

From the foregoing results and discussion, it could be concluded that low cost waste biomass viz. SD was highly efficient and has immense potential as "biomaterial" for the removal of hexavalent chromium from aqueous industrial solutions.

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