Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes

Feng-Chin Wu [a], Ru-Ling Tseng [b], Ruey-Shin Juang [c,*]

[a] *Department of Chemical Engineering, National Lien-Ho Institute of Technology, Miao-Li 360, Taiwan, ROC*
[b] *Department of Safety, Health and Environmental Engineering, National Lien-Ho Institute of Technology, Miao-Li 360, Taiwan, ROC*
[c] *Department of Chemical Engineering, Yuan Ze University, Chung-Li 320, Taiwan, ROC*

Abstract

The adsorption capacities and rates of Cu(II) and a commercial reactive dye RR222 on flake- and bead-types of chitosans prepared from three fishery wastes (shrimp, crab, and lobster shells) were compared at 30°C. It was shown that all equilibrium isotherms could be well fitted by the Langmuir equation. The adsorption capacity of Cu(II) on flake- and bead-types of chitosans appeared to be comparable, but the adsorption capacity of RR222 on bead type was much larger than that on flake type by a factor of 2.0–3.8. The rates of dye adsorption on both types of chitosans indicated different controlling mechanisms. In addition, the bead type of chitosans exhibited a greater rate compared to the flake type. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fishery wastes; Chitosan; Flake; Bead; Comparative adsorption; Metal; Dye

1. Introduction

It was known that liquid-phase adsorption process is very efficient for the removal of colors, odors, and organic pollutants from process or waste effluents. Activated carbons

---

* Corresponding author. Tel.: +886-34638800 ext. 555; fax: +886-3-4559373; e-mail: cejuang@ce.yzu.edu.tw

(powdered and granular forms) are the most widely used adsorbents because they have an excellent adsorption capability for common organic matters, but their use is usually limited due to high cost [1–4]. This has lead many workers to search for cheaper or more effective substitutes such as fly ash, silica gel, zeolite, lignin, seaweed, wool wastes, agricultural wastes (e.g. bagasse pith, maize cob, coconut shell, rice husk, etc.), chitin, chitosan, and clay materials (e.g. fuller's earth, diatomaceous earth, bentonite, kaolinite, montmorillonite, etc.). Compared to activated carbons, they have been already studied with varying success for the removal of pollutants from aqueous streams, especially for heavy metals and reactive dyes [4,5].

Chitosan is a partially acetylated glucosamine biopolymer found in the cell wall of some fungi such as the *Mucorales* strains. However, it mainly results from deacetylation of chitin [6,7]. Of these alternatives, chitosan appears to be more economically attractive for this purpose since chitin is the second abundant polymer in nature next to cellulose. Furthermore, chitosan has many useful features such as hydrophilicity, biocompatibility, biodegradability, and anti-bacterial property. This biopolymer is also a known sorbent, effective in the uptake of transition metals since the amino groups on chitosan chains serve as coordination sites [7]. In contrast to chitin, the adsorption ability of metals with chitosan is superior due to its higher content of amino functional groups [6,8].

A series of experiments will be conducted in our laboratory to evaluate the possibility of the use of chitosan as adsorbent for industrial pollution control. Although many equilibrium and kinetic studies on metal and dye adsorption using chitosan or chitin have been made [9–17], to our best knowledge, the roles of the sources of chitosan preparation and the types of chitosans were little studied. The aim of this paper was to compare the adsorption behavior of flake- and bead-types of chitosans prepared from three fishery wastes. The equilibria and kinetics of adsorption of one heavy metal, Cu(II), and one commercial reactive dye, RR222, on these chitosans from water were investigated. These information will be useful for further application in treatment of practical waste effluents.

2. Materials and methods

2.1. Preparation of chitosans from fishery wastes

In this work, the chitosans were prepared from three fishery wastes (shrimp, lobster, and crab shells). The shells were first immersed in 5 wt.% NaOH for 18 h to remove proteins (solid shells/solutions = 10% w/w) and in 10 wt.% HCl for 18 h to remove all mineral materials (mainly, $CaCO_3$). The resulting insoluble solid is the so-called chitin. The chitin (40 g) was deacetylated in 50 wt.% NaOH (800 g) at 90°C for 3 h. The final flake (or powder) type of chitosan were filtered and washed three times with deionized water (Millipore Milli-Q). They were dried at 50°C in a vacuum for 12 h and finally sieved in the size range 16–30 mesh for further processing.

The chitosan flakes (1 g) were fully dissolved in 1 mol/dm^3 acetic acid solutions (0.1 dm^3). The resulting viscous solutions were gradually poured into another solution

(1 dm^3) containing 15 g NaOH and 25-cm^3 ethanol (95 wt.%) through a 0.8-mm i.d. needle. The whole solutions were settled for 24 h and the chitosan beads was obtained. These beads were also dried at 50°C in a vacuum for 12 h. The mean particle size was 2.39 (shrimp), 3.11 (crab), and 2.93 mm (lobster).

2.2. Measurements of physical properties of the chitosans

Several physical properties of chitosans were measured in this work. The degree of deacetylation was determined following the method of Guibal et al. [9]. The BET surface area was measured from N$_2$ adsorption isotherms with sorptometer (Porous Materials, Model BET-202A). The molar mass was determined by the Mark–Houwink equation from viscosity measurements of solutions containing different amounts of chitosan in 0.1 mol/dm^3 acetic acid and 0.2 mol/dm^3 NaCl [18]. The yield was calculated as the ratio of the weight of final chitosan to that of initial raw wasted shells.

2.3. Adsorption experiments

Analytical reagent grade CuSO$_4$ (Merck) was used. The commercial reactive dye Sumifix Super Scarlet 2 GF (Reactive Red 222, RR222) was offered from Sumitomo Chemical, Japan and used as received. It had vinyl sulfone/monochlorotriazine bifunctional groups. The aqueous solutions were prepared by dissolving the solutes into deionized water to the required concentrations without pH adjustment.

In equilibrium experiments, an amount of chitosan (0.1 g) and 0.1 dm^3 of an aqueous phase were placed in a 0.25-dm^3 glass-stoppered flask and stirred for 5 days using a bath controlled at 30°C (Firstek Model B603, Taiwan). Preliminary experiments showed that the adsorption studied was complete after 3 days. After equilibrium, the aqueous-phase concentration of Cu(II) was analyzed with a Shimadzu atomic absorption spectrophotometer (Model AA68). The concentration of dye was measured with a Hitachi UV/Visible spectrophotometer (U-2000). Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium q_e (g/kg) was obtained as follows

$$q_e = (C_0 - C_e)V/W \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations, respectively (g/m^3), V is the volume of the solution (m^3), and W is the weight of chitosan used (kg).

The batch contact-time experiments were made in a Pyrex glass vessel of 100 mm i.d. and 130 mm high, fitted with four glass baffles, 10 mm wide. In each run, an aqueous solution (0.8 dm^3) was poured and agitated by using a Cole-Parmer Servodyne agitator with six blades, flat-bladed impeller (12 mm high, 40 mm wide). The stirring speed was 500 rpm because above that the agitation has little effect on adsorption. An amount of dry chitosan (0.48 g) was then added into the vessel and the timing was started. The whole vessel was immersed in a water bath controlled at 30°C (Haake Model K-F3). At preset time intervals, aqueous samples (5 cm^3) were taken and the concentration was analyzed.

3. Results and discussion

3.1. Physical properties of the chitosans

Chitin can be basically treated as a poly(*N*-acetyl-D-glucosamine) helix and occurs in three polymorphic forms which differ in the arrangement of molecular chains within the crystal cell [8]. α-Chitin has a rhomb crystalline form where the chains are arranged in an anti-parallel fashion and is more tightly compacted. On the other hand, β-chitin has a monoclinic crystalline form where the chains are parallel and is more loose. The chitin produced from the above three fishery wastes is mostly of the α form.

Table 1 lists the properties of the three chitosans prepared here. The basis is 100 g of raw fishery wastes. It is found that the yields of chitin and chitosan decrease in the order shrimp > lobster > crab. The corresponding ratio of the yield of chitosan to chitin is 0.697, 0.731, and 0.772, respectively, which is less than the theoretical value of 0.793. On the other hand, the degree of deacetylation and molar mass are comparable. The BET surface areas for flake- and bead-types of chitosans are about 4–6 and 30–40 m^2/g, respectively. In addition, the surface area decreases in the order for different sources: crab > lobster > shrimp.

3.2. Equilibrium adsorption

Fig. 1 shows the equilibrium adsorption of Cu(II) at 30°C on ''shrimp'' chitosan. It is seen that the adsorption ability of Cu(II) on both types of chitosans is comparable. The same trends are also observed for other two sources of chitosan preparation (not shown). It is known that the adsorption of transition metal ions on chitosan is mainly effected via coordination with the unprotonated amino groups ($-NH_2$) of chitosan [7,19]. Based on the BET surface area of chitosans, the unusually larger adsorption capacity of Cu(II) on flake type of chitosan at high C_e (> 35 g/m^3) can be explained by the pore-blockage mechanism [20]. This mechanism indicated that the distribution of solutes sorbed may be determined by intraparticle diffusion rate of the solutes into the porous matrix, which is in turn by the concentration gradient of solutes and the sorbent particle porosity. At low C_e, the initial flux through the matrix is low and so Cu(II) binds with amino sites near the outer surface of the particle. Eventually, the adsorbed Cu(II) clogs the pores near the outer surface so Cu(II) can no longer diffuse to active sites deep within the interior surface. In this case the solute is mostly loaded in a shell near the outer surface of the particle. In contrast, at high C_e the initial flux is high and so Cu(II) shoots deep into the

Table 1
Physical properties of chitosan flakes prepared from fishery wastes[a]

Source	Chitin (g)	Chitosan (g)	Degree of deacetylation (%)	Molar mass	Intrinsic viscosity
Shrimp	21.0	14.6	80.9	7.93×10^5	7.66
Crab	10.8	8.3	76.3	7.97×10^5	7.69
Lobster	17.3	12.7	77.9	7.44×10^5	7.16

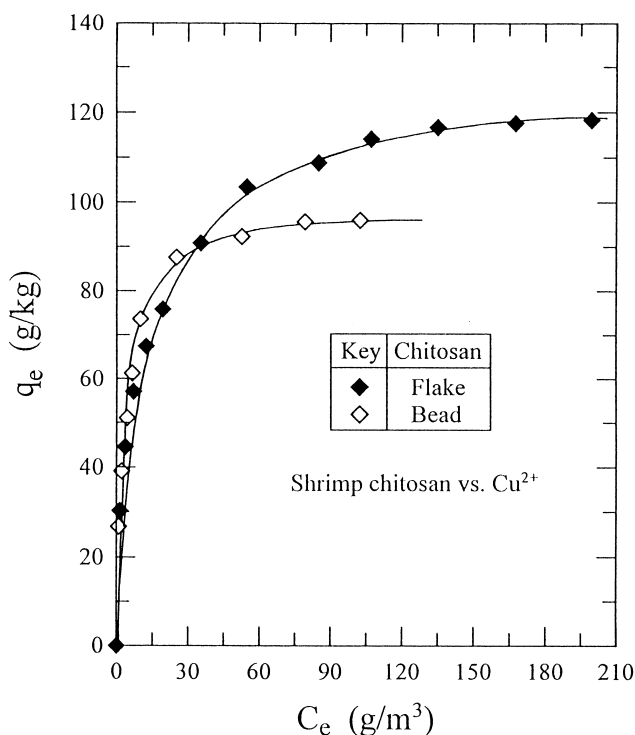[a] Basis: 100 g of fishery wastes.

Fig. 1. Equilibrium adsorption of Cu(II) on the chitosans prepared from shrimp shell.

interior matrix until the pores are finally clogged. This behavior is more pronounced for flake type of chitosan because it has a more restricted pore structure (a smaller pore volume) and/or a more steric hindrance of the amino groups in the particle.

Adsorption isotherm is important to describe how solutes interact with adsorbent and so is critical in optimizing the use of adsorbent. Correlation of isotherm data by empirical or theoretical equations is thus essential to practical operation. The widely used Langmuir equation is given as:

$$C_e/q_e = (1/K_L q_{mon}) + (1/q_{mon})C_e \qquad (2)$$

where q_{mon} is the amount of adsorption corresponding to complete monolayer coverage. K_L is the Langmuir constant. A linearized plot of (C_e/q_e) vs. C_e gives K_L and q_{mon}. Table 2 lists the calculated results. The fit is quite well for Cu(II) adsorption on both types of chitosans under the concentration range studied (correlation coefficient, $R >$ 0.998).

The equilibrium adsorption of dye RR222 at 30°C on chitosans prepared from three fishery wastes is shown in Fig. 2. It is found that all these isotherms are well fitted by the Langmuir equation (Table 2). Unlike Cu(II) adsorption, the bead type of chitosan gives a higher capacity for RR222 (q_{mon}) than the flake type by a factor 2.0–3.8, depending on the sources of fishery wastes. This is probably because the chitosan

Table 2
Parameters in the Langmuir equation obtained for solute adsorption on chitosans prepared from fishery wastes at 30°C[a]

Source	Type	Cu(II)			RR222		
		K_L	q_{mon}	$R\,(-)$	K_L	q_{mon}	$R\,(-)$
Shrimp	Flake	0.11	123.1	0.998	0.054	494	0.992
	Bead	0.24	103.8	0.999	0.204	1026	0.995
Crab	Flake				0.036	293	0.995
	Bead				0.185	1106	0.995
Lobster	Flake				0.052	398	0.998
	Bead				0.203	1037	0.998

[a]Unit: K_L (m^3/g) and q_{mon} (g/kg).

''bead'' has a much higher BET surface area (i.e. more loose pore structure) than the ''flake'', which facilitates the adsorption of RR222, a rather larger molecule than Cu(II) [21]. It should be noted that the order of q_{mon} for different sources is exactly identical to that of surface area, i.e., crab > lobster > shrimp.
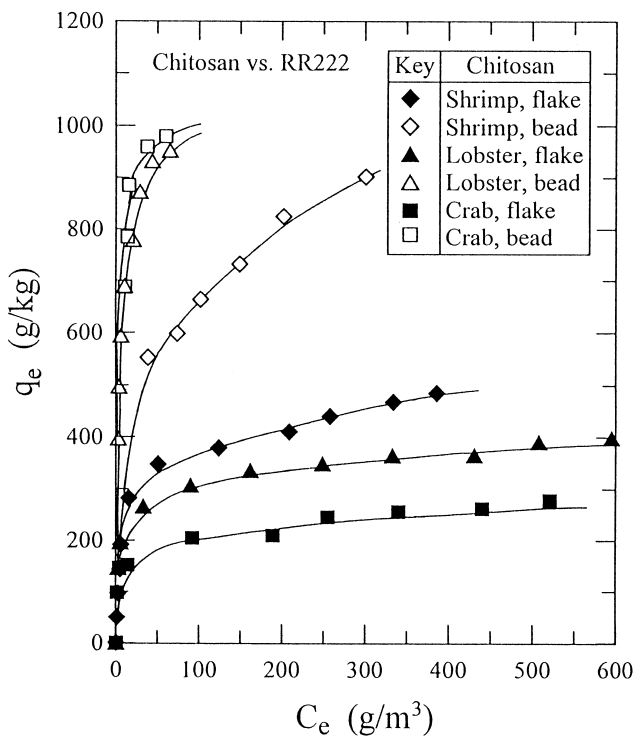

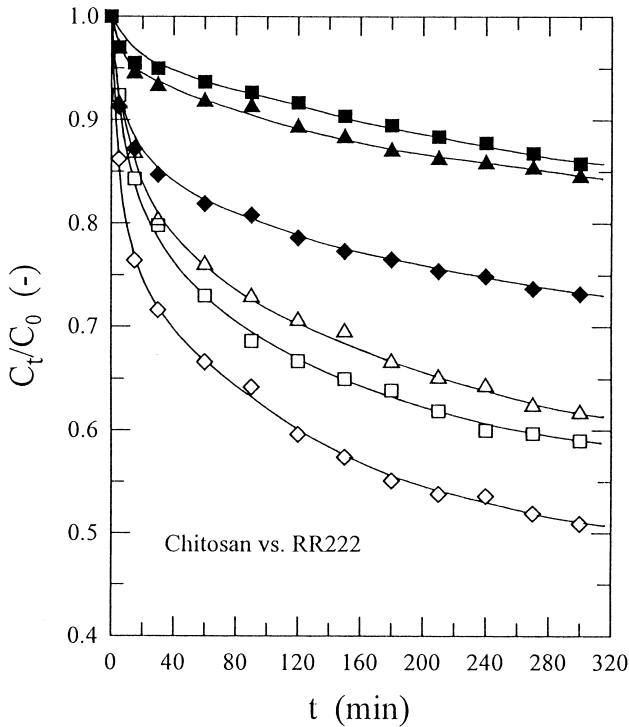Fig. 2. Equilibrium adsorption of RR222 on the chitosans prepared from fishery wastes.

Fig. 3. Time profiles of aqueous-phase concentration for RR222 adsorption on different chitosans. $C_0 = 1020-1180$ g/m^3. The meaning of each symbol is identical to that shown in Fig. 2.

3.3. Adsorption rates: pseudo first- and second-order equations

Fig. 3 shows the time profiles of adsorption of RR222 on chitosans. It is found that the adsorption is faster using bead type of chitosan. In order to examine the controlling mechanism of adsorption such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. A simple kinetic analysis of adsorption is the pseudo first-order equation in the form [22,23]:

$$dq_t/dt = k_1(q_e - q_t) \tag{3}$$

where q_t is the amount of adsorption at time t and k_1 is the rate constant of pseudo first-order adsorption. After integration and applying the initial condition $q_t = 0$ at $t = 0$, Eq. (3) becomes to

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

In addition, a pseudo second-order equation based on adsorption equilibrium capacity may be expressed in the form [22,23]:

$$dq_t/dt = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the rate constant of pseudo second-order adsorption. Integrating Eq. (5) and applying the initial condition, we have

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{6}$$

or equivalently,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

It is noticed that, compared to Eq. (6), Eq. (7) has an advantage that k_2 and q_e can be calculated from the intercept and slope of the plot of (t/q_t) vs. t and there is no need to know any parameter beforehand.

Figs. 4 and 5 show the results. As reported earlier, the pseudo first-order equation is expressed in a range of reaction only, although it has been adequately used to describe adsorption reactions [22–24]. For pseudo second-order equation (Fig. 5), a two-step linear relationship is obtained using flake type of chitosan. Since this equation is based on the adsorption capacity, it predicts the behavior over the ''whole'' range of studies
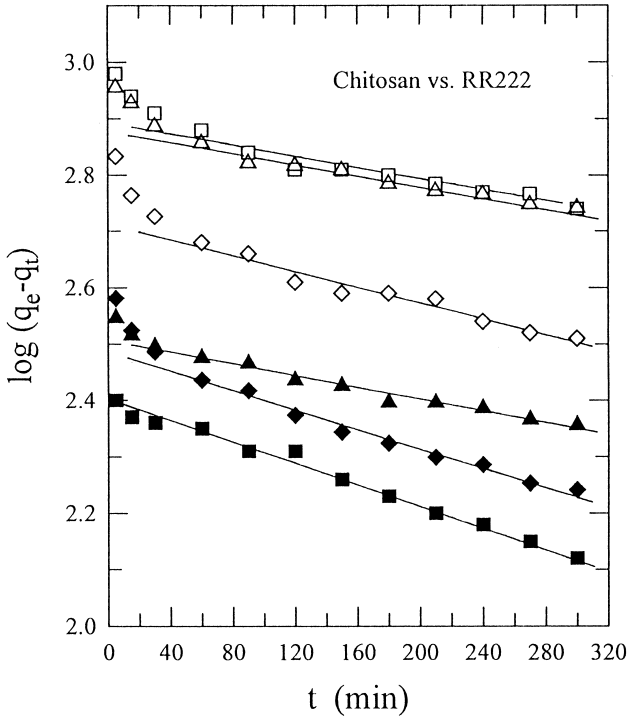

Fig. 4. Test of pseudo first-order equation for RR222 adsorption on different chitosans. The meaning of each symbol is identical to that shown in Fig. 2.
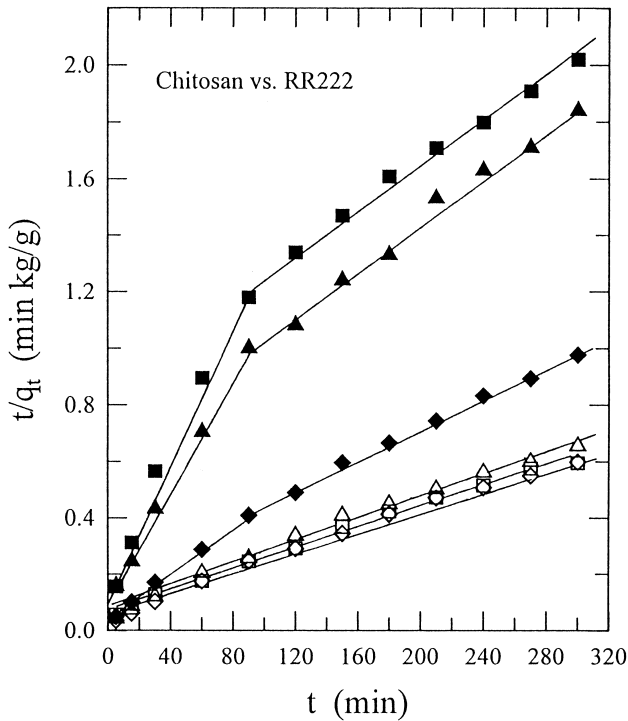
Fig. 5. Test of pseudo second-order equation for RR222 adsorption on different chitosans. The meaning of each symbol is identical to that shown in Fig. 2.

supporting the validity, and is in agreement with chemisorption being the rate-controlling. Thus, the present findings remain uncertain about the adsorption mechanisms.

3.4. Adsorption mechanism: intraparticle diffusion model

Because the above two models cannot give definite mechanisms, another model is desired. Intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [25]. Fractional approach to equilibrium changes according to a function of $(Dt/r^2)^{1/2}$, where r is the particle radius and D is the diffusivity within the particle. The initial rates of intraparticle diffusion are obtained by linearization of the curve $q_t = f(t^{1/2})$. Fig. 6 shows the results.

Previous work showed that such plot may present a multi-linearity [26], which means that two or more steps occur. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is controlled [27]. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution [28]. A good correlation of rate data in this model justifies the adsorption mechanisms [12].
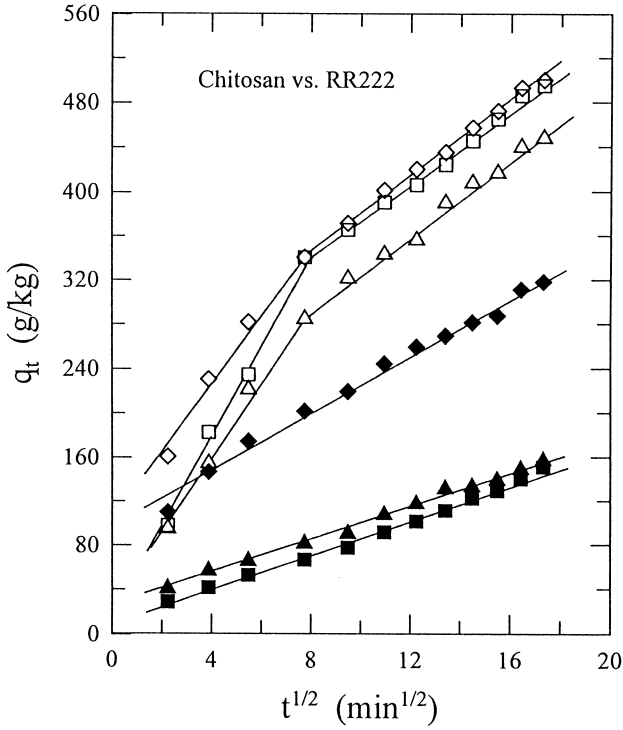
Fig. 6. Test of intraparticle diffusion model for RR222 adsorption on different chitosans. The meaning of each symbol is identical to that shown in Fig. 2.

The slope of the line in each stage is termed as the rate parameter $k_{p,i}$ ($i = 1$–3). The external surface adsorption (stage 1) is less apparent (Fig. 6). Such phenomena have been seen for adsorption of reactive dyes and the chelated anions on chitosans [13,17]. The stage 1 is completed within about 5 min. The stage of intraparticle diffusion control (stage 2) is then attained and extended to 60 min for bead type of chitosan. The rate parameters $k_{p,2}$ for both types of chitosans are listed in Table 3. It is clearly seen that the adsorption on bead type of chitosan is much faster than on flake types by a factor of 2.7–5.8.

Table 3
Rate parameters of intraparticle diffusion for RR222 adsorption on chitosans

Source	Flake type	Bead type	
	$k_{p,2}$ (g/kg min$^{1/2}$)	$k_{p,2}$ (g/kg min$^{1/2}$)	$k_{p,3}$ (g/kg min$^{1/2}$)
Shrimp	12.9	35.2	15.9
Crab	7.7	44.6	15.5
Lobster	8.1	34.5	15.8

When the bulk and surface dye concentrations start to drop, the third stage for bead type of chitosan is due to a drop in diffusion rate (Fig. 6). It is noticed that stage 3 is absent for flake type of chitosan over the whole range studied. The much longer period of intraparticle diffusion for these chitosans is likely due to their tighter pore structure.

In summary, compared to flake type of chitosan the high capacity and high rate of adsorption on bead type provide the potential possibility for industrial pollution control, especially for high-molecular-weight solutes.

4. Conclusions

Physical properties such as the degree of deacetylation, molar mass, surface area, and the yield of the chitosans prepared from three fishery wastes are measured. Equilibrium and kinetics of adsorption of Cu(II) and reactive dye RR222 on flake- and bead-types of the chitosans are compared at 30°C. The following results are obtained.

(1) For the chitosans prepared from the three wastes, the adsorption capacity of Cu(II) on flake- and bead-types of chitosans is comparable. However, the bead type of chitosan has a higher capacity for RR222 than the flake type by a factor 2.0–3.8, which is likely because RR222 is a rather larger molecule than Cu(II). All isotherm data can be well fitted by the Langmuir equation (Table 2).

(2) Both pseudo first-order and second-order equations cannot successfully confirm the mechanism. The intraparticle diffusion model shows the external surface adsorption to complete within 5 min only. The stage of intraparticle diffusion control is extended to 60 min for bead type of chitosan. The rate parameter $k_{p,2}$ indicates that the adsorption on bead type of chitosan is much faster than on flake types by a factor of 2.7–5.8. The much longer period of intraparticle diffusion for flake type of chitosan is likely due to their tighter pore structure.

(3) Compared to flake type of chitosan, the high capacity (Table 2) and high rate (Table 3) of adsorption on bead type of chitosan provide their potential possibility for industrial pollution control, especially for high-molecular-weight pollutants.

Nomenclature

C_e	Solute concentration in the aqueous phase at equilibrium (g/m^3)
C_t	Solute concentration in the aqueous phase at time t (g/m^3)
C_0	Initial solute concentration in the aqueous phase (g/m^3)
D	Diffusivity in the particle (m^2/s)
k_1	Rate constant of pseudo first-order adsorption defined in Eq. (3) $(1/min)$
k_2	Rate constant of pseudo second-order adsorption defined in Eq. (5) $(g/kg\ min)$
$k_{p,i}$	Rate parameter of intraparticle diffusion model $(g/kg \cdot min^{1/2})$
K_L	Parameter of the Langmuir equation (m^3/g)
q_e	Amount of adsorption at equilibrium (g/kg)
q_{mon}	Amount of adsorption corresponding to monolayer coverage (g/kg)

q_t	Amount of adsorption at time t (g/kg)
r	Radius of the particle (m)
R	Correlation coefficient
t	Time (min)
V	Volume of the solution (m^3)
W	Amount of the dry chitosans used (kg)

References

[1] A.K. Bhattacharya, C. Venkobachar, Removal of cadmium(II) by low cost adsorbents, J. Environ. Eng. ASCE 110 (1984) 110–122.

[2] G. McKay, G.R. Prasad, P.R. Mowli, Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials, Water Air Soil Pollut. 29 (1986) 273–283.

[3] M.M. Nassar, M.S. El-Geundi, Comparative cost of color removal from textile effluents using natural adsorbents, J. Chem. Technol. Biotechnol. 50 (1991) 257–264.

[4] M.S. El-Geundi, Adsorbents for industrial pollution control, Adsorpt. Sci. Technol. 15 (1997) 777–787.

[5] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[6] T.C. Yang, R.R. Zall, Adsorption of metals by natural polymers generated from seafood processing wastes, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 168–172.

[7] E. Onsoyen, O. Skaugrud, Metal recovery using chitosan, J. Chem. Technol. Biotechnol. 49 (1990) 395–404.

[8] R.A.A. Muzzarelli, Chitin and its derivatives: new trends of applied research, Carbohydr. Polym. 3 (1983) 53–75.

[9] E. Guibal, I. Saucedo, M. Jansson-Charrier, B. Delanghe, P. Le Cloirec, Uranium and vanadium sorption by chitosan and derivatives, Water Sci. Technol. 30 (9) (1994) 183–190.

[10] E. Guibal, C. Milot, J.M. Tobin, Metal-anion sorption by chitosan beads: equilibrium and kinetic studies, Ind. Eng. Chem. Res. 37 (1998) 1454–1463.

[11] C.P. Huang, Y.C. Chung, M.R. Liou, Adsorption of Cu(II) and Ni(II) by pelletized biopolymer, J. Hazard. Mater. 45 (1996) 265–277.

[12] M. Jansson-Charrier, E. Guibal, J. Roussy, B. Delanghe, P. Le Cloirec, Vanadium(IV) sorption by chitosan: kinetics and equilibrium, Water Res. 30 (1996) 465–475.

[13] R.S. Juang, R.L. Tseng, F.C. Wu, S.H. Lee, Adsorption behavior of reactive dyes from aqueous solutions on chitosan, J. Chem. Technol. Biotechnol. 70 (1997) 391–399.

[14] G. McKay, H.S. Blair, J.R. Gardner, Adsorption of dyestuffs on chitin. External mass transfer processes, J. Appl. Polym. Sci. 27 (1982) 4251–4261.

[15] G. McKay, H.S. Blair, J.R. Gardner, Rate studies for the adsorption of dyestuffs on chitin, J. Colloid Interface Sci. 95 (1983) 108–119.

[16] G. McKay, Mass transfer processes for the adsorption of dyestuffs on chitin, Chem. Eng. Process. 21 (1987) 41–51.

[17] F.C. Wu, R.L. Tseng, R.S. Juang, Role of pH in metal adsorption from aqueous solutions containing chelating agents on chitosan, Ind. Eng. Chem. Res. 38 (1999) 270–275.

[18] G.A.F. Roberts, J.G. Domszy, Determination of viscometric constants for chitosan, Int. J. Macromol. 4 (1982) 374–379.

[19] O.A.C. Monteiro Jr., C. Airoldi, Some thermodynamic data on copper–chitin and copper–chitosan biopolymer interactions, J. Colloid Interface Sci. 212 (1999) 212–219.

[20] G.L. Rorrer, T.Y. Hsien, J.D. Way, Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water, Ind. Eng. Chem. Res. 32 (1993) 2170–2178.

[21] H. Ishii, M. Koyama, T. Mitani, Removal of organic acids by highly swollen chitosan beads, J. Environ. Sci. Health A 30 (1995) 945–950.

[22] Y.S. Ho, G. Mckay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Trans. IChemE. 76B (1998) 332–340.

[23] Y.S. Ho, G. Mckay, Comparative sorption kinetic studies of dyes and aromatic compounds onto fly ash, J. Environ. Sci. Health A 34 (1999) 1179–1204.

[24] D. Sarkar, D.K. Chattoraj, Activation parameters for kinetics of protein adsorption at silica-water interface, J. Colloid Interface Sci. 157 (1993) 219–226.

[25] W.J. Weber, J.C. Morris, Advances in water pollution research: removal of bio-logically resistant pollutants from waste waters by adsorption, in: Proc. Int. Conf. on Water Pollution Symposium, Vol. 2, Pergamon, Oxford, 1962, pp. 231–266.

[26] G. McKay, H.S. Blair, A. Findon, Sorption of metals by chitosan, in: H. Eccles, S. Hunt (Eds.), Immobilization of Ions by Biosorption, Ellis Horwood, Chichester, 1986, pp. 59–69.

[27] G. McKay, M.S. Otterburn, A.G. Sweeney, The removal of color from effluent using various adsorbents: III. Silica: rate processes, Water Res. 14 (1980) 15–20.

[28] G. McKay, Adsorption of dyestuffs from aqueous solutions using activated carbon, J. Chem. Technol. Biotechnol. 33A (1983) 196–204.