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BIOSORPTION OF HEAVY METAL AND DYES: A PROMISING TECHNOLOGY LEATHER WASTEWATER TREATMENT

E. Rosales[1], M. Pazos[1], M.A. Sanromán[1] and T. Tavares[2]
1 Dpt. Chemical Engineering, University of Vigo, Campus As Lagoas, Marcosende 36310, Vigo Spain email: emiliorv@uvigo.es, mcurras@uvigo.es, sanroman@uvigo.es
2 IBB – Instituto de Biotecnologia e Bioengenharia, Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal email: ttavares@deb.uminho.pt

ABSTRACT

The presence of dyes and heavy metals is usual in industrial processes like chrome tanning in tannery industry and their removal may be an environmental problem. Different techniques were developed and applied for the treatment of dyes and heavy metals in effluents. Among them, adsorption showed to be an economic, simple operation and an effective technique. Zeolites have a strong affinity for cations of transition metals, but only little affinity for anions and non-polar organic molecules. The application of a zeolite to heavy metal removal may be improved by the presence of microorganisms. The aim of this work is the treatment of an effluent containing dyes and toxic metals. Several operation parameters such as pH, concentration and kinetic behavior were studied. This innovative process for treating dyes and heavy metal effluents showed that the zeolite-biomass system is able to perform the removal of a combination of Azure B and chromium(VI). A mixture of dye and metal solutions was treated reaching a removal higher than 50% in the case of chromium (VI) and higher than 99% for dye, in 8 days.

Keywords: Azure B, chromium, biosorption

INTRODUCTION

Industrial processes like chrome tanning of tannery industry use dyes and heavy metals and their removal may be an environmental problem. These industrial processes are based on chemical processes involving several organic and inorganic compounds such as: acids, chromium salts, dyes, auxiliaries and other chemical additives [1]. Direct discharge of dye effluents can cause serious problems to the environment due to their high organic loading, toxicity and aesthetic pollution related to colour. Another environmental problem is the presence of heavy metals in the effluent. Under certain environmental conditions, they may accumulate to toxic levels and cause ecological damage.

Different techniques were developed and applied for the treatment of dyes and/or heavy metals in effluents. Among them, adsorption showed to be an economic, simple operation and an effective technique. Nowadays, the use of clay materials is being investigated by their cost and potential for ion exchange. Zeolites have a strong affinity for cations of transition metals, but only little affinity for anions and non-polar organic molecules [2]. The application of a zeolite to heavy metal removal may be improved by the presence of microorganisms.

The aim of this work is the treatment of an effluent which contains dyes and toxic metals such as Azure B and chromium (VI). In previous reports, the chromium removal by an adsorption process has been studied and prior to study the mixture pollutants, it is necessary to know the characteristics of the adsorption process behaviour when the effluent contains a dye as pollutant. Therefore, in this work a sequential study has been proposed. Initially, the adsorption process of Azure B dye in zeolite has been studied. Furthermore, a low-cost system combining the biosorption properties of a microorganism with the ion-exchange properties of a zeolite has been developed to remove simultaneously the chromium and dye from the effluent. This innovative process combines the reduction of chromium (VI) to chromium (III) by the bacterium *A. viscosus* with adsorption of the dye and chromium in a zeolite.

MATERIALS AND METHODS

Dye

Dye solutions were prepared with Azure B purchased from Aldrich (CAS Number 531-55-5). Aqueous solutions were prepared according to the experiments in concentrations between 1.5-2500 mg/L.

Metal

Chromium solutions were prepared by diluting $K_2Cr_2O_7$ (Riedel-de Haen) in distillated water.

Zeolite

NaY zeolite (relationship Si/Al 2.83, BET area 700 m^2/g) was used as support. Prior to use, the faujasite zeolite NaY (Zeolyst International) was pre-treated by calcination at 500 ºC during 8 h under a dry air stream.

Microorganism

A. viscosus was obtained from the Spanish Type Culture Collection of the University of Valencia. A medium with 10 g/L of glucose, 5 g/L of peptone, 3 g/L of malt extract and 3 g/L of yeast extract was used for growth and maintenance of the microorganism.

Dye batch adsorption

Erlenmeyer flasks (250 mL) containing 1 g of zeolite in 150 mL of different Azure B solutions were employed. Isotherm studies were made with concentration solutions of Azure B between 1.5-2500 mg/L. Kinetic studies were made at a concentration of 10 mg/L for 15 minutes.
To study the effect of pH on dye removal, pH values range from 2 to 7.5. The solution pH was regularly maintained at the desired value using H_2SO_4 or NaOH (0.1 M) solutions.
All the experiments were performed in a rotary shaker at 150 rpm and 28ºC.

Batch biosorption

A. viscosus biofilm formation was prepared according to Quintelas and Tavares [3]. Bacterium was harvested during the exponential phase of the growth curve. The experiments were performed with 250 mL Erlenmeyer flasks containing 1 g of zeolite covered with biofilm (bacterium concentration 5 g/L) and 150 mL of the different solutions mixture of dye and chromium at concentrations: 100 mg/L chromium with 100, 150, 300, 450, 600 mg/L of dye. All biosorption experiments were performed in a rotary shaker at 150 rpm, temperature 28ºC.
Samples of 1 mL were taken, centrifuged and analysed for dye and chromium determination. These experiments were performed twice, being the experimental error margin below 3%.

Azure B determination

The dye content was measured spectrophotometrically (T60 UV Visible, PG Instruments) in the supernatant based on the constructed calibration curves at maximum absorption wavelength (648 nm). The sample was diluted with distilled water if the absorbance exceeded the range of calibration curve.

Chromium determination

Hexavalent chromium was quantified by measuring absorbance at 540 nm of the purple complex of chromium (VI) with 1,5-diphenylcarbazide in acidic solution (T60 UV Visible, PG Instruments). For total chromium determination, the chromium (III) was first oxidized to chromium (VI) at high temperature by the addition of an excess of potassium permanganate previous to the reaction with 1,5-diphenylcarbazide. The chromium (III) concentration was calculated by the difference between the total chromium and chromium (VI) concentration.

Azure B and chromium adsorption uptake and removal percentages

The amount of dye or chromium adsorbed and the percentages of removal were calculated using the following equations:

$$q = (C_i - C_f)\cdot V / M \quad (1)$$
$$D = 100\cdot(C_i - C_f) / C_i \quad (2)$$

where q is the dye uptake (mg/g); C_i and C_f the initial concentration and the concentration through time in the solution (mg/L) respectively; V is the solution volume (L); M is the mass of adsorbent (g) and D the percentage of dye or chromium removal (%).

RESULTS AND DISCUSSION

Azure B adsorption. Effect of pH and Azure B concentration

Initially the effect of the solution pH on the Azure B adsorption capacity of the zeolite was studied. The work was done at the pH values of 2, 4, 6 and 7.5 in order to obtain adsorption equilibrium data. In all cases, adsorption showed a linear rising with instantaneous uptake followed by a stationary state and the dye uptake profiles were high with values from 1.30 to 1.42 $mg_{dye}/g_{zeolite}$. The best results, obtained at pH 4, may be related to the surface charge density decreasing with an increase in the solution pH. Therefore, the electrostatic repulsion between the positively charged dye and the surface of adsorbents is lowered, which may result in an increase in the extent of adsorption. The low uptake value obtained at pH 6 and 7.5 can be explained by a greater concentration of the OH^- in the system which makes a competitive reaction with the zeolite.

The effect of the Azure B concentration on zeolite adsorption was investigated under the equilibrium conditions at pH 4. As shown in Fig.1, when the dye concentration was among 10-120 mg/L the dye removal percentages were nearly constant (98.26-99.33%). The maximum removal percentage was 99.33% obtained with 60 mg/L of Azure B. For higher concentrations the dye removal decreased significantly. The maximum adsorption capacity attained was 140.953 $mg_{dye}/g_{zeolite}$ at an Azure B initial concentration of 2500 mg/L.

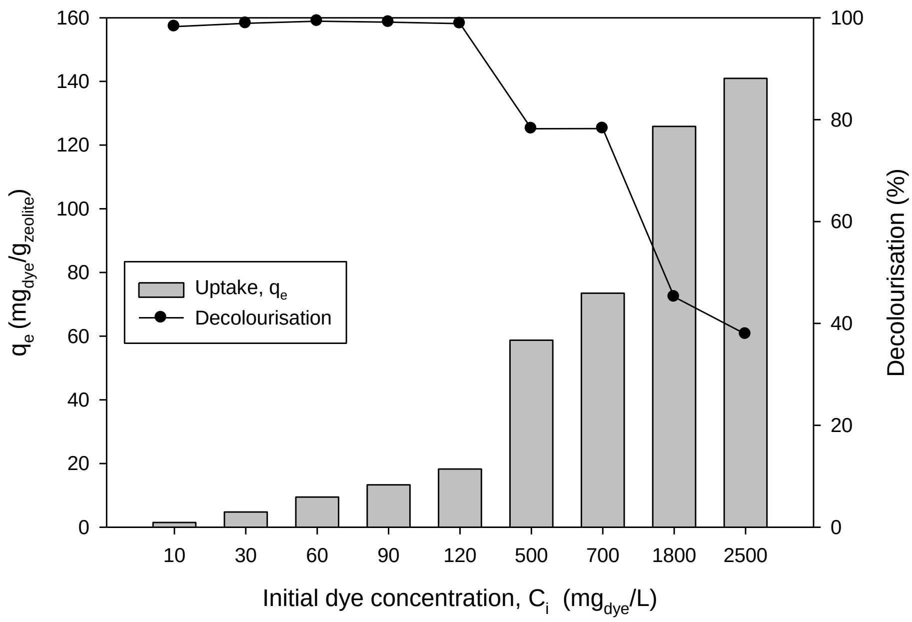

Fig. 1 Uptake and decolourisation values obtained from different initial Azure B concentrations in presence of zeolite dosage 1 g and pH 4.

Azure B adsorption isotherms

In order to optimize the design of an adsorption system to remove pollutants from effluent, it was required to establish the most appropriate correlation of equilibrium curves, commonly known as adsorption isotherms. The equations of the four analysed models along with the isotherm constants and correlation coefficients are presented in Table 1.The results of the present study indicated that the Langmuir model did not fit the experimental data due to low correlation coefficient value which suggested that homogeneous and monolayer mode of adsorption was not suitable in the present case. The Freundlich model exhibited good fit to the experimental sorption data suggesting the heterogeneous mode of adsorption since correlation coefficient value was 0.9968. Furthermore, the n_F value, which is related to the distribution of bonded ions on the adsorbent surface, was found to be 3.011 indicating that adsorption of dye onto zeolite is favoured [4]. A suitable explanation for the adsorption mechanism would be that the stronger binding sites were initially occupied, with the binding strength decreasing with increasing degree of site occupation. The abilities of the three-parameter models, Redlich-Peterson and Sips, were examined to model the equilibrium data. In terms of correlation coefficient values, the three-parameter models were better than the two-parameter models as expected from the number of parameters involved in the models. Thus, the three-parameter models suggested a non-monolayer sorption. The best representation of the experimental results of the adsorption isotherms was obtained using the Redlich-Peterson model. The β_{RP} value indicates that the adsorption system was between the two limiting behaviours.

Table 1. Adsorption isotherms parameters for Azure B onto NaY zeolite

Model	**Equation**	**Constants**	**R^2**
Langmuir	$q_L = q_{max}\cdot b_L\cdot C_f / (1 + b_L\cdot C_f)$	b_L=0.0049 [L/mg] q_{max}=154 [mg/g]	0.9723
Freundlich	$q_F = K_F\cdot C^{1/nF}$	K_F=12.443 [$mg^{1-1/n}\cdot L^{1/n}/g$] n_F=3.011	0.9968
Redlich-Peterson	$q_{RP} = K_{RP}\cdot C_f / (1 + a_{RP}\cdot C_f^{\beta RP})$	K_{RP}=100.114 [L/g] a_{RP}=7.356 [L^{β}/mg^{β}] β_{RP}=0.6808	0.9974
Sips	$q_S = K_S\cdot C_f^{\beta S} / (1+a_S\cdot C_f^{\beta S})$	K_S=12.057 a_{RP}=0.0078 β_S=0.3491	0.9969

Azure B adsorption kinetics

In order to develop applications of the system, operation control and adsorption kinetic are very important to the process design. The system was adjusted to the pseudo-second order kinetics, described by Ho & McKay [5]

$$q_t = q_e - q_e/(1+q_e\cdot k_2\cdot t) \qquad (4)$$

where q_t is the amount of solute sorbed at time t ($mg_{dye}/g_{zeolite}$), q_e is the amount of solute sorbed at equilibrium ($mg_{dye}/g_{zeolite}$) and k_2 the second order equilibrium rate constant (g/(mg·min)).

The pseudo-second order kinetics provides an excellent fit between the predicted curves and the experimental values, whereas the first-order kinetics did not fit well to the experimental data. This fact was confirmed by a good linearization of the data with R^2>0.999. Pseudo-second-order adsorption rate constant (k_2) and equilibrium uptake values (q_e) were determined from the slope and the intercepts of the plots in the linearized form of the pseudo-second-order model. The calculated q_e values (q_e=1.4182 $mg_{dye}/g_{zeolite}$) also agrees very well with the experimental data (q_e=1.4172 $mg_{dye}/g_{zeolite}$). The best fit of the second-order expression suggests that the chemisorption mechanism is involved in the adsorption.

***A. viscosus*-zeolite system. Model effluent treatment**

In this study, the biosorbent obtained by combination of zeolite and *A. viscosus* has been tested in order to degrade an effluent like chrome tanning of tannery industry. Several initial dye concentrations were studied and the obtained data are shown in Fig.2. In all cases, the dye was the first pollutant to be removed with a level higher than 99% after one hour. The chromium removal was favoured by the presence of *A. viscosus* which is suggested to reduce the chromium (VI) to its oxidation state chromium (III), thus it is more easily adsorbed in zeolite. The chromium exhibits two adsorption stages typical of biosorption kinetics: first associated with external cell surface reaching a removal of approximately 40% in one day, followed by intracellular accumulation/reaction.

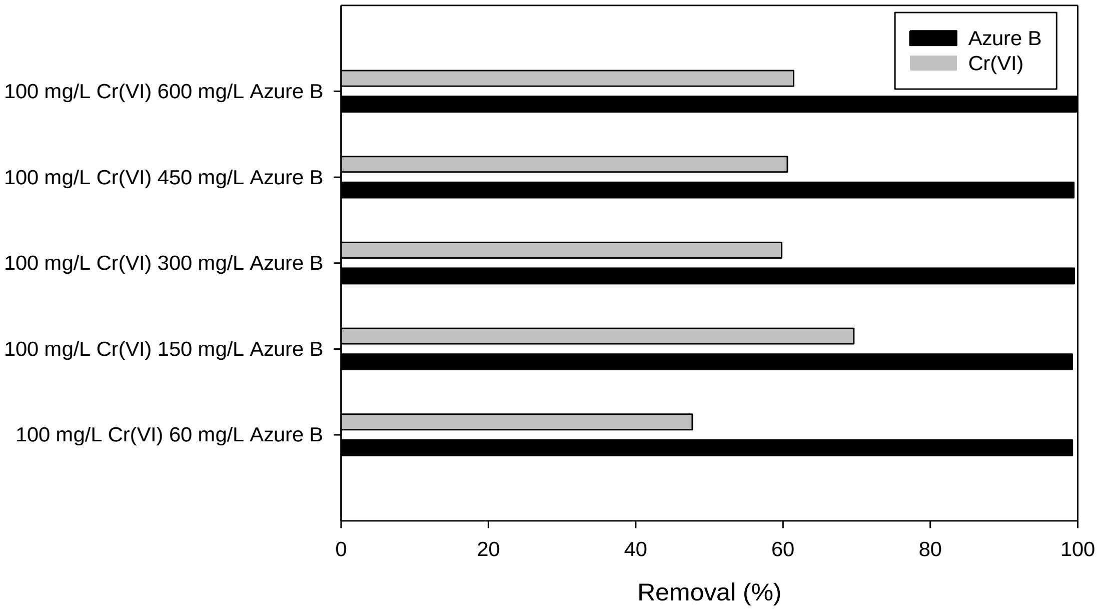

Fig. 2 Removal degree into zeolite-*A.viscosus* system for a mixture of Azure B and chromium (VI) after 8 days.

CONCLUSIONS

The results obtained in this work demonstrated that Azure B can be effectively removed by adsorption in zeolite NaY. Adsorption isotherms of Azure B on the zeolite were studied using Langmuir, Freundlich, Sips and Redlich-Peterson isotherm models. Among all the tested isotherm models for the description of adsorption equilibrium isotherms of Azure B on zeolite, the best fitting models were Redlich–Peterson and Sips. Kinetic studies on sorption of Azure B on zeolite revealed that pseudo-second-order model showed the best fit to the experimental data suggesting that a chemisorption mechanism is involved in the adsorption.

The innovative zeolite-biomass system showed that this process is able to perform the removal of a combination of Azure B and chromium reaching a removal levels higher than 50% in case of chromium (VI) and more than 99% for Azure B. The presence of the bacterium facilitates the reduction of the chromium (VI) and the consequent adsorption to the NaY zeolite and reduction of the toxicity of the effluent. The system appears to be a promising process to the removal of both pollutants simultaneously (inorganic and organic pollutants) reducing the pollutant charge and toxicity.

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REFERENCES

[1] S. Hammami, A. Ouejhani, N. Bellakhal, M. Dachraoui, Application of Doehlert matrix to determine the optimal conditions of electrochemical treatment of tannery effluents J. Hazard. Mater. 163 (2009) 251-258.

[2] M. Vaca Mier, R. Lopez Callejas, R. Gehr, B.E. Jimenez Cisneros, P.J.J. Alvarez, Heavy metal removal with mexican clinoptilolite: Multi-component ionic exchange, Water. Res. 35 (2001) 373-378.

[3] C. Quintelas, T. Tavares, Removal of chromium(Vi) and cadmium(II) from aqueous solution by a bacterial biofilm supported on granular activated carbon, Biotechnol.Lett. 23 (2001) 1349-1353.

[4] A.S. Özcan, B. Erdem, A. Özcan, Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite, Colloids Surf.A Physicochem.Eng.Asp. 266 (2005) 73-81.

[5] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451-465.

[6] B. Silva, H. Figueiredo, C. Quintelas, I.C. Neves, T. Tavares, Zeolites as supports for the biorecovery of hexavalent and trivalent chromium, Microporous Mesoporous Mater. 116 (2008) 555-560.