Journal of Chemical Technology and Biotechnology *J Chem Technol Biotechnol* **80**:164–168 (2005)
DOI: 10.1002/jctb.1171

Quaternized biomass as an anion exchanger for the removal of nitrate and other anions from water

Chinnaiya Namasivayam[1,2]* and Wolfgang H Höll[2]

[1] *Department of Environmental Sciences, Bharathiar University, Coimbatore 641 046, India*
[2] *Institute for Technical Chemistry, Section WGT, Karlsruhe Research Center, PO Box 3640, D-76021 Karlsruhe, Germany*

Abstract: Dried Chinese Reed (*Miscanthus sinensis*), a fast growing plant, was used as a model biomass for the development of anion exchangers using a quaternization agent, *N*-(3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHMAC), and a cross-linking agent, epichlorohydrin. Anions studied include nitrate, phosphate, perchlorate and sulfate. Batch mode adsorption studies were conducted using aqueous solutions of anions. Detailed kinetics were studied for nitrate removal. Parameters studied included anion concentration, agitation time, adsorbent dose, and pH. Adsorption equilibrium occurred in 10 min for all the anions studied. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms. The presence of phosphate, perchlorate, fluoride and sulfate lowered the adsorption significantly. The effects of pH on adsorption and desorption show that ion exchange is involved in the adsorption process. The adsorption capacity of the cross-linked and quaternized Chinese Reed for nitrate, sulfate, phosphate and perchlorate was found to be 7.55, 13.25, 16.61 and 10.07 mg of anion per g of the anion exchanger, respectively.

Keywords: quaternized biomass; anion exchanger; nitrate; adsorption isotherms; pH effect

1 INTRODUCTION

Drinking-water sources in developing and under-developed countries are facing serious threat from contamination problems due to both man-made industrial and agricultural activities and natural sources such as minerals. In many developing countries ground water is used for drinking purposes and it is polluted with nitrate, sulfate, perchlorate and phosphate. Though cost-effective methods are available for the removal of pollutant cations from water, decontamination of pollutant anions at low cost is a challenging problem. The guidelines for drinking water prescribed by the WHO for fluoride, nitrate and sulfate are 1.5, 50 and 250 mg dm^{-3}, respectively.[1] California, USA, has set a provisional standard for perchlorate of 18 µg dm^{-3}.[2] Germany's drinking water limit for phosphate is 6.7 mg dm^{-3}.[3] Increased nitrate concentrations in public water supplies presents a potential health hazard due to reduction to nitrite in the gastrointestinal human tract. Nitrite causes methemoglobinemia (cyanosis or 'blue baby syndrome') and both nitrate and nitrite have potential to form carcinogenic *N*-nitroso compounds.[4] Sulfate is one of the least toxic anions; however, catharsis, dehydration, and gastrointestinal irritation have been observed at high concentrations.[5] Perchlorate is a human health concern due to its ability at high doses to interfere with iodine uptake and the ability of the thyroid to regulate hormones and metabolism.[2] Phosphates cause toxic cyanobacterial blooms in water.[6]

The present treatment methods for anion removal from drinking water using ion exchange resins, ultrafiltration, reverse osmosis and activated carbon adsorption are efficient; but they are expensive, especially in poor countries.[7] Hence new materials are being investigated for anion removal, including microbial degradation,[8] activated alumina,[7] amine-modified biomass,[9] kaolinite, bentonite, charfines, lignite and nirmali seeds[10] and soil.[11] These methods are either time-consuming, inefficient or cumbersome. Development of simple and low-cost anion exchangers from indigenous materials could help facilitate the practice of better and less time- consuming water treatment in poor countries. Recently, dried Chinese Reed, a fast growing plant, has been used as an adsorbent for the removal of dyes, phenols, anilines,[12] and Cr(III);[13] and quaternized Hanf Sativa has been studied for the removal of anionic dyes[12] in this laboratory. In the present study, dried Chinese Reed

---

* Correspondence to: Chinnaiya Namasivayam, Bharathiar University, Coimbatore 641 046, India
E-mail: cnamasi@vsnl.com

Contract/grant sponsor: Forschungscentrum Karlsruhe [FZK], Germany
(*Received 2 December 2003; revised version received 21 June 2004; accepted 21 June 2004*)

has been used as a model biomass to prepare anion exchangers by quaternization. To improve the yield and capacity of the anion exchanger, epichlorohydrin was used as a cross- linking agent. Detailed kinetic studies were carried out for the removal of nitrate by the resulting quaternized and cross-linked Chinese Reed. The adsorption capacity was also determined for the removal of other anions, sulfate, perchlorate, and phosphate, from water.

2 EXPERIMENTAL

2.1 Materials

Dried Chinese Reed of particle size 5–50 mm (Agricultural Research Institute, Karlsruhe, Germany) ground and sieved to <0.6 mm particle size was used for the preparation of anion exchangers using the method reported by Laszlo,[14] with some modifications. Biomass (30 g) was soaked in 50 cm^3 of 5 mol dm^{-3} NaOH for 90 min. *N*-(3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHMAC) (Fluka) (30 cm^3) was added and the resulting mixture stirred and left in an air oven at 70 °C for 4 h with intermittent stirring. The reaction mixture was washed with water and finally rinsed with dilute HCl at pH 2. The product, in the chloride form, was filtered and dried in air overnight. For cross-linking, the biomass was treated with 5 mol dm^{-3} NaOH and epichlorohydrin (Aldrich) for 6 h prior to quaternization. The particle size distribution of the final product was: 0.25–0.5 mm (85%) and 0.15–0.25 mm (15%). Solutions of nitrate, sulfate, phosphate, and perchlorate were prepared from $NaNO_3$, Na_2SO_4, KH_2PO_4 and $NaClO_4.H_2O$ (E Merck), respectively.

2.2 Methods

2.2.1 Adsorption studies

Adsorption experiments were carried out by agitating the desired weight of adsorbent with 50 cm^3 of anion solution of the desired concentration and pH at 175 rpm and 25 °C in a rotary shaker. The samples were withdrawn from the shaker at predetermined time intervals and the supernatant solution separated from the adsorbent by 0.45 µm membrane filtration. Fluoride was estimated using a fluoride ion selective electrode (Mettler Toledo, Switzerland). Other anions were estimated using a Dionex DX-500 Ion Chromatograph. The effect of agitation time was studied with 0.4 g of adsorbent and different concentrations of NO_3^- (10–40 mg dm^{-3}) at pH 5.8. The effect of adsorbent dosage was studied using different adsorbent doses (0–1.0 g) and 50 cm^3 of 10 mg dm^{-3} NO_3^- solutions for 10 min. The effect of pH was studied over the range 3.0–10.0 by adjusting the pH of 10 mg dm^{-3} NO_3^- solutions with dilute HCl, $HClO_4$ and NaOH solutions and then agitated with 0.2 g of adsorbent for 10 min. The Langmuir isotherm was obtained using the equilibrium data from the time curves. The Freundlich isotherm was derived using the data of adsorbent dose effect.

2.2.2 Desorption studies

Adsorbent (0.2 g) used for the adsorption of 10 mg dm^{-3} NO_3^- solution at pH 5.8 was separated from the solution by 0.45 µm membrane filtration and washed gently with water to remove any unadsorbed NO_3^-. Several such samples were prepared. The spent adsorbent samples were then agitated for 10 min with 50 cm^3 of distilled water, adjusted to different pH values from 3.0 to 11.2 using dilute HCl, $HClO_4$ and NaOH solutions. The desorbed NO_3^- was determined as before.

All experiments were performed in duplicate and the results were reproducible within ±4% and the mean values were taken for calculation and data analysis.

3 RESULTS AND DISCUSSION

3.1 Effects of agitation time and concentration of NO_3^- on adsorption

The equilibrium reached in 10 min for all NO_3^- concentrations is shown in Fig 1. The percentage equilibrium removal was found to be 92, 90, 89 and 85% for 10, 20, 30, and 40 mg dm^{-3} NO_3^-, respectively. It is clear that the removal of NO_3^- depends on its initial concentration.

3.2 Effect of adsorbent dosage

Figure 2 shows the effect of adsorbent dose on the removal of NO_3^-. Increasing the adsorbent dose increased the percentage removal of NO_3^-, which is due to the increase in the total surface area of the adsorbent used.

3.3 Adsorption isotherms

Adsorption data for a wide range of adsorbate concentrations and adsorbent doses have been treated by Langmuir and Freundlich isotherms, two widely used models. The Langmuir model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is uniform for all the adsorbent sites, and that there is no transmigration of adsorbate molecules in the plane

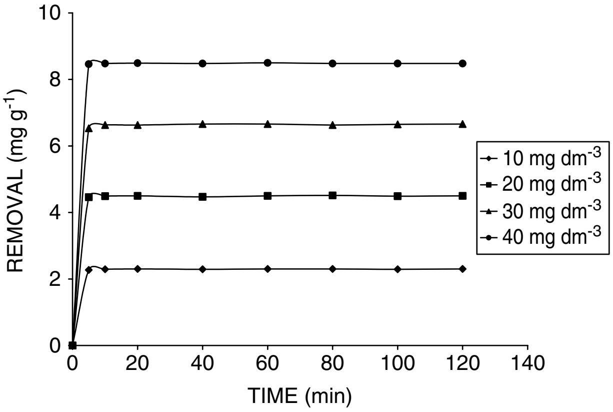

Figure 1. Effect of agitation time and concentration of NO_3^- on removal: adsorbent dose: 0.4 g/50 cm^3; initial pH: 5.8; 175 rpm.

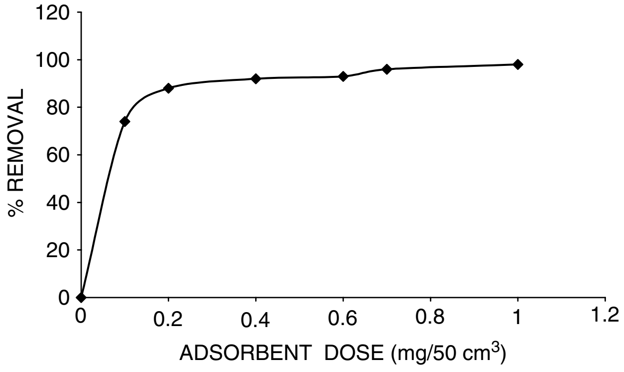

Figure 2. Effect of adsorbent dose on removal of NO_3^-: initial pH: 5.8; agitation time: 10 min; solution volume: 50 cm^3; NO_3^- concentration: 10 mg dm^{-3}.

of the adsorbent surface. Langmuir isotherms were obtained by agitating fixed amounts of the adsorbent and different concentrations of the adsorbate solution for a constant time that is greater than the equilibrium time. The Langmuir isotherm is represented by eqn (1):[15]

$$C_e/q_e = 1/Q_o b + C_e/Q_o \qquad (1)$$

where C_e is the equilibrium concentration (mg dm^{-3}) and q_e is the amount adsorbed (mg g^{-1}) at equilibrium time. Q_o is related to adsorption capacity and b to energy of adsorption. Figure 3 shows that the Langmuir plot is linear. Values of Q_o and b were evaluated and were found to be 7.55 mg g^{-1} and 0.22 dm^3 mg^{-1}, respectively. The essential characteristics of Langmuir isotherm can be expressed by the equilibrium parameter, R_L, a dimensionless constant that indicates the type of isotherm defined by:[16]

$$R_L = 1/(1 + bC_o) \qquad (2)$$

where b is the Langmuir constant and C_o is the initial nitrate concentration (mg dm^{-3}). Calculated R_L values were found to be between zero and one, which indicates favorable adsorption.[16]

The Freundlich equation is basically empirical, but is often useful as a means for data description, and assumes that the adsorbent surface sites have a spectrum of different binding energies. The Freundlich isotherms were obtained in the same way as the Langmuir isotherm and are represented by the following equation:[17]

$$\log(x/m) = \log k_f + 1/n \log C_e \qquad (3)$$

where x is the amount adsorbed (mg) and m is the adsorbent dose used (g). The magnitude of the exponent 'n' gives an indication of the favorability for adsorption and k_f is the capacity of the adsorbent/adsorbate system. In the current studies the adsorption also obeyed the Freundlich isotherm model (Fig 4). Values of n and k_f were calculated respectively from the slope and intercept of the Freundlich plots and were found to be 1.16 and 1.51, respectively.

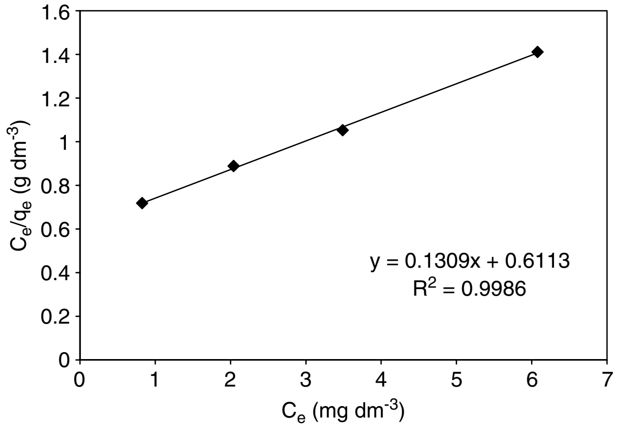

Figure 3. Langmuir plot for the adsorption of NO_3^-.

3.4 Effect of pH

The effect of pH on the adsorption is shown in Fig 5 with removal increasing from 65% at pH 3.0 (HCl) to 88% at pH 5.8, and then decreased to 79% at pH 7.5 and remained constant to pH 10.0. The lower removal at pH 3.0 is due to competition of chloride ions from the HCl medium. In $HClO_4$ medium the removal was lower than in the HCl medium, because of greater competition of the perchlorate ions for the adsorbent sites compared with the chloride ions. At pH values above 6.0, the number of negatively charged adsorbent sites increased and this slightly decreased the adsorption of NO_3^- due to electrostatic repulsion. Figure 5 also shows the final pH vs initial pH for tests where the curve referred to as 'final pH without NO_3^-' was obtained under the conditions $[NO_3^-] = 0$. The pH decrease observed in the blank curve may be explained by the exchange of Cl^- ions of the anion exchanger with OH^- ions of the bulk solution and/or desorption of other anions originally present in the adsorbent. When NO_3^- is present in solution, its uptake will free Cl^- and/or some more OH^- ions and the pH will be higher than in the blank over the pH range <9.0. At an initial pH >9.0, the final pH was found to be lower in the presence of NO_3^- than in its absence. This may be due to the high concentration of

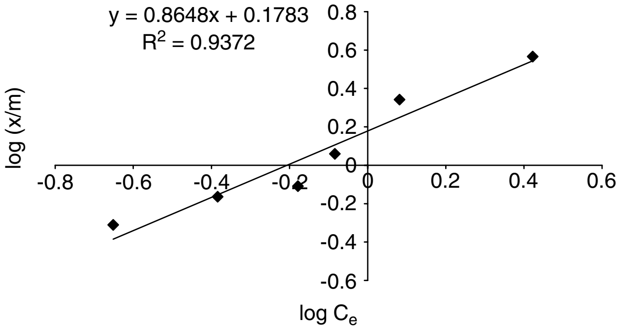

Figure 4. Freundlich plot for the adsorption of NO_3^-.

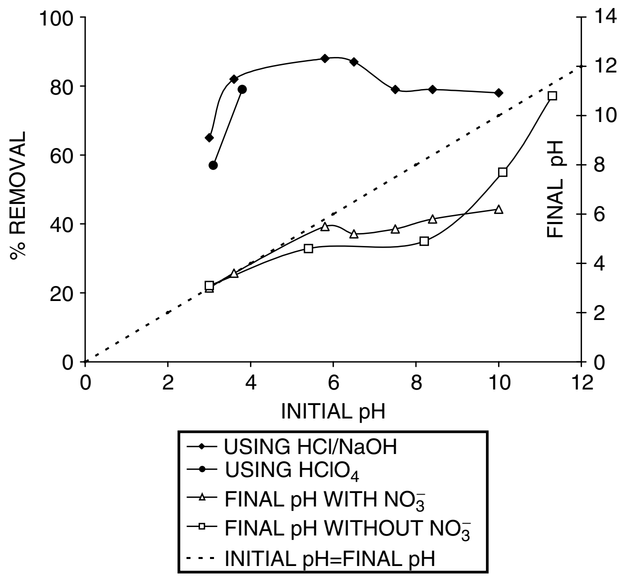

Figure 5. Effect of initial pH on adsorption of NO_3^- and final pH: adsorbent dose; 0.2 g/50 cm^3; NO_3^- concentration: 10 mg dm^{-3}; agitation time: 10 min.

OH^- ions competing with NO_3^- ions to displace Cl^- ions present in the adsorbent.

3.5 Desorption studies

Regeneration of spent adsorbent and recovery of nitrate would make the treatment process more economic. Also, desorption studies help elucidate the mechanism of adsorption. Desorption increased from 9.3 to 92.0%, as the pH was increased from 8.5 to 11.2 (Fig 6). The increasing concentration of OH^- in bulk solution displaces NO_3^- from the adsorbent. This shows that the quaternized biomass behaves like an ion exchanger. The observed desorption was 31% and 41% at pH 3.0 for HCl and $HClO_4$ media, respectively, due to the displacement of NO_3^- ions from the NO_3^--laden adsorbent by Cl^- and ClO_4^- ions from the acids, with ClO_4^- being the stronger competitor.

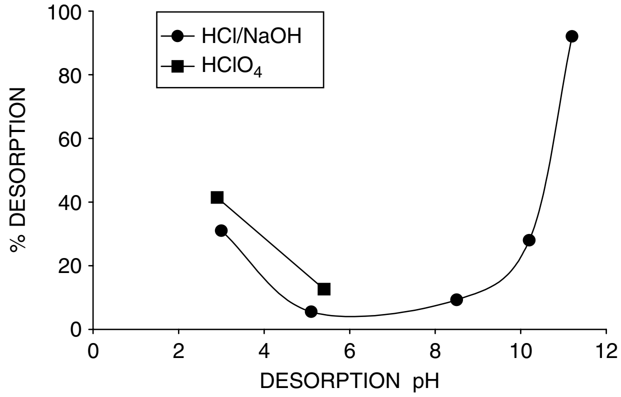

Figure 6. Effect of pH on desorption of NO_3^- from NO_3^--loaded adsorbent: adsorption conditions: adsorbent dose: 0.2 g/50 cm^3; NO_3^- concentration: 10 mg dm^{-3}; agitation time: 10 min, 175 rpm.

3.6 Effect of other anions

In the present study all the tests were carried out with a single anion, ie nitrate solutions. However, in real systems several other ions, which can compete with nitrate, will possibly be present. Table 1 presents studies on the influence of phosphate, perchlorate, fluoride, and sulfate on the removal of nitrate and the corresponding release of chloride in the solution, along with the removal of the other anion. This shows that the above anions are also adsorbed on the quaternized biomass. Detailed kinetic studies on the removal of these and other oxyanions like arsenate, selenate, chromate, vanadate, bromate, bromide, and iodide by the quaternized biomass will be reported elsewhere.

3.7 Adsorption capacity of cross-linked and quaternized Chinese Reed for other anions

Langmuir plots for the adsorption of other anions: sulfate, phosphate and perchlorate are shown in Fig 7. The adsorption capacity for sulfate, phosphate, and perchlorate was found to be 13.25, 16.61 and 10.07 mg of anion per g of the anion exchanger, respectively.

4 CONCLUSION

The present study shows that cross-linked and quaternized biomass acts as a potential anion

Table 1. Effect of other anions on nitrate removal

Anion	% NO_3^- removal	% Removal of the other anion	Chloride release (mg dm^{-3})
No anion	88	—	9.9
PO_4^{3-} (100 mg dm^{-3})	66	47	25.8
ClO_4^- (100 mg dm^{-3})	61		27.7
F^- (100 mg dm^{-3})	41		39.6
SO_4^{2-} (100 mg dm^{-3})	15	68	51.7

Conditions: 10 mg dm^{-3} NO_3^-, 0.2 g adsorbent/50 cm^3, pH 5.8, 10 min agitation time at 175 rpm.

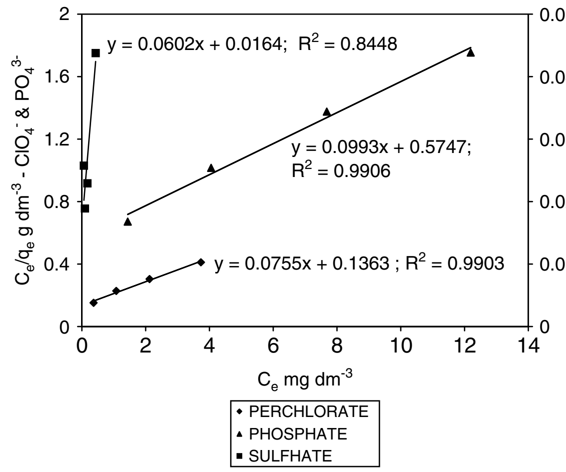

Figure 7. Langmuir isotherm plots for the adsorption of sulfate, phosphate, and perchlorate ions.

exchanger for the removal of anions from water. Adsorption equilibrium occurred very fast, within 10 min. Adsorption equilibrium data for nitrate removal follow both the Langmuir and Freundlich isotherms. The pH effect and desorption studies confirm that removal of nitrate occurs through ion exchange on the quaternized biomass. The presence of sulfate, fluoride, phosphate, and perchlorate considerably lowered the uptake of nitrate. Since the raw materials are abundant, they may be used as a low-cost and natural resource for the removal of anions and may be an alternative to more expensive materials such as activated carbon and ion exchange resin.

ACKNOWLEDGEMENTS

One of the authors (CN) is grateful to Forschungscentrum Karlsruhe [FZK], Germany for the award of visiting scientist program and Bharathiar University for granting sabbatical leave. The authors are thankful to Professor Dr R Nueesch, Director, ITC-WGT, FZK for the facilities.

REFERENCES

1 *WHO Guidelines for Drinking-Water Quality, Health Criteria and Other Supporting Information*, 2nd edn. World Health Organization, Geneva, Vol 2, pp 940–949 (1996). and Addendum to Vol 2, pp 281–283, (1998).

2 Kim K and Logan BE, Fixed bed bioreactor treating perchlorate-contaminated water. *Env Engg Sci* **17**:257–265 (2000).

3 Mavrov V, Fähnrich A and Chimiel H, Treatment of low-contaminated waste water from the food industry to produce water of drinking quality for reuse. *Desalination* **113**:197–203 (1997).

4 Van Leeuwen FXR, Safe drinking water: the toxicologist's approach. *Food Chem Technol* **38**:S51–S58 (2000).

5 *WHO Guidelines for Drinking-Water Quality, Recommendations*, 2nd edn. World Health Organization, Geneva. Vol 1, pp 122–130 (1993).

6 Hester RE and Harrison RM, *Agricultural Chemicals and the Environment*. The Royal Society of Chemistry, Cambridge (1996).

7 Lounici H, Addour L, Belhocine D, Grib H, Nicolas S, Bariou B and Mameri N, Study of a new technique for fluoride removal from water. *Desalination* **114**:241–251 (1997).

8 Logan B, Assessing the outlook for perchlorate remediation. *Environ Sci Technol* **35**:483A–487A (2001).

9 Baes AU, Okuda T, Nishijima W, Shoto E and Okada M, Adsorption and ion exchange of some ground water anion contaminants in an amine modified coconut coir. *Wat Sci Technol* **35**:89–95 (1997).

10 Srimurali M, Pragathi A and Karthikeyan J, A study on removal of fluoride from drinking water by adsorption onto low-cost materials. *Environ Pollut* **99**:285–289 (1998).

11 Zevenbergen C, Van Reeuwijk LP, Frapporti G, Louws RJ and Schuiling RD, A simple method for defluoridation of drinking water at village level by adsorption on Ando soil in Kenya. *Sci Tot Environ* **188**:225–232 (1996).

12 Kräuter A, Sorption Organischer Wasserschadstoffe an Abgestorbene Pflanzliche Biomasse. PhD thesis, Karlsruhe Technical University, Karlsruhe, Germany (2000).

13 Namasivayam C and Hoell WH, Chromium(III) removal in tannery wastewaters using Chinese Reed (*Miscanthus sinensis*), a fast growing plant. *Holz Roh Werkst* **62**:74–80 (2004).

14 Laszlo JA, Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from wastewater. *Tex Chem Color* **28**:13–17 (1996).

15 Langmuir I, The adsorption of gases on plane surface of glass, mica and platinum. *J Amer Chem Soc* **40**:1361–1364 (1918).

16 McKay G, Blair HS and Gardner JK, Adsorption of dyes on chitin. 1. Equilibrium studies. *J Appl Poly Sci* **27**:3043–3057 (1982).

17 Freundlich H, Uber die Adsorption in Losungen. *Z Phy Chem* **57**:387–470 (1985).