Sorption of Cr(III) from aqueous solutions by spent brewery grain

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Abstract

Two types of spent brewery grains were tested for Cr(III) uptake from aqueous solutions: not treated spent grains (NTSG), obtained by abundant washing of spent grain obtained from a Portuguese brewing industry with distilled water, and treated spent grain (TSG), prepared by treating NTSG with NaOH 0.5 M for four hours followed by washing with distilled water.

Both materials were mixed with chromium solutions (50 and 100 mg Cr(III)/L), varying medium pH from 3 to 5. Maximum metal uptake occurred at pH 5. Langmuir isotherm model well describes Cr(III) biosorption by NTSG and TSG. The maximum uptake capacity obtained was 17.84 mg Cr(III)/g NTSG and 13.87 mg Cr(III)/g TSG. Considering that Langmuir constant, *b*, reflecting the affinity between the sorbent and the sorbate is lower for NTSG (0.0749 L/mg) it is possible to conclude that the alkalis treatment does not improve spent grain uptake capacity for Cr(III).

1 Introduction

Industrial activities such as electroplating, mining, metal processing, dyeing and textile produce wastewater contaminated with heavy metals (Goyal et al, 2003; Zouboulis et al, 2004). The discharge of these untreated wastewater into natural water bodies cause serious environmental problems because metals tend to accumulate in living tissues throughout the food chain (Zouboulis et al, 2004).

Traditional treatments for these wastewater include chemical precipitation, membrane processes, ion exchange and adsorption onto activated carbon (Bailey et al, 1999; Low et al, 2000; Tarley and Arruda, 2004). Several studies refer natural products, available in large quantities, and waste products from industry or agriculture as potential inexpensive sorbents. Bailey et al (1999) defines low cost sorbent as a product that requires little processing, is abundant in nature, or is a by-product or waste material from another industry, also referring cost as an important parameter for comparing sorbent materials.

Considering these perspectives, solid wastes produced by brewing industries such as spent grain and spent yeast can be faced as interesting alternatives to activated carbon or ion-exchangers. The present work studies the effect of medium pH and spent grain pre-treatment on Cr(III) sorption from liquid solutions. The spent grains used were obtained from a Portuguese brewing industry – UNICER.

2 Materials and Methods

2.1 Spent Grain preparation

Spent brewery grain was prepared according to Low et al (2000). The authors tested acid (HCl) and base (NaOH) treatments, indicating that maximum sorption was obtained with 0.5 M NaOH treated spent grain. Fresh spent grain (SG) was washed thoroughly with distilled water, dried at 60 ºC and

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screened through a 1 mm sieve. This final product is subsequently named as NTSG (not treated spent grain). Part of NTSG was treated with 0.5 M NaOH solution for 4 h at room temperature. Excess of NaOH was removed by washing with distilled water until constant supernatant pH was reached in successive washings. Spent grain treated with NaOH - TSG (treated spent grain) was dried at 60ºC.

2.2 Chromium solutions

Chromium (III) solutions were prepared dissolving $CrCl_3.6H_2O$ in distilled water. The solutions pH was adjusted with HCl 0.1 M or NaOH 0.1 M.

2.3 Effect of solution pH

The study of the effect of medium pH was carried out with Cr(III) solutions with initial concentration of 50 and 100 mg Cr(III)/L. The experiments were carried out in 250 mL flasks, with 100 mL of metal solution with pH adjustments varying from 3 to 5. Within this pH range Cr(III) does not precipitate.

Half a gram of NTSG or TSG was mixed with chromium solution and flasks were incubated at 30ºC with orbital shaking (150 rpm). Samples were collected at equilibrium (after 96 h), preserved with concentrated HNO_3 (pH < 2) and analysed by Atomic Absorption Spectroscopy (AAS).

2.4 Isotherms

One hundred mililitres of Cr(III) solutions with initial concentration ranging from 25 to 400 mg Cr(III)/L were prepared in 250 mL flasks. Solutions pH was adjusted to 5 with NaOH 0.1 M, mixed with 0.5 g of NTSG or TSG and incubated at 30ºC with orbital shaking (150 rpm). Samples were collected at different time intervals until equilibrium was reached and preserved with concentrated HNO_3 (pH < 2). Chromium concentration was analyzed by AAS.

3 Results and Discussion

3.1 Effect of solution pH

Solution pH is one of the most important environmental factors affecting biosorption. It has influence in site dissociation and in solution chemistry of heavy metals (Özer and Özer, 2003). Figure 1 shows the percentage of initial Cr(III) concentration removed by spent grain at different solution pH. Data indicates that Cr(III) sorption onto NTSG and TSG increases with increasing pH, with maximum removal being observed at pH 5.

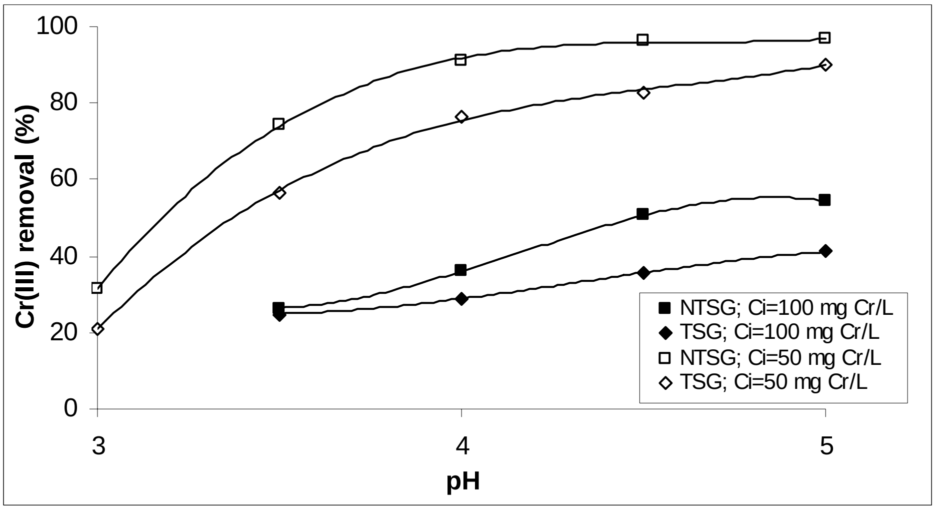

Figure 1 – Effect of solution pH on Cr(III) uptake.

According to Cr(III) speciation with medium pH (Ramos et al, 1995) at low pH the dominant specie is Cr^{3+}. At high H_3O^+ concentrations spent grain biding sites may be occupied by protons limiting the approach of metal cations due to the electrostatic repulsive forces.

Ramos et al (1995) also stated that the predominant species at pH 5 are $Cr(OH)^{2+}$ (70 %) and $Cr(OH)_4^{5+}$ (20 %). The changes in Cr(III) speciation and the fact that higher pH may turn biomass surface negatively charged, can explain the higher metal uptake at pH 5.

3.2 Isotherms

Equilibrium experiments were conducted with initial metal concentrations from 25 to 400 mg Cr(III)/L. Metal equilibrium concentration was reached after 44 h (Ci = 25 mg Cr(III)/L) to 168 h (Ci = 400 mg Cr(III)/L). Figure 2 presents Cr(III) sorption isotherms for NTSG and TSG.

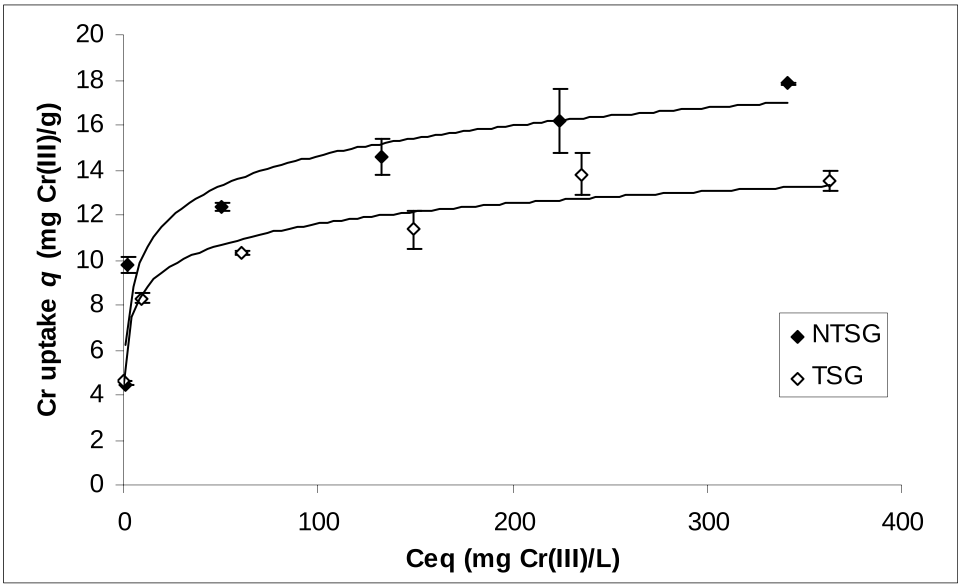

Figure 2 – Cr(III) sorption isotherms.

The sorption isotherm relationship can be mathematically expressed (Volesky, 2004). Among the existing mathematical models for single-sorbate isotherms, Freundlich and Langmuir are the most commonly used in literature.

Freundlich model: $$q = kC_{eq}^{(1/n)}$$ (eq. 1)

Langmuir model: $$q = q_{\max} \frac{bC_{eq}}{1 + bC_{eq}}$$ (eq.2)

Where:

q is the adsorption capacity at the equilibrium sorbate concentration C_{eq} (mg of sorbate adsorbed/g sorbent);

C_{eq} is the final equilibrium concentration of sorbate remaining in solution (mg sorbate/L);

k and n are Freundlich constants;

q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of sorbate adsorbed/g sorbent) it can also be interpreted as the total number of binding sites available for biosorption (Volesky, 2004);

b is a Langmuir constant related to the affinity between the sorbent and the sorbate (L/mg).

The relationship between b and the affinity constant K can be expressed by eq. 3 (Volesky, 2004).

$$b = \frac{1}{K} \qquad \text{(eq.3)}$$

According to eq. 3, b represents the reverse of the affinity. Therefore, the higher K and the smaller b, the higher is the affinity of the sorbent to the sorbate.

Langmuir isotherm considers sorption as a chemical phenomenon. This model assumes that all sorption sites are uniform and that sorption is restricted to a monolayer The Freundlich isotherm relationship is exponential. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges of C_{eq} (Volesky, 2004).

Data obtained from the equilibrium studies was fitted with both Freundlich and Langmuir models according to equations 1 and 2. Plots are presented in figure 3. Table 1 summarises the constants values calculated from data fitting. It is possible to observe that Langmuir model better fits experimental results.

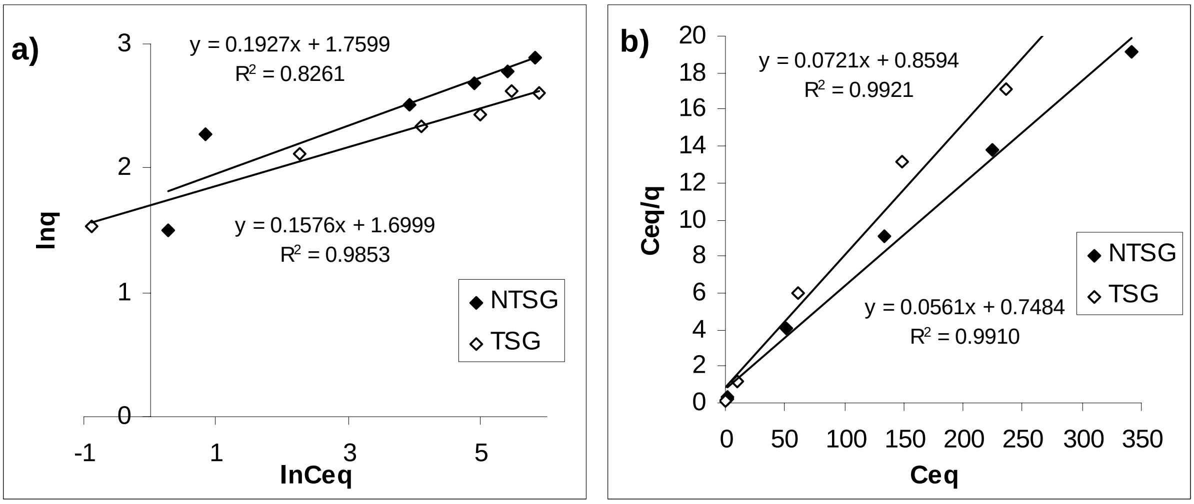

Figure 3 – Data fitting with a) Freundlich model and b) Langmuir model.

Table 1 – Freundlich and Langmuir constants.

Sorbent	Freundlich			Langmuir		
	K	N	R^2	q_{max}	b	R^2
NTSG	5.812	5.189	0.8261	17.84	0.0749	0.9910
TSG	5.473	6.344	0.9853	13.87	0.0839	0.9921

Evaluating q_{max} and b values for the two sorbents in study, it is possible to point out NTSG as the best sorbent for Cr(III) as it reveals the higher sorption uptake capacity and the higher affinity for the metal.

Table 2 presents q_{max} values found in literature for several types of biomass residues. Comparing these values with NTSG data it is possible to consider this brewing residue as a potential biosorbent for wastewater contaminated with Cr(III).

Table 2 – q_{max} values for residual biomass used as biosorbent for heavy metals.

Biomass	q_{max} (mg/g)	Reference
Spent brewery grain (with NaOH 0.5 M treatment)	17.3 mg Cd/g 35.5 mg Pb/g	Low et al (2000)
Spent grain (treatment with 1 M HCl)	18.94 g Cr(VI)/g	Low et al (2001)
Carrot residues (washed with 0.5 M HCl and distilled water until constant pH)	45.09 mg Cr(III)/g 32.74 mg Cu/g 29.61 mg Zn/g	Nasernejad et al (2005)
Medicago sativa (Alfalfa)	7.1 mg Cd/g 7.7 mg Cr(III)/g 0.0 mg Cr(VI)/g 43.0 mg Pb/g 4.9 mg Zn/g	Gardea-Torresdey et al (1998)
Tree fern	7.58 mg Zn/g 10.6 mg Cu/g 39.8 mg Pb/g	Ho et al (2002)
Olive pomace	7.0 mg Cd/g 4.3 mg Cu/g 15.7 mg Pb/g	Pagnanelli et al (2003)

4 Conclusions

Data obtained in the present study indicate that solution pH has an important effect on Cr(III) uptake by spent grain. The maximum uptake capacity obtained for both NTSG and TSG was observed when solution pH was adjusted to 5. The calculated Langmuir isotherm parameters indicate the higher q_{max} (17.84 mg Cr(III)/g) for NTSG, demonstrating that alkali treatment does not improve spent grain uptake capacity. Compared to other residual biomasses, the NTSG tested can be considered has a promising biosorbent to treat wastewater contaminated with Cr(III).

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