Adequacy of isotherm adsorption of black 5 reactive dye for crosslinked chitosan microspheres

Irene Yukiko Kimura[1]*, Valfredo Tadeu Fávere[2], Amarildo Otávio Martins[2], Viviane Aparecida Spinelli[2] and Atche Josué[2]

[1]*Departamento de Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, Paraná, Brasil.*
[2]*Departamento de Química, Universidade Federal de Santa Catarina, CP 476, 88040-900, Florianópolis, Santa Catarina, Brasil.*
**Author for correspondence. e-mail: kimurai@hotmail.com*

ABSTRACT. Chitosan microspheres with average diameter 1.03 ± 0.06 mm and degree of deacetylation of 72.5% were employed as adsorbent for reactive dye black 5. Chitosan was characterized through infrared spectroscopy (IR), ^{13}C NMR spectrum and deacetylation degree (DD%), and crosslinked with glutaraldehyde 2.5% (w/v) to increase its resistance in acid medium. Corresponding isotherms were obtained in acid and alkaline solutions. Experimental data were fitted by Langmuir's, extended Freundlich's and Nernst's isotherms. Adsorption was more effective in acid medium and adjusted better the Langmuir's isotherm.

Key words: adsorption, chitosan microsphere; reactive dye.

RESUMO. Adequação da isoterma de adsorção do corante reativo preto 5 pelas microesferas de quitosana reticulada. Microesferas de quitosana, com diâmetro médio 1,03 ± 0,06 mm e grau de desacetilação de 72,5%, foram empregadas como adsorvente para o corante reativo preto 5. A quitosana foi caracterizada através de espectroscopia no infravermelho (IV), RMN ^{13}C e grau de desacetilação (GD%) e reticulada com glutaraldeído 2,5% (m/v) para aumentar a sua resistência em meio ácido. As isotermas correspondentes foram obtidas em soluções ácidas e alcalinas. Dados experimentais foram plotados usando as isotermas de Langmuir, Freundlich estendida e Nernst, mostrando que a adsorção foi mais efetiva em meio ácido e ajustando melhor a isoterma de Langmuir.

Palavras-chave: adsorção, microesfera de quitosana, corante reativo.

Dyes present in large volumes in textile waste water are major polluting agents. The use of reactive dyes by textile industries has largely increased, due to the high reactivity of such compounds with fibers and to the color stability thereafter. Nevertheless, reactive dyes consist of rather stable molecules resistant to degradation by light, and chemical or biological processes (Zollinger, 1991).

Chitosan is a copolymer formed by β (1→4)-2-amino-2-deoxy-D-glycopyranose and β (1→4)-2-acetamide-2-deoxy-D-glycopyranose, obtained by the alkaline hydrolysis of chitin (Muzzarelli, 1978; Gacén and Gacén, 1996). Chitosan has been found to be a promising polymeric material of great scientific interest due to its properties and wide range of application (Mathur and Narang, 1990).

Many textile wastewaters are highly acid. This limits the use of chitosan as adsorbent for dye removal, as this compound is highly soluble in such environments. Current research presents a detailed evaluation on the adsorption of a reactive dye containing the vinylsulfone group using reticulated chitosan microspheres. Crosslinking of chitosan was necessary to stabilize the microspheres in acid medium as well as to grant the material the mechanical strength necessary for the adsorption studies in dynamic systems.

A number of studies analyses adsorption as a means of dye removal from textile waste water (Mckay *et al.,* 1982; Laszlo, 1994; Kim *et al.,* 1997). A variety of adsorbents has been employed, including activated carbon (Mckay, 1979), turf (Poots *et al.*, 1976), silica (Mckay and Alexander, 1977), alumina (Moreira *et al.*, 1998), cellulose (Laszlo, 1995) and, more recently, chitin and chitosan (Muzzarelli, 1978; Mckay *et al.,* 1982; Laszlo, 1994; Laszlo, 1995; Kim *et al.,* 1997; Nawar and Doma, 1995).

Several adsorption isotherms are quite well established for adsorption processes in aqueous solution involving equilibrium and adsorption capacity of monocomponent systems. Langmuir's isotherm (Mckay *et al.*, 1982; Kim *et al.,* 1997; Yoshida *et al.*, 1993), which has been frequently used, may be expressed by

$$\theta = \frac{KC_e}{1 + KC_e} \tag{1}$$

where θ is the local coverage ratio ($\theta = q/q_m$), q is the adsorbed quantity (mg/g) and q_m is the maximum adsorption quantity (mg/g), C_e is the dye concentration in equilibrium (mg/L) and K is related to the adsorption energy required for the formation of a monolayer.

More recently, the extended Freundlich isotherm has also been applied to interpret experimental adsorption results. The adsorbent surface is considered to be non-homogeneous, therefore revealing the possibility of several adsorption sites. The total surface is divided into sites of identical groups with adsorption energy Q and the isotherm is obtained from an exponential distribution of adsorption energies. The integral equation of the complete adsorption isotherm is given by:

$$\theta_T = \int_\Delta N(Q)\theta(Q)dQ \tag{2}$$

where θ_T is the total ratio of relative coverage by the surface monolayer, N(Q) is the number of sites with adsorption energy lying between Q and Q + dQ , θ(Q) is the ratio of local coverage by individual sites and follows Langmuir's isotherm $\theta = KC_e/(1+KC_e)$, Q represents the difference between the adsorption energy of solute and solvent for a given site, and Δ is the integration region corresponding to all possible values for the adsorption energy.

Integration of above equation results in the final expression for the total coverage of the adsorption surface:

$$\theta_T = \frac{(KC_e)^m}{\text{sen}(m\pi)/(m\pi)} - \frac{m}{(1-m)}\frac{KC_e}{(1+KC_e)} - \frac{m}{(1-m)}\frac{1}{(2-m)} \tag{3}$$
$$\frac{(KC_e)^2}{(1+KC_e)^2} - \frac{m}{(1-m)}\frac{1}{(2-m)}\frac{2}{(3-m)}\frac{(KC_e)^3}{(1+KC_e)^3} - \ldots$$

where *m* characterizes the degree of energetic heterogeneity of the system. This expression shows that Freundlich's modified isotherm is a function of K, *m* and C_e (Rocha *et al.*, 1997).

Nernst's isotherm is linear, and may be expressed as:

$$\theta = KC_e \tag{4}$$

where the angular coefficient K corresponds to the ratio between dye solubility in water and in the solid phase (Gonzales-Davila *et al.*, 1990).

Material and methods

Reactive Remazol Black 5 dye (55% pure, Aldrich Chemical Company, Inc.) was employed without previous purification. All other reagents employed herein were of an analytical grade and supplied by Merck. Figure 1 illustrates the structure of the Black 5 reactive dye containing vinylsulfone groups (Colour Index, 1971).

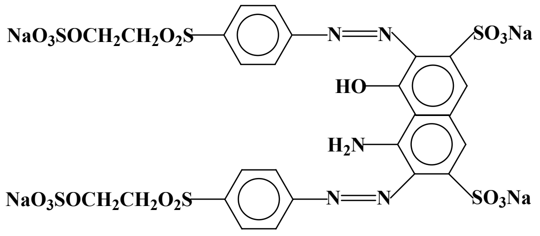


Figure 1. Structure of the Black 5 Reactive Dye

Synthesis of chitosan: Chitin (10.0 g) has been previously prepared according to an adaptation of Hackman's method (Hackman, 1955). The compound was submitted to a deacetylation reaction using Broussignac's method (Broussignac, 1970). Synthesized chitosan was purified and dissolved in 3% (m/v) acetic acid, and filtered to eliminate insoluble residues. The material was then dried in a Mini Spray Dryer Büchi B-191, resulting in particles of approximately 25 µm.

Characterization of chitosan: Infrared patterns were obtained from 400 to 4000 cm^{-1}, using an FT Perkin Elmer 16 PC infrared spectrophotometer. Chitosan films were prepared by dissolving 200 mg of the polymer in 20.0 mL of 3% (m/v) acetic acid in a petri dish. The acid slowly evaporated at room temperature.

NMR^{13}C patterns were obtained using a ^1H ^{13}C Nuclear Magnetic Resonance spectrometer Brucker AC - 200 F. 100 mg of the polymer were dissolved in a solution containing 0.4 mL glacial acetic acid and 2.5 mL D_2O. The sample was centrifuged and an aliquot was analyzed.

The deacetylation degree (%DD) was estimated by conductometric titration, using a Micronal B 330 conductivimeter and an automatic Schott Geräte T

80/20 titration system. 200 mg of chitosan were transferred to a 600 mL vial containing 450 mL of a solution of 0.001 mol/L NaCl and 5.0 mL of 1.0 mol/L HCl. Titration was carried out after polymer dissolution with an addition of 0.5 mL of 0.100 mol/L NaOH under nitrogen in 20 seconds intervals (Raymond *et al.*, 1993). The degree of deacetylation estimated thereby was 72.5% (4.50 mmols amino groups/g of chitosan).

Preparation of chitosan microspheres: Chitosan (2.5 g) was dissolved in 100 mL of 5% (m/v) acetic acid. A viscous solution was obtained and dripped, using an Ismatec peristaltic pump coupled to a bath containing 2.0 mol/L NaOH solution. Gel microspheres were rinsed in distilled water so that neutral pH could be attained (Rorrer *et al.*, 1993).

Crosslinking of chitosan microspheres: Chitosan microspheres were placed in a glutaraldehyde 2.5 % (m/v) solution at a ratio of 1.5 mL of solution per gram of gel microspheres. The mixture was set for 24 hours at room temperature. The material was rinsed in distilled water to remove the remainder of the crosslinking agent. Subsequently, the microspheres were placed in acetone during 24 hours and dried at room temperature (Rorrer *et al.*, 1993). Figure 2 illustrates the crosslinked chitosan.

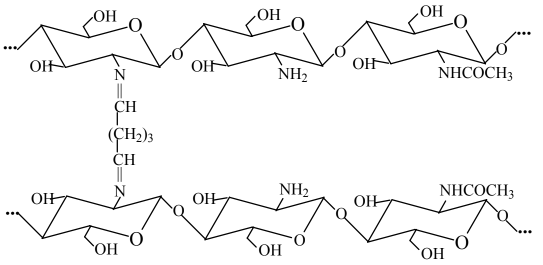
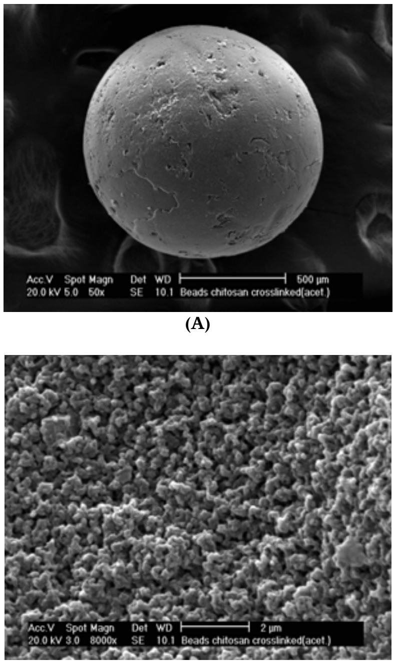


Figure 2. Structure of the crosslinked chitosan

After crosslinking, the content of free amino groups (NH_2) was determined by acid-base titration. 300 mg of microspheres were placed in 100 mL of a standard HCl 0.100 mol/L solution during 24 hours aiming at the protonation of free amino groups. A 25.0 mL aliquot of the supernant was removed and titrated with NaOH 0.100 mol/L. The results showed the presence of 48.0% of free amino groups (2.98 mmols/g).

Scanning Electron Microscopy (SEM): The morphology of the microspheres was analyzed under a Philips XL30 Scanning Electron Microscope. The average size of the microspheres was 1.03 ± 0.06 mm and the external surface depicted only limited porosity. Figure 3 shows SEM images of chitosan microsphere with morphology details.



(A)

(B)

Figure 3. SEM photomicrographs: (a) whole chitosan microsphere at 50X; (b) external surface of microsphere at 8000X

Determination of reactive dye in solution: The concentration of reactive Black 5 in solution was carried out from the analytical curve obtained in a UV-Vis Hitachi U3000 spectrophotometer with λ_{max} = 599 nm. Figure 4 shows the curve λ_{max} for reactive black 5.

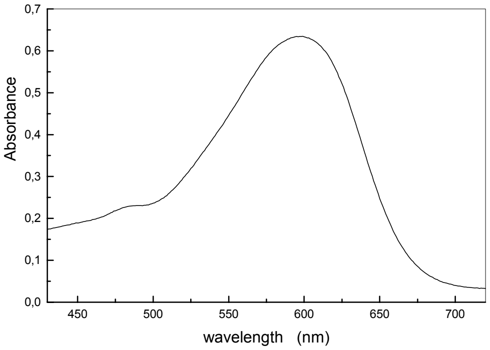


Figure 4. Spectrum of maximum wavelength (λ_{max} = 599 nm) of the black 5 reactive dye in whole range of pH

Adsorption isotherms: Isotherms were obtained by the batch method. Flasks were maintained at 25.0 ± 0.5 °C and contained 100 mg of chitosan microspheres, and 50.0 mL dye solution (10.0 – 70.0 mg/L). The ionic strength of the solution was controlled by NaCl (μ = 0.100 mol/L) and pH adjusted with a buffer solution. The system was continuously stirred at 150 rpm during 24 hours. The material was centrifugally separated from the solution and the concentration of dye in solution was determined by UV-Vis spectrophotometry.

Results and discussion

Figure 5 illustrates the infrared spectrum measured for chitosan. Its absorption band at 3454 cm^{-1} is rather intense as a consequence of OH and water stretching vibrations, whereas the band at 2900 cm^{-1} corresponds to C-H stretching vibrations. The bands at 1654 and 1380 cm^{-1} may be attributed to deformation vibrations of medium intensity of N-H bonds from primary amines and of low intensity from C-H bonds of the CH_3 group. Small contents of residual acetamide groups may be found in the polymeric chain as a consequence of incomplete deacetylation of chitosan. The band at 1068 cm^{-1} corresponds to the stretching vibrational of C-O bonds from primary alcohol (Muzzarelli, 1978; Domszy and Roberts, 1985).

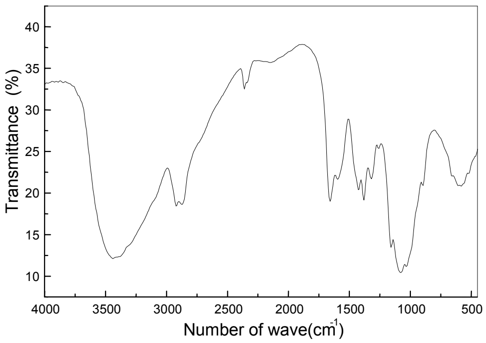


Figure 5. Espectrum of the chitosan infrared

The NMR ^{13}C patterns showed that the chemical displacement of the anomeric C_1 carbon at 98 ppm was clearly distinguished from other signals. Two closest signals at 80 ppm corresponded to C_4. The displacement of secondary C_3 and C_5 carbons was 77 ppm. Signals at 60 ppm and 56 ppm might be attributed to C_6 and C_2, respectively. Due to the fact that the polymer is not to be 100% deacetylated, the corresponding lines C=O and CH_3 still appear with displacement around 177 and 21 ppm, respectively. Figure 6 shows the ^{13}C NMR spectrum measured for chitosan.

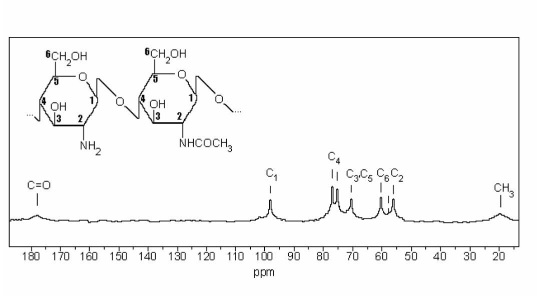


Figure 6. Spectrum of the chitosan ^{13}C NMR

Figure 7 illustrates plots for total coverage of solid phase (θ_T) as a function of the concentration of adsorbate in liquid phase (C_e).

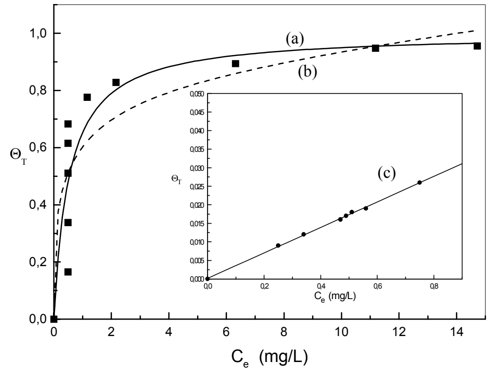


Figure 7. Adsorption isotherm of the black 5 reactive dye by chitosan microspheres. (a) Langmuir (pH 2), (b) Extended Freundlich (pH 2) and (c) Nernst (pH 10). 100 mg chitosan microspheres, T = 25.0 ± 0.5 °C, μ = 0.100 mol/L

From equation 3 it could be observed that *m* is equal to 0.27 for black 5 dye. Low values of *m* indicate a lesser degree of energetic heterogeneity for adsorption, and therefore surfaces indicating just one adsorption site, i.e., the experimental plots, are better fitted using Langmuir's isotherm than the extended Freundlich's one. The former considers the overall surface as divided into groups of identical sites having the same adsorption energy. In this case, the main chitosan adsorption sites for pH < 3 are the $-NH_3^+$ groups that may adsorb $-SO_3^-$ anions from the dye by ionic interaction. The maximum capacity (q_m) of black 5 reactive dye (28.9 ± 2.8) mg/g was obtained from the non-linear method.

For pH 10, the adsorption of the dye by chitosan microspheres was rather limited. Adsorption plots fitted a linear isotherm similar to a Nernst's one. The value of the partition coefficient (K) obtained was 0.034 ± 4.796.10^{-4} L/g. A linear adsorption isotherm suggests that the solutes do not interact strongly with specific surface sites on the adsorbent (Podoll apud Gonzales-Davila, 1990), indicating a non-specific interaction of the dye on the chitosan. In alkaline media, the chitosan amino groups are not protonated and do not interact with the sulfonate groups of the dye. The little adsorption that takes place may be attributed to van der Waals interaction and hydrogen bonds.

Therefore, this support polymer may be used for the removal of reactive dyes of textiles wastewaters effluents.

Acknowledgements

The authors would like to acknowledge the financial support granted by UFSC, CAPES – PICD and UEM.

References

BROUSSIGNAC, J. Un haut polymère natural peu connu dans l'industrie le chitosane. *Chim. Ind. Gén. Chim.*, v. 99, n. 9, p. 1241-1247, 1970.

COLOUR INDEX. USA: Society of Dyers and Colourist and American Association of Textile Chemists and Colourists, 1971.

DOMSZY, J. G.; ROBERTS, A. F. Evalution of infrared spectroscopic technique for analyzing chitosan. *Makromol.*, v. 186, p. 1671-1677, 1985.

GACÉN, J.; GACÉN, I. Quitina y quitosano. Nuevos materiales textiles. *Boletín Intexter*, v. 110, p. 67-71, 1996.

GONZALES-DAVILA, M. *et al*. The adsorption of Cd(II) and Pb (II) to chitin in seawater. *J. Coll. Interface Sci.*, San Diego, v. 137, n. 1, p. 102-109, 1990.

HACKMAN, R. H. Adsorption of proteins to chitin. *Aust. J. Biol. Sci.*, Collingwood, v. 5, p. 530-537, 1955.

KIM, Y. C. *et al*. Effect of deacetylation on sorption of dye and chromium on chitin. *J. Appl. Polym. Sci.*, New York, v. 63, p. 725-736, 1997.

LASZLO, J. A. Removing acid dyes from textile wastewater using biomass for decolorization. *Am. Dyest. Rep*, Secancus, v. 83, p. 17, 1994.

LASZLO, J.A. Waste color removal from textile effluents. *Textile Chem. Color.*, Davis, v. 86, n. 4, p. 17-21, 1995.

MATHUR, N. K.; NARANG, C. K. Chitin and chitosan, versatile polysaccharides from marine animals. *J. Chem. Educ.*, Beijing, v. 67, n. 11, p. 938-942, 1990.

MCKAY, G. Waste color removal from textile effluents. *Am. Dyest. Rep.*, Secancus, v. 86, n. 4, 29-36, 1979.

MCKAY, G.; ALEXANDER, F. The removal of basic dye from effluent using fluidized beds of silica. *Chem. Engineer*, n. 319, p. 243-248, 1977.

MCKAY, G. *et al*. Adsorption of dyes on chitin. I. Equilibrium studies. *J. Appl. Polym. Sci.*, New York, v. 27, p. 3043-3047, 1982.

MOREIRA, R. F. P. M. *et al*. Adsorption of textiles dyes on alumina. Equilibrium studies and contact time effects. *Braz. J. Chem. Engi.*, São Paulo, v. 15, n. 1, p. 221-228, 1998.

MUZZARELLI, R. A. A. *Chitin*. Oxoford: Pergamon Press, 1978.

NAWAR, S.S.; DOMA, H.S. Removal of dyes from effluents using low-cost agricultural by-products. *Sci. Total Environ.*, Amsterdam, v. 79, p. 271-275, 1989.

POOTS, V.J.P. *et al*. The removal of acid dye from effluent using natural adsorbents – Part I Peat. *Water Research*, Kidlington, v. 10, p. 1067-1070, 1976.

RAYMOND, L. *et al*. Degree of deacetylation of chitosan using conductometric titration and solid-state NMR. *Carbohydr. Res.,* Oxford, v. 246-336, p. 331, 1993.

ROCHA, M. S. *et al*. Freendlich's isotherm extended by statistical mechanics, *J. Coll. Int. Sci.*, San Diego, v. 185, p. 493-496, 1997.

RORRER, L. G. *et al.* Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water. *Ind. Eng. Chem. Res.*, Washington D.C., v. 32, n. 9, p. 2170, 1993.

YOSHIDA, H. *et al.* Adsorption of acid dye on cross-linked chitosan fibers: equilibria. *Chem. Eng. Sci.*, Kidlington, v. 48, n. 12, p. 2267-2272, 1993.

ZOLLINGER, H. *Color Chemistry*: Syntheses, properties and applications of organic dyes and pigments. New York: UCH Publishers, 1991.

Received on January 29, 2001.
Accepted on September 24, 2001.