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Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization

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Abstract

The enhancement of abilities for the removal of reactive dyes and immobilization of tyrosinase onto highly swollen chitosan beads was demonstrated compared to the use of common chitosan flakes. Chitosan was prepared from natural cuttlebone wastes. It was shown that the adsorption capacity of dyes at 30°C using swollen chitosan beads was around five times greater than that using common chitosan flakes. The adsorption of dyes using swollen beads was faster by 10–40% depending on the types of dyes. Finally, the capacity of tyrosinase immobilization onto swollen beads was about 14 times greater than chitosan flakes, which was reflected by the higher yield of 3,4-dihydroxyphenylalanine from tyrosine and ascorbic acid in the heterogeneous catalytic system.

Keywords: Capacity enhancement; Swollen chitosan beads; Color removal; Tyrosinase immobilization

1. Introduction

Chitosan is a partially acetylated glucosamine biopolymer which exists in the cell wall of some fungi such as the Mucorales strains. In fact, it mainly results from deacetylation of chitin [1,2]. Chitosan is a widely used sorbent for transition metals and organic species because both amino (-NH_2) and hydroxy (-OH) groups on chitosan chains can serve as coordination and reaction sites [3,4]. This biopolymer is also an ideal support for enzyme immobilization because it has many features such as hydrophilicity, biocompatibility, biodegradability and anti-bacterial property [5–7]. In addition to this, chitosan appears

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to be economically attractive because chitin is the second-most abundant polymer in nature next to cellulose [8,9].

In our laboratory, the adsorption of various dyes and divalent metals from aqueous solutions, in the absence or presence of strong complexing agents such as EDTA, citrate and tartrate, onto chitosan "flakes" has been examined [10–15]. However, the adsorption capacities were only comparable to those obtained using commercially available activated carbons. A series of work will thus, be made to improve the adsorption ability of chitosan materials. In this paper, an attempt was first made to enhance the ability only via physical modification of such adsorbents. Two model systems, that is, color removal and enzyme immobilization, were evaluated for this purpose.

Among the use of chitosan flakes prepared from four fishery wastes including shrimp shell, lobster shell, crab shell and cuttlebone, it has been found that the cuttlebone-made flakes gives the highest adsorption capacity for Cu(II), Ni(II) and Cd(II) ions [15]. This is because the chitin produced from cuttlebone wastes is mostly of β-form and those from other three fishery wastes are mostly of α-form [16]. The larger degree of water swelling of β-chains in cuttlebone-made chitosan enlarges the pore volume to a larger extent, thus, improving the adsorption ability. In this regard, the cuttlebone wastes were selected as raw materials to prepare chitosan adsorbents in this work.

2. Experimental

2.1. Preparation of chitosan flakes and swollen beads

Dried cuttlebone wastes were immersed in 5 wt.% NaOH for 18 h to remove proteins and then in 5 wt.% HCl for 18 h to remove $CaCO_3$ (the weight ratio of wastes to solutions was 1:10). The resulting insoluble solid (40 g), chitin, was deacetylated in 50 wt.% NaOH (800 g) at 90°C for 3 h. The final product, chitosan, was washed three times with deionized water (Millipore Milli-Q) and dried at 50°C in a vacuum. Prior to use as adsorbent, the chitosan "flakes" were ground and sieved into a particle size range of 1.00 to 1.41 mm.

Three physical properties of chitosan flakes, degree of deacetylation, molar mass and BET surface area, were measured. The former was found to be 96.6 mol % following the method of Guibal et al. [17]. The molar mass was measured to be 1.85×10^6 by the Mark–Houwink equation from the viscosity data of solutions containing different amounts of chitosan in 100 mol m^{-3} acetic acid and 200 mol m^{-3} NaCl [18]. The BET surface area was found to be 11.8 m^2 g^{-1} based on N_2 adsorption isotherms using sorptometer (Porous Materials Inc., Model BET-202A).

The highly swollen chitosan beads was prepared in an usual manner [19]. An aliquot of chitosan flakes (1 g) was completely dissolved in 100 cm^3 of 1 mol dm^{-3} acetic acid. The resulting solution was sprayed into 125 cm^3 deionized water (Millipore Milli-Q) containing 15 g NaOH and 25 cm^3 ethanol through a thin nozzle (diameter, 0.8 mm). The chitosan beads were formed and washed with deionized water until the solution became neutral. The diameter of wet beads was about 2.8 mm. The BET surface area of swollen beads was not measured because the drying was difficult.

2.2. Adsorption of dyes

The commercial-grade reactive dyes were purchased from Sumitomo Chemical Co. Ltd., Japan and used as received. They were Sumifix Super Scarlet 2 GF (Reactive Red 222, RR222), Sumifix Super Yellow 3 RF (Reactive Yellow 145, RY145) and Sumifix Super Navy Blue BF (Reactive Blue 222, RB222). They all had monochlorotriazine and vinyl sulfone bifunctional groups [11]. Acetic acid and other inorganic chemicals were the products of Merck as analytical-grade reagents. The solutions were prepared by dissolving the dyes in deionized water without pH adjustment.

Kinetic experiments were made in a Pyrex vessel of 100 mm i.d. and 130 mm high, fitted with four glass baffles, 10 mm wide. An aqueous solution (0.6 dm^3) was poured and agitated 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 the agitation above this has little effect on adsorption rate. An amount of chitosan was added into the vessel and the timing was started. The vessel was immersed in a bath controlled at 30°C (Haake Model K-F3). Samples (5 cm^3) were taken at preset time intervals and the concentrations of dyes were measured with a Hitachi UV-visible spectrophotometer (Model U-2000). The amount of adsorption at time t, q_t (g kg^{-1}), was obtained as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 and C_t are the liquid-phase concentrations at the initial and time t, respectively (g m^{-3}), V is the volume of solution (m^3), and W is the weight of chitosan used (kg).

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 tests had shown that the equilibrium was achieved after 4 days. After equilibrium, the liquid-phase concentration of dyes was similarly analyzed. Each run was at least duplicated under identical conditions. The amount of adsorption at equilibrium q_e (g kg^{-1}) was obtained as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_e (g m^{-3}) is the liquid-phase concentration of solute at equilibrium.

2.3. Immobilization of tyrosinase

An amount of chitosan flakes or beads (0.5 g) was cross-linked by contacting with 10 cm^3 of 10 wt.% glutaraldehyde (Merck) in a shaker for 24 h at 30°C. This renders them insoluble in acidic media and improve resistance to chemical and biological degradation [20]. Cross-linking can also enhance the mechanical strength and abrasion resistance of the beads so that the beads are suitable for use in a packed column. After washing with deionized water three times, the cross-linked chitosan was stored in a vessel containing phosphate buffer (pH 6) at 4°C. The tyrosinase solution (10 cm^3, pH 6) was poured into the vessel and shaken for 24 h at 30°C. The resulting chitosan was washed with deionized water three times.

Ten milliliter of solution containing 0.01 g tyrosine (Merck) and 10 mmol ascorbic acid (Merck) was mixed with tyrosinase-immobilized chitosan for 24 h at 30°C. Samples were immediately taken from the upper layer of the solution and the concentrations of species were analyzed by HPLC (Jasco, Model PU-986) with a Nova-Pak C18 column (Waters, 4 μm) and an UV detector at 254 nm. The mobile phase contained 25 mol m^{-3} phosphate buffer (pH 6) and was flowed at 1 cm^3 min^{-1}.

3. Results and discussion

3.1. Equilibrium adsorption

Fig. 1 shows the equilibrium adsorption of reactive dyes at 30°C on the chitosan flakes and swollen beads. It is found that the amount of adsorption decreases in the order RR222 > RB222 > RY145 and this sequence is much less apparent using chitosan flakes. Furthermore, the adsorption capacity significantly increases using swollen chitosan beads compared to the use of chitosan flakes.

The isotherm is important to describe how solutes interact with adsorbents and so is critical in optimizing the use of adsorbents. The known Langmuir equation is given by

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_{mon}}\right) + \left(\frac{1}{q_{mon}}\right) C_e \tag{3}$$

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) versus C_e gives K_L and q_{mon} (not shown). Table 1 lists the calculated results. The fit is well for all adsorption systems under the concentration range

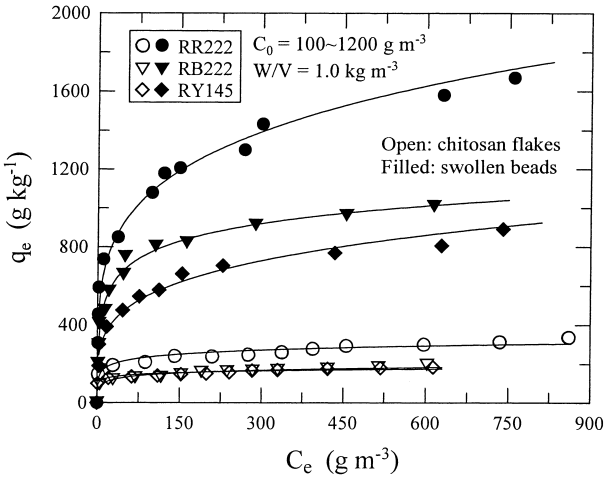

Fig. 1. Equilibrium adsorption of dyes from aqueous solutions using chitosan flakes and swollen beads (the solid curves are calculated by the Langmuir equation).

Table 1
Parameters in the Langmuir equation obtained at 30°C

Dye	Type of chitosan	Langmuir		
		K_L ($m^3\,g^{-1}$)	q_{mon} ($g\,kg^{-1}$)	R^2
RR222	Swollen bead	0.0295	1653	0.988
	Flake	0.0169	339	0.990
RB222	Swollen bead	0.0574	1009	0.997
	Flake	0.0251	199	0.991
RY145	Swollen bead	0.0352	885	0.992
	Flake	0.0270	188	0.994

studied (correlation coefficient, $R^2 > 0.988$). It is found that the adsorption capacities of three reactive dyes (q_{mon}) using highly swollen chitosan beads are about five times greater than that using chitosan flakes. For example, the maximum q_{mon} for RR222 using swollen beads is $1653\,g\,kg^{-1}$.

3.2. Kinetics of adsorption

Fig. 2 shows the time profiles of solid-phase concentrations (q_t) for adsorption of dyes. It is seen that the use of swollen beads enhances the processes at the initial stage of adsorption. In order to examine the mechanism of adsorption such as mass transfer and chemical reaction, a suitable kinetic model is needed.

The large number and array of different chemical groups on chitosan chains (e.g. -NH_2, -OH) imply that there are many types of chitosan-dye interaction [4]. Any kinetic or mass

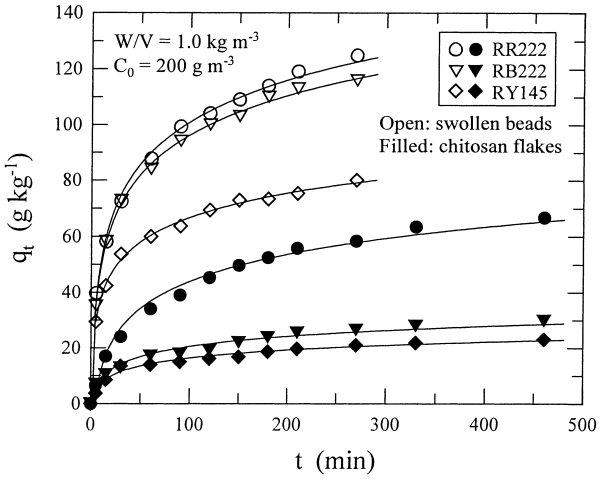

Fig. 2. Time profiles of solid-phase concentrations of dyes using chitosan flakes and swollen beads.

transfer representation is probably to be global. From a system design viewpoint, a lumped analysis of adsorption rates is sufficient to practical operation. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [21,22]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

where k_1 is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (4) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

Also, a pseudo-second-order equation based on equilibrium adsorption is expressed in the form [21,23]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

where k_2 is the rate constant of pseudo-second-order adsorption. This model assumes that the rate-limiting step may be chemical adsorption. Thus, it must be initially assumed that the adsorption obeys the Langmuir equation as confirmed above. Integrating Eq. (6) and applying the initial conditions, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{1}{q_{e2}}t \tag{7}$$

It is noted that k_2 and q_{e2} in Eq. (7) can be obtained from intercept and slope of the plot of (t/q_t) versus t without knowing any parameter beforehand.

Because the above two equations cannot give definite mechanism, the intraparticle diffusion model was tested. Weber and Morris [24] indicated that the fraction of solute adsorbed can be expressed in terms of the square root of time. A plot of fraction of solute absorbed against $t^{1/2}$ may be used to estimate the intraparticle diffusion rate in the linear range. That is, the fractional approach to equilibrium changes according to a function of $(Dt/r^2)^{1/2}$, where r is the particle radius and D the diffusivity of solute within the particle. The initial rates of intraparticle diffusion are thus, obtained by linearization of the curve $q_t = f(t^{1/2})$ [25].

Previous studies have shown that such plots may present a multi-linearity, indicating that two or more steps occur [26,27]. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage where intraparticle diffusion is rate-controlled. The third portion is final equilibrium stage where intraparticle diffusion starts to slow down due to low solute concentrations in the solution. A good correlation of the rate data in this model can justify the mechanisms. In general, the slope of the lines in each stage is termed as the rate parameter $k_{p,i}$ (i = stage number).

As indicated above, the validity of these models is checked in Figs. 3–5 by each linear plot of $\log(q_e - q_t)$ versus t, (t/q_t) versus t, and q_t versus $t^{1/2}$, respectively. Table 2 lists the results. Based on the correlation coefficients, the adsorption of three dyes RR222, RB222

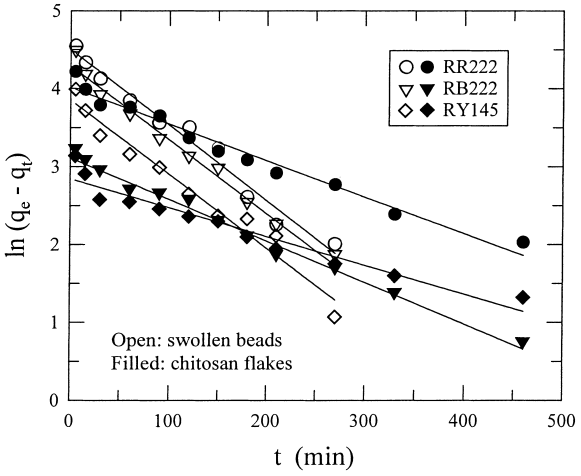

Fig. 3. Test of pseudo-first-order equation for adsorption of dyes using chitosan flakes and swollen beads.

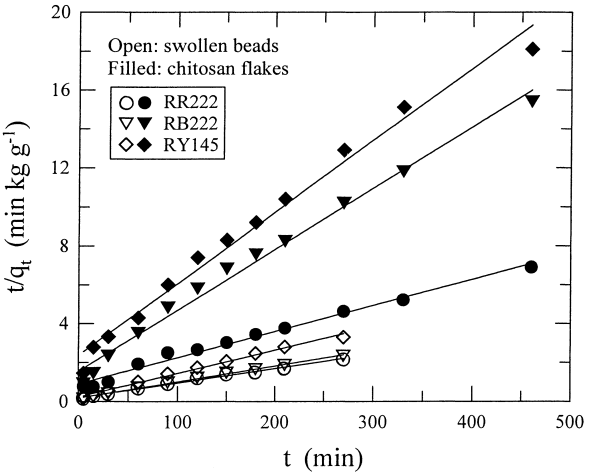

Fig. 4. Test of pseudo-second-order equation for adsorption of dyes using chitosan flakes and swollen beads.

Table 2
Kinetic parameters for dye adsorption onto chitosan at 30°C ($C_0 = 200\,g\,m^{-3}$)[a]

Dye	Chitosan	First-order		Second-order			Intraparticle	
		k_1	R^2	k_2	q_{e2}	R^2	$k_{p,2}$	R^2
RR222	Bead	9.1×10^{-3}	0.957	2.9×10^{-4}	135	0.990	6.06	0.962
	Flake	4.7×10^{-3}	0.971	2.0×10^{-4}	74.3	0.986	3.05	0.946
RB222	Bead	9.5×10^{-3}	0.981	6.8×10^{-4}	122	0.996	5.37	0.934
	Flake	5.3×10^{-3}	0.979	6.1×10^{-3}	31.9	0.989	1.21	0.969
RY145	Bead	1.1×10^{-2}	0.915	6.3×10^{-3}	86.5	0.993	3.35	0.939
	Flake	3.7×10^{-3}	0.966	5.7×10^{-3}	26.7	0.988	0.91	0.904

[a] Unit: k_1 (min^{-1}), k_2 ($kg\,g^{-1}\,min^{-1}$), $k_{p,2}$ ($g\,kg^{-1}\,min^{-1/2}$), q_{e2} ($g\,kg^{-1}$).

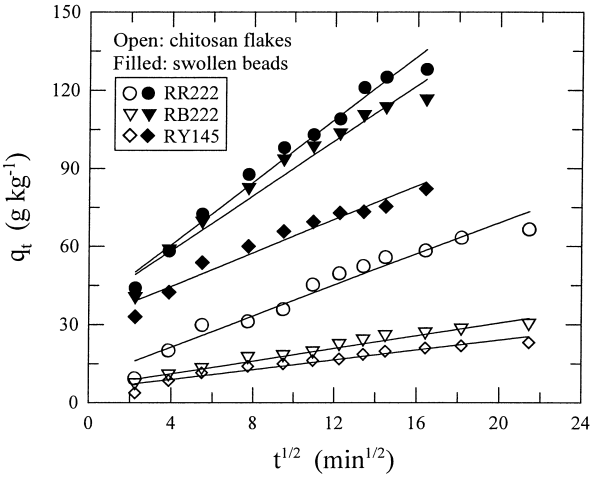

Fig. 5. Test of intraparticle diffusion model for adsorption of dyes using chitosan flakes and swollen beads.

and RY145 can be best described by the pseudo-second-order equation. It is also found that the adsorption of dyes onto swollen beads is faster by the ranges from 10% (RB222, RY145) to 40% (RR222), compared to the use of chitosan flakes.

Literature review showed that most adsorption reported can be represented as pseudo-first-order rate equation [21,28]. For all systems examined here, this model is restricted to a limited range of reactions, as also found earlier [29]. For pseudo-second-order equation, a two-step linear relation is obtained although the range of first step is much shorter (Fig. 4). Because this equation is based on equilibrium adsorption (q_e), it predicts the behavior over the "whole" range of studies supporting the validity and agrees with chemisorption (chemical reaction) being rate-controlling [21,23].

3.3. Reactions on tyrosinase-immobilized chitosan

Fig. 6 shows the chromatograms of reaction mixtures between tyrosine and ascorbic acid using immobilized tyrosinase onto chitosan flakes and swollen beads, respectively. The enzymatic reaction can be represented as follows [30,31]:

$$\text{tyrosine} \overset{\text{tyrosinase, } O_2}{\rightarrow} \text{dopaquinone} \overset{\text{ascorbic acid}}{\rightarrow} \text{3, 4-dihydroxyphenylalanine}$$

It is found that the peak area of product 3,4-dihydroxyphenylalanine while using swollen chitosan beads has a ratio of about 14 (498, 189/35, 800) compared to immobilization of tyrosinase onto chitosan flakes. This is mostly attributed to an increase in the capacity of tyrosinase immobilization onto swollen beads.

Finally, it should be noted that the capacity increment of tyrosinase immobilization is much greater than that of dye adsorption. The stronger affinity of cross-linked chitosan chains to tyrosinase, rather than reactive dyes, is probably the main reason.

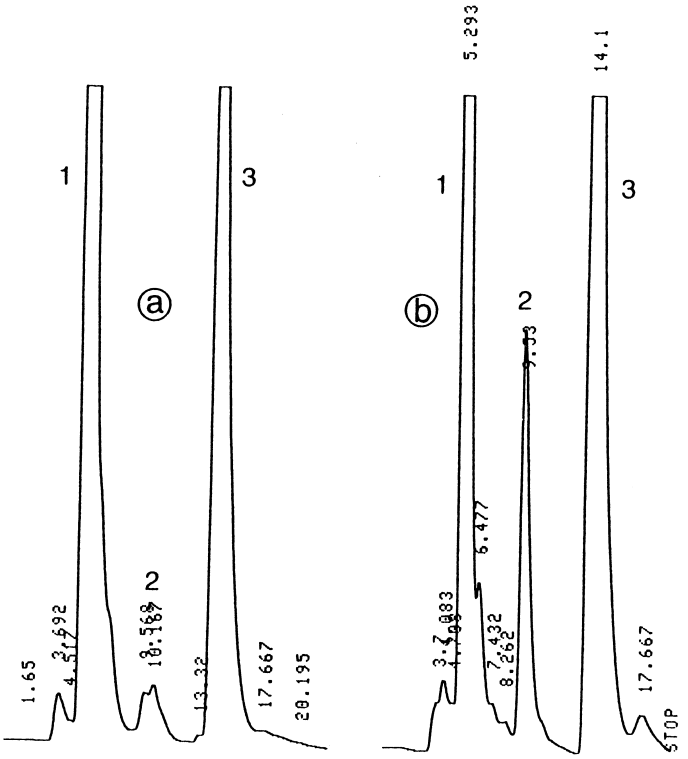

Fig. 6. Chromatogram of reaction mixtures for tyrosinase-immobilized onto (a) chitosan flakes and (b) swollen beads. Peak identification: ascorbic acid (1), 3,4-dihydroxy-phenylalanine (2) and tyrosine (3).

4. Conclusions

The abilities of removal of three reactive dyes (RR222, RB222, and RY145) and of immobilization of tyrosinase using flake-type and highly swollen bead-type of chitosans at 30°C were compared. The adsorption isotherms could be well fitted by the Langmuir equation. The capacity of dye adsorption (q_{mon}) using swollen chitosan beads was about five times, up to 1653 g kg^{-1}, greater than that using chitosan flakes. The adsorption process could be best described by the pseudo-second-order equation, indicating the controlling nature of chemisorption (chemical reaction). The rate of dye adsorption, in terms of rate constant, using swollen beads was larger by the ranges from 10% (RB222, RY145) to 40% (RR222). Based on the yield of 3,4-dihydroxyphenylalanine for reaction of tyrosine and ascorbic acid in the tyrosinase-immobilized system, the immobilization capacity of tyrosinase onto swollen beads was around 14 times greater than onto chitosan flakes. In addition, the capacity increment of tyrosinase immobilization was much greater than dye adsorption. The highly swollen chitosan beads proposed in this work showed promising potential for applications to enzyme immobilization and color removal.

Nomenclature

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 of solute in the particle ($m^2\,s^{-1}$)
$k_{p,2}$	rate parameter of intraparticle diffusion ($g\,kg^{-1}\,min^{-1/2}$)
k_1	rate constant of pseudo-first-order adsorption defined in Eq. (4) (min^{-1})
k_2	rate constant of pseudo-second-order adsorption defined in Eq. (6) ($kg\,g^{-1}\,min^{-1}$)
q_e	amount of adsorption at equilibrium defined in Eq. (2) ($g\,kg^{-1}$)
q_t	amount of adsorption at time t defined in Eq. (1) ($g\,kg^{-1}$)
r	radius of the particle (m)
R	correlation coefficient
t	time (min)
V	volume of the solution (m^3)
W	weight of dry chitosan used (kg)

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