Biosorption of hexavalent chromium from paint industrial effluent by *Saraca indica* leaves using with and without gel entrapment method

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Abstract: Raw agricultural wastes are affordable adsorbents for the removal of heavy metals from aqueous solutions. In this research, the use of *Saraca indica* leaves (as an eco-friendly and low cost adsorbent) having the ability to remove toxic hexavalent chromium (Cr(VI)) from paint industrial effluent has been investigated. Parameters such as biosorbent quantity, initial metal-ion concentration, and contact time in with and without immobilised batch experiments have been studied. The results revealed that *Saraca indica* leaves absorb over 86% of Cr (VI) ions from solutions with increasing adsorbent dosage. Adsorption isotherms were compared with Langmuir and Freundlich adsorption models and experimental data were found to fit the models. Also adsorption kinetic models were studied and found to best fit the pseudo second order model. The present study showed that such a low cost material could be used efficiently for the removal of Cr(VI) from paint industrial effluent.

Keywords: adsorption isotherms; chromium (VI); low cost; *Saraca indica*; sorbent.

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1 Introduction

Metals discharged into water bodies are not biodegraded (Witek-Krowiak et al., 2011), but they undergo chemical or microbial transformations, creating a large impact on the environment and public health.

Chromium has long been used in electroplating, leather tanning, metal finishing and chromate manufacturing industries (Prakasham et al., 1999). Normally in contaminated water chromium is primarily present in the form of hexavalent Cr(VI) as chromate (CrO_4^{2-}) and dichromate $(Cr_2O_7^{2-})$. Potable waters containing more than 0.05 mgl^{-1} chromium are considered to be toxic (Arief et al., 2008). The conventional treatment methods used for this purpose include chemical precipitation, lime coagulation, ion exchange, chemical oxidation, electro dialysis, ultra-filtration and solvent extraction (Baral, Das and Rath, 2006). However, chemical processes are inefficient, energy intensive and prohibitively expensive (Arief et al., 2008). Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater and water supplies (Dakiky, Manassra and Mer'eb, 2002). However water decontamination by using sorbents like activated carbon and synthetic resins are rather expensive (Fourest and Volesky, 1995).

Biosorption, an alternative process, is the uptake of heavy metals from aqueous solutions by biological materials. Biosorption of metals by biomass has been much explored in recent years. (Choudhury et al., 2012) Different forms of inexpensive, non-living plant materials such as agricultural waste materials and seaweeds, moulds, yeasts and other dead microbial biomass has been widely investigated as potential biosorbent for heavy metal (Orhan and Buyukgungor, 1993). The basic components of the agricultural waste materials biomass include hemi cellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch containing a variety of functional groups that facilitate metal complexation which helps the sequestering of heavy metals (Idowu, Oni and Adejumo, 2011).

In the present work, leaves of *Saraca indica* are used as the biosorbent. It is considered to be economic and ecofriendly due to its unique chemical composition, availability in abundance, renewable, low cost and more efficient for heavy metal remediation. The powdered form provides some difficulties associated with separation of biomass after adsorption, mass loss after regeneration and small particle size which makes it difficult to be used in column applications (Aathithya and Balakrishnan, 2013). Therefore, modification of raw biomass can improve the sorption capacity. The modification can be achieved by physical processes, chemical processes, and chemical entrapment of the biomass to form membranes, beads, pellets or granular biosorbents. (Bhatti, Nasir and Hanif, 2010; Suresh and Babu, 2009).

As an option, Alginate has been applied in preparation of beads for biosorption. The idea is to entrap the biomass and prevent its loss, while substrates and products are allowed to pass through the support material (Sharmila, Rebecca and Saduzzaman, 2012; Donghee, Yun and Park, 2010).

The aim of this work was to immobilise the biomaterial within Calcium alginate bead and to investigate the effectiveness of *Saraca indica* leaf for the removal of hexavalent chromium from paint industrial effluent. Finally, kinetic study describes the adsorbate uptake over the time. So it is possible to decide the minimum residence time of the adsorbate in the solid-liquid interface and reactor dimensions (Hermes and Nurayani, 2002). Langmuir and Freundlich were used as kinetic models to identify the mechanism reaction of bio sorption process.

2 Materials and methods

2.1 Adsorbate

The industrial effluent was collected from paint industry located at Hosur industrial area, Tamilnadu, India. The total chromium concentration was determined using atomic absorption spectrophotometer (AAS).The sample was stored in a cool dry place to carry out further studies.

2.2 Adsorbents

Saraca indica were collected at Coimbatore Institute of Technology campus, Coimbatore. Adsorbent I-V was washed thoroughly in running water to remove impurities and any adhering particles. The leaves were dried at room temperature for 20 days until it became crisp. The dried leaves were crushed and blended to be powdered and sieved. 1.676 mm mesh size particles were collected and stored in an airtight container for further use to avoid contact with moisture in atmosphere.

2.3 Preparation of immobilised adsorbents

$$\text{Sodium alginate } (0.5\,\text{g}) + \text{adsorbent } (1\,\text{g})$$
$$\downarrow$$
$$\text{Calcium chloride } (0.2\,\text{M})$$
$$\downarrow$$

Calcium alginate beads entrapped with adsorbent.

(Mahamadi and Zambara, 2012). Beads of 3–5 mm in diameter were formed by extrusion through a 5 ml pipette tip. Figure 1 represents the beads formed. The beads were left to harden in the $CaCl_2$ solution for about 12 h and were subsequently washed with distilled water several times. After removing residual water with paper towels, the beads were used for the following experiments.

Figure 1 *Saraca indica* - Calcium alginate beads (see online version for colours)

2.4 Experimental procedure

Experiments were carried out in batch process without beads (WB), beads (B).The samples were collected at 15 min time interval and analysis of hexavalent chromium.

2.5 Analysis

The concentration of hexavalent chromium was determined by spectrophotometric method using 1,5-diphenylcarbazide at 540 nm.

2.6 Adsorption isotherms and kinetics

The adsorption isotherms and kinetic models were done according to the following models: Freundlich model, Langmuir model, Pseudo-first order, Pseudo-second order, Elovich Model and Intra-particle diffusion model. (Hamadi et al., 2001).

3 Results and discussion

3.1 Effect of time with removal of Cr(VI)

The experiments were carried out for different time intervals with constant number of Calcium alginate beads for different initial concentrations. It had been noticed that as time increases the removal of Cr(VI) increases for different concentrations of hexavalent chromium. The graph has been plotted between removal percentage of Cr(VI) and contact time and shown in Figure 2. It had been noted that the removal percentage at the end of 3 hours is 86, 83 and 76% for concentration of 50, 100 and 200 mg/l. (Tables 1 and 2).

Figure 2 Effect of concentration of Cr(VI) with respect to time (see online version for colours)

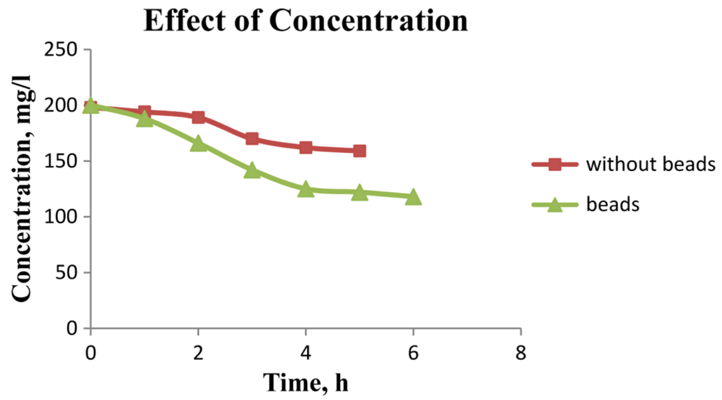

Table 1 Isotherm parameters: Langmuir, Freundlich

	Langmuir isotherm		*Freundlich isotherm*		
Type	R^2	*b*	R^2	*n*	k_f
WB	0.995	0.001 L/mg	0.98	1.098	0.040
B	0.99	0.001 L/mg	0.99	1.098	0.040

Table 2 Kinetic parameters

	Pseudo-first order model			*Pseudo-second order model*		
Type	R^2	k_1	q_e	R^2	k_2	q_e
WB	0.99	0.0253	0.095	0.95		
B	0.99	0.0253	0.095	0.9193	0.297	1.55

The removal of Cr(VI) from aqueous solution by *Saraca indica* - Calcium alginate beads were carried out in a batch experimental system was investigated, and the following conclusions are obtained.

The calcium alginate beads did not reduce Cr(VI) to Cr(III). The rate of adsorption of Cr(VI) onto *Saraca indica* - Calcium alginate beads were higher and the maximum percentage removal was 86%. Also the batch adsorption experiments revealed that the percentage removal increased with an increase in metal ion concentration, whereas it decreased with an increase in contact time and adsorbent dosage.

The isotherm models that fits best is the Freundlich isotherm model (Figures 3 and 4) which confirms the adsorption of Cr(VI) onto the adsorbents. The kinetics for adsorption of Cr(VI) best described by the pseudo first order model. The results indicated the following order to fit the kinetic models: Pseudo first order (Figure 5); Pseudo second order (Figure 6).

Figure 3 Adsorption Langmuir isotherm of Cr(VI) on *Saraca indica* with and without immobilisation (see online version for colours)

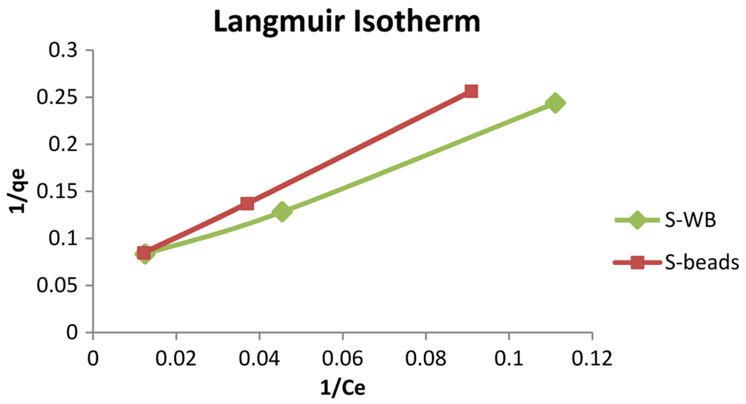

Figure 4 Adsorption Freundlich isotherm of Cr(VI) on *Saraca indica* beads (see online version for colours)

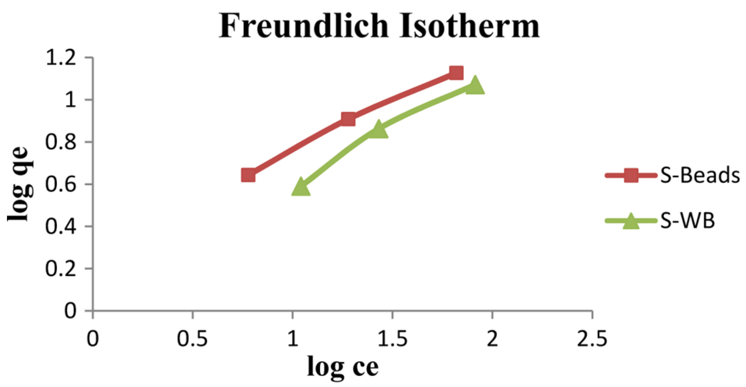

Figure 5 Pseudo first order plot for the adsorption of Cr(VI) on *Saraca indica* beads (see online version for colours)

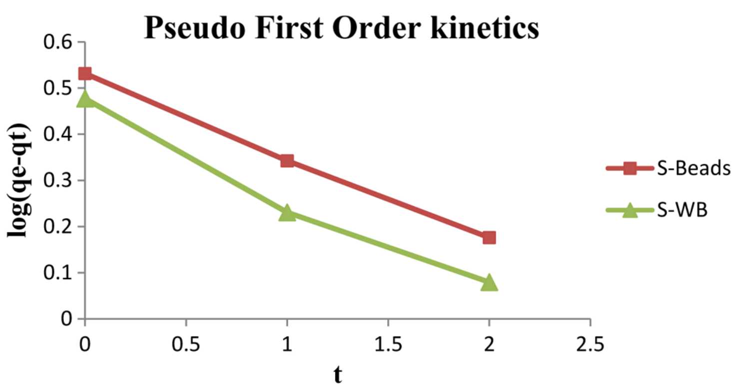

Figure 6 Pseudo second order plot for the adsorption of Cr(VI) on *Saraca indica* beads (see online version for colours)

4 Conclusion

The use of *Saraca indica* leaf beads as adsorbents seems to be an economical and effective alternative over other conventional methods. Finally, this work shows that the *Saraca indica* leaves can be used as efficient biosorbent for Cr(VI) removal form wastewater. However, further research should attempt to improve the adsorption capacity of adsorbents and apply this method to the removal of metals in large scale.

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