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Removal of Methyl Red, a cationic dye, Acid Blue 113, an anionic dye, from wastewaters using chitin and chitosan: influence of copper ions

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ABSTRACT

Chitin and chitosan were employed as biosorbent for removal of methyl red (MR), a cationic dye and azo dye, and acid blue (AB113), an anionic dye in single-component systems and in the presence of Cu(II) ions. Kinetic studies indicate that AB113 adsorption on chitin and chitosan in a single-component system follows pseudo-first order kinetics while the pseudo-second order rate model provided the best correlation of the kinetic data for MR adsorption on both chitin and chitosan. For the single system, AB113 adsorption isotherm follows the Langmuir model while MR adsorption follows the Freundlich isotherm. Among the tested models, the multi-component three-parameter Redlich–Peterson model showed the best fit for both the Cu(II)-AB113 and Cu(II)-MR adsorption equilibrium data both on chitin and chitosan. In the single-dye and binary metal-dye systems, chitosan exhibits relatively higher affinity and capacity than chitin.

Keywords: Industrial wastewaters; Chitin; Chitosan; Acid Blue 113; Methyl Red; Adsorption; Multi-component adsorption

1. Introduction

Wastewater from textile and dye manufacturing industries as well as pulp and paper industries contains dye stuff, suspended solids, and other soluble substances such as organics and heavy metals. Dyes and heavy metal ions are important pollutants, causing environmental and health problems to human being and aquatic animals. Dyes and pigments are emitted into wastewaters and produce difficult to treat water contamination, as the colour tends to persist even after the conventional removal processes. Removal of dyes and heavy metals from wastewater can be achieved by several techniques, such as precipitation [1], flocculation [2], adsorption [3], ion exchange [4], and membrane separation [5–6]. Photo-catalysis, mainly using TiO_2-anatase [7] and Fenton process [8] can only be used in the removal of dyes. The conventional techniques used for dyes and heavy metal removal are expensive, have low efficiency [9]. Adsorption using low-cost adsorbents is believed to be the simplest and most cost-effective technique [10,11].

Much attention has recently been focused on various biosorbent materials such as fungal or bacterial biomass and biopolymers that can be obtained in large quantities from these microorganisms and that are harmless to nature [12,13]. Application of chitinous products in wastewater treatment has received considerable attention in recent years [14,15]. Chitosan is derived by deacetylation of the naturally occurring biopolymer chitin which is the second most abundant aminopolysaccharide in the world after cellulose [16]. Chitin, low cost material, is extracted from the exoskeleton of crustaceans, the cuticles of insects, and the cells walls of fungi [17]. Chitin is a linear homopolymer composed of β(1–4)-linked N-acetyl glucosamine. It is an aminopolymer and has acetamide groups at the C–2 positions in place of the hydroxyl groups [18].

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Chitosan is a polysaccharide composed by polymers of glucosamine and N-acetyl glucosamine. It has produced by partial deacetylation of chitin. The fully deacetylated chitosan is rarely obtained due to the risks of undesired side reactions and chain depolymerization. Chitosan and chitin are of commercial interest due to their high percentage of nitrogen, biodegradability, biocompatibility, film-forming ability, bioadhesivity, polyfunctionality, hydrophilicity and adsorption properties. Most of the properties of chitosan can be related to its cationic nature [16–18] . The ability of the anionic dyes to adsorb onto chitosan beads is often attributed to the surface charge which depends on the pH of the medium. Dye adsorption occurred through electrostatic attraction on protonated amine groups. Chitosan had a positively charged surface below pH 6.4 (point of zero potential). When pH is decreased more protons becomes available to protonate the amine group of chitosan with the formation of a large number of cationic amines. This results in increasing dye adsorption by chitosan due to increased electrostatic interactions [19–21].

The production of chitosan derivatives for the treatment of wastewater containing metal ions has been investigated by various researchers in recent years [22,23]. Among these chitosan derivatives, carboxymethyl chitosan is an amphoteric ether derivative containing active carboxyl (–COOH), hydroxyl (–OH), and amino ($-NH_2$) groups in a molecule [24]. A new chitosan derivative with zwitter ionic characteristics has been synthesized by quaternization of the amine group of chitosan and esterification of hydroxyl groups with EDTA dianhydride and has been used for the removal of cationic species (Cu^{2+}, Co^{2+}, Ni^{2+}) and anionic species in a single aqueous solution [25]. Chitosan composites with inorganic substances have also caused much attention recently in many research fields such as catalysis or photocatalysis. A novel core-shell organic-inorganic hybrid material of surface imprinted chitosan-TiO_2 composite has been prepared with methyl orange as the template [26]. A kind of biocomposite has been prepared by the intercalation of chitosan in bentonite and the cross-linking reaction of chitosan with glutaraldehyde [27]. Removal of methyl orange from aqueous solutions has been investigated in batch system. Up to now, the research on the adsorption of metal ions or dyes by chtin-chitosan or modified chitosan has mainly focused on single-component systems. However, relatively less work has been performed to elucidate the details of the adsorption behavior of anionic dye-cation or cationic dye-cation in multi-component systems, which are frequently encountered composition of industrial effluents. In our previous study, as Cu(II) ions and crystal violet dye have cationic properties, their dual adsorption characteristics by chitin and chitosan has been proved to be competitive and antagonistic [28].

Adsorption equilibrium is established when the amount of dye being adsorbed onto the adsorbent is equal to the amount being desorbed. The equilibrium adsorption isotherms are obtained by plotting the concentration of the dye in the solid phase versus that in the liquid phase. Three isotherm models, Langmuir, Freundlich and Redlich-Peterson, was tested to describe the equilibrium adsorption of AB113 and MR from single-component systems on chitin and chitosan.

The Langmuir model assumes that all sites are energetically equivalent [29].

$$q_{eq} = \frac{q_s \; bC_{eq}}{1 + bC_{eq}} \tag{1}$$

where q_{eq} (mmol/kg) is the amount of adsorbate per unit weight of adsorbent in equilibrium with a solution concentration, C_{eq} (mmol/L); q_s is the maximum amount of sorbed material required to give a complete monolayer on the surface, b is the ratio of adsorption/ desorption rates and $a = q_s\, b$.

The Freundlich model assumes a logarithmic decrease in the heat of sorption with the fraction of surface covered by the sorbed solute [30]:

$$q_{eq} = K_F C_{eq}^{1/n} \tag{2}$$

where K_F and $1/n$ are the adsorption capacity parameter and isotherm non-linearity factor, representing adsorption intensity, respectively.

Another isotherm equation such as a three-parameter isotherm proposed by Redlich-Peterson seems to more adequately fit the broad range of equilibrium data [31].

$$q_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{\beta}} \tag{3}$$

If β is equal to 1, then Eq. (3) becomes the Langmuir equation. If $a_R C_{eq} \beta$ is much greater than 1, then it becomes the Freundlich equation. If $a_R C_{eq} \beta$ is much less than 1, which occurs at low concentrations, then it becomes a linear isotherm equation. Although the Langmuir and Freundlich models have been widely used to define equilibrium parameters of fungal biosorption, the application of the Redlich-Peterson equation to biosorption is scarce in the literature. The three parameter isotherm of Redlich-Peterson that has been empirically developed for multi-component mixtures is given as [32]:

$$q_{i,eq} = \frac{K_{R,i} C_{i,eq}}{1 + \sum_{j=1}^{N} a_{R,i} C_{j,eq}^{\beta_j}} \tag{4}$$

In addition to equilibrium studies, the kinetics of the sorption has to be determined in order to establish the time course of the dye uptake. The study of sorption kinetics in waste water treatment is also important as it provides deep understanding of the reaction pathways and the mechanism of sorption reactions. Two sorption kinetic models were tested in this study for the sorption of AB113 and MR onto chitin/chitosan: Pseudo-first order rate equation of Lagergren and the pseudo-second order kinetic rate equation.

The pseudo-first order equation of Lagergren is generally expressed as follows [33]:

$$\frac{dq}{dt} = k_{s1}(q_{eq} - q) \tag{5}$$

where q_{eq} and q are the amount of component sorbed per unit weight of sorbent at equilibrium and at any time t, respectively (mmol g^{-1}) and k_{s1} is the rate constant of pseudo-first order sorption (1 min^{-1}). After integration and applying boundary conditions, for $t = 0$, $q = 0$, the integrated form of Eq. (1) becomes [34] :

$$\log\left(q_{eq}-q\right)=\log\left(q_{eq}\right)-\frac{k_{s1}}{2.303}t \tag{6}$$

If the rate of sorption is a second order mechanism, the pseudo-second order kinetic rate equation is expressed as [35]:

$$\frac{dq}{dt}=k\left(q_{eq}-q\right)^2 \tag{7}$$

where k is the rate constant of pseudo-second order sorption (g mmol^{-1} min^{-1}). Integrating this equation for the boundary conditions for $t = 0$, $q = 0$ gives:

$$\frac{t}{q}=\frac{1}{kq_{eq}^2}+\frac{1}{q_{eq}}t \tag{8}$$

The intercept of the linearised pseudo-second order rate equation gives the second order rate constant, k.

In this study, the adsorption behavior of MR, a cationic dye, and AB113, an anionic dye in single-component systems and in the presence of Cu(II) ions was investigated. Mutual interactions of MR, AB113 and Cu(II) ions were evaluated, synergistic and antagonistic interactions between the dyes and Cu(II) ions were defined. The accordance of multi-component or competitive adsorption of the dyes and Cu(II) ions to the multi-component Redlich-Peterson model was examined.

2. Materials and methods

Chitin prepared from shrimp shells [poly (N-acetyl-1,4-β-D-glucopyranosamine)] $(C_8H_{13}NO_5)n$ (CAS1398-61, practical grade, powder (SIGMA)) and chitosan [2-amino-2-deoxy-(1,4)-β-D-glucopyranan; poly(1,4-β-D-glucopyranosamine)] (CAS9012–76–4, (ALDRICH)) were used for simultaneous removal of MR and AB113 and Cu(II) ions. Chitosan prepared by the partial deacetylation of chitin in hot alkali has a degree of deacetylation 75–85%. Chitosan has low molecular weight, approximately 50,000–190,000 daltons based on viscosity. Before utilization of the sorbents, the chitin and chitosan were ground and sieved into particle diameter d_p(µm) – $400 < d_p < 550$. Batch kinetics and equilibrium experiments were conducted at a constant temperature (25°C), in an orbital agitated incubator operated at 150 rpm, using 250-mL flasks. The sorption media consisted of a total volume of 150 mL. Batch type contact studies were continued for 24 h. Preliminary experiments to estimate the optimum pH, temperature and sorbent quantity for the adsorption of MR, AB113 dyes and Cu(II) ions from the aqueous solution by chitin and chitosan were set. The maximum adsorption for MR, AB113 dyes and Cu(II) ions in the single-component systems was obtained at pH 5.0, at 25°C and when a amount of chitin and chitosan of 0.8 g was used [36]. Experiments that examined the effect of Cu(II) ions on the adsorption of MR and AB113 by chitin and chitosan were also performed at pH 5.0, at 25°C and using 0.8 g of the adsorbent. The Cu(II) solutions in the concentration range of 25–200 mg/L were prepared to required concentrations by diluting 1 g/L stock solution of Cu(II) dissolving $Cu(NO_3)_2{\cdot}3H_2O$ in distilled water. The concentrations of MR, AB113 dyes were held constant at 100, 200, 300, 400, and 500 mg/L. The pH value of the solutions was adjusted to pH 5.0 by using 0.1 M NaOH and HNO_3. Before mixing the chitin and chitosan flakes with the dyes and metal-bearing solution, 3 mL samples were taken from the sorption media. Subsequently, samples were taken at 2–5 min intervals at the beginning of sorption and at 15–30–60 min intervals before adsorption equilibrium was reached and then centrifuged at 19,000 g for 5 min. The concentration of remain Cu(II) ions in the supernatant liquid was determined using an atomic absorption spectrophotometer (Thermo Scientific ICE 300 AA) with an air-acetylene flame. The concentration of unadsorbed MR and AB113 in the sorption medium was analyzed via UV visible spectrophotometer (Thermo Genesys 10s Model) at 450 nm and 580 nm, respectively.

3. Results and discussion

In this study, the adsorption of AB113 and MR dyes in single systems and Cu(II) ion-dye stuffs in binary systems on chitin and chitosan was investigated. The results were given in terms of initial adsorption rates, amount of adsorbed material per unit weight of adsorbent at equilibrium and adsorption efficiency. The compliance of equilibrium removal of heavy metal and dye stuff to adsorption isotherms and kinetic models was investigated and the values of adsorption parameters were determined.

3.1. Single-component adsorption of AB113 by chitin and chitosan

The maximum initial adsorption rate of AB113 on chitin was obtained as 1.165 mg/g-min at an initial AB113 concentration of 200 mg/L while a maximum initial adsorption rate of 1.943 mg/g-min at an initial AB113 concentration of 500 mg/L was reached by chitosan. The highest adsorption efficiency for AB113 was achieved with the value of 82.5% in the adsorption onto chitin at 100 mg/l initial concentration, then decreased to 70.8% at 500 mg/l initial concentration. The adsorption efficiency of AB113 on chitosan also decreased with increasing initial dye concentration from 86.2% to 70.7% in the initial concentration range of 100–500 mg/L. The maximum adsorbed amounts of AB113 removal per unit weight of chitin and chitosan at 500 mg/l initial dye concentration were found as 66.7 mg/g and 66.4 mg/g, respectively. The adsorption equilibrium data were analysed using the non-linear Langmuir, Freundlich and Redlich-Peterson adsorption equilibrium models. The adsorption model constants were estimated from the adsorption data of AB113 on chitin and chitosan by using a Microsoft Office 2013 Excel software. The adsorption isotherms for the AB113 adsorption on chitin and chitosan are given in Fig. 1a

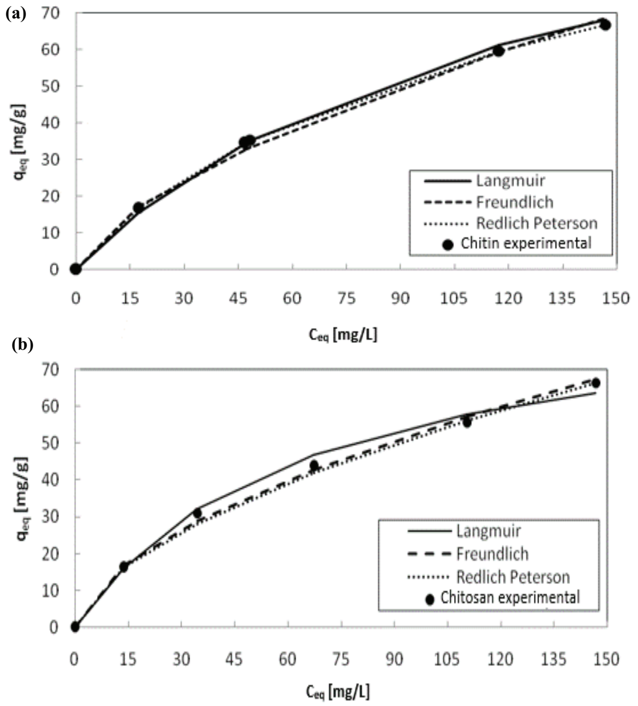

Fig. 1. The adsorption isotherms for AB113 adsorption on a) chitin and b) chitosan, respectively. The Langmuir, Freundlich and Redlich-Peterson model profiles are presented in full, dushed and dot lines, respectively, whereas the symbols denote experimentally obtained values.

and 1b, respectively. In the figures where AB113 adsorption equilibrium data are shown, the Langmuir, Freundlich and Redlich-Peterson model profiles are presented in full, dushed and dot lines, respectively, whereas the symbols denote experimentally obtained values. The Freundlich and Redlich-Peterson isotherms adequately fitted the equilibrium adsorption data. However, the equilibrium adsorption of AB113 both on chitin and chitosan was represented better by the Langmuir model (Table 1). The maximum amount of adsorbed AB113 required to give a complete monolayer on the surface for chitin, q_s, was higher than that for chitosan. Chitin and chitosan have a finite capacity for the AB113 at equilibrium, a saturation point is reached where no further adsorption can occur.

Kinetic aspects of the adsorption of AB113 by chitin and chitosan were investigated using the pseudo first order kinetic model of Lagergren and the pseudo-second order model and the first and second order rate constants were compared. Adsorption kinetics of AB113 showed the best fit to pseudo first order kinetic model (Tables 2, 3). The pseudo first order rate constants for the adsorption of AB113 by chitin and chitosan were found to be 0.012 (1/min) and 0.009 (1/min), respectively. Fig. 2a and 2b shows the kinetic curves plotted q_t against t and plots of the linearized form of the pseudo-first order model for the adsorption of AB113 onto chitin at various initial AB113 concentrations for contact times of 180 min. When adsorption is proceeded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first-order rate equation of Lagergren. A true first order sorption reaction log q_{eq} should be equal to the intercept of a plot of log(q_{eq} −

Table 1
The Langmuir, Freundlich and Redlich-Peterson adsorption constants for the AB113 adsorption by chitin and chitosan

Langmuir Model	a (L·g^{-1})	b (L·mg^{-1})	q_s (mg·g^{-1})	R^2	RPE (%)
Chitin	1.020	0.008	125	0.938	13.08
Chitosan	1.436	0.016	90.9	0.998	3.83
Freundlich model	K$_F$ (mg$^{(1-1/n)}$ g^{-1}·L^{-n})	1/n	n	R^2	RPE (%)
Chitin	2.705	0.648	1.543	0.868	14.17
Chitosan	3.658	0.583	1.715	0.993	3.54
Redlich-Peterson model	a$_R$ (mg$^{\beta+1}$·g^{-1}·L$^{-\beta}$)	K$_R$ (L·g^{-1})	β	R^2	RPE (%)
Chitin	0.037	1.305	0.783	0.861	13.68
Chitosan	3.195	12.72	0.428	0.995	2.85

Table 2
Change of the pseudo-first order rate constants with concentration for AB113 adsorption on chitin and chitosan

Chitin				Chitosan			
C_i (mg/L)	k_1 (1/min)	R^2	RPE (%)	C_i (mg/L)	k_1 (1/min)	R^2	RPE (%)
98.44	0.012	0.957	10.17	100.17	0.012	0.952	27.22
203.80	0.009	0.953	5.13	200.34	0.012	0.920	1.89
300.35	0.012	0.986	0.15	300.52	0.009	0.950	3.97
407.59	0.009	0.982	1.67	405.49	0.009	0.996	6.58
502.52	0.012	0.977	4.25	500.86	0.009	0.997	4.81

Table 3
Change of the pseudo-second order rate constants with concentration for AB113 adsorption on chitin and chitosan

Chitin				Chitosan			
C_i (mg/L)	k_2 (g/mg-min)	R^2	RPE (%)	C_i (mg/L)	k_2 (g/mg-min)	R^2	RPE (%)
98.44	0.004	0.980	5.51	100.17	0.004	0.988	3.14
203.80	0.002	0.978	4.27	200.34	0.001	0.868	2.81
300.35	0.0004	0.858	10.57	300.52	0.001	0.892	2.01
407.59	0.0002	0.793	14.83	405.49	0.0004	0.915	2.88
502.52	0.001	0.712	33.69	500.86	0.0003	0.896	1.00

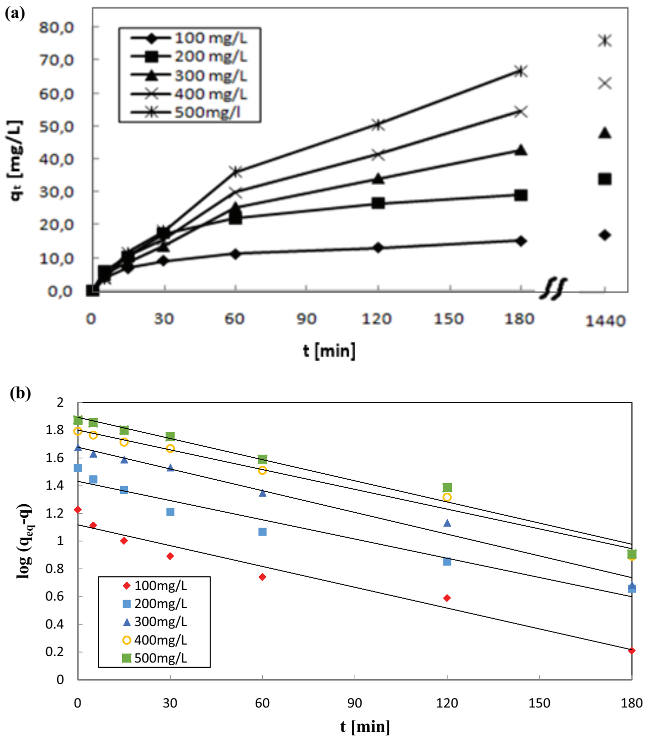

Fig. 2. a) The adsorption curves and b) the linearized form of the pseudo-first order model for adsorption of AB113 onto chitin at various initial AB113 concentrations.

q) vs. t. The parameter log q_{eq} of pseudo-first order sorption rate expression is a regulatable parameter which is often not found equal to the intercept of a plot of log ($q_{eq} - q$) vs. t. As adsorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the amount sorbed at equilibrium. The differences in experimental and theoretical q_{eq} values can be explained that there is a time lag, difficult to quantify, possibly due to a boundary layer or external resistance controlling at the beginning of the sorption. Another disadvantage of this model is that the pseudo-first order sorption rate expression does not fit well the experimental data for the whole range of contact time and the plots are only linear over the first 30 min. However, in case of AB113 adsorption by chitin-chitosan, the Lagergren equation seems to characterize the 180 min range of contact time.

3.2. Single-component adsorption of MR by chitin and chitosan

The initial adsorption rates of MR by chitin and chitosan increased with increasing initial MR concentration and determined as 3.5 mg/g-min and 4.8 mg/g-min, respectively. In the adsorption of MR on chitin, adsorption efficiency was increased from 35.5% to 44.7% with increasing initial MR concentration in the range 100–500 mg/L. Similarly the adsorbed amount of MR at equilibrium on chitin increased from 6.8 mg/g to 42.3 mg/g. The adsorption efficiency of MR on chitosan was also increased from 49.2% to 56.5% with increasing concentrations of MR. The adsorbed amount of MR at equilibrium on chitosan changed from 9.5 mg/g to 53.9 mg/g. As the adsorption of MR by both chitin and chitosan did not show saturation kinetics, and the adsorbed amount of MR at equilibrium on chitin and chitosan increased with increasing initial MR concentration, the equilibrium uptake data were not represented with the Langmuir model. Adsorption isotherms of MR on chitin and chitosan were computed from the empirical Freundich and Redlich-Peterson isotherm models and the comparison between experimental values (denoted by symbols) and computed values (denoted by dushed and dot lines) is shown in Fig. 3a and 3b, respectively. The Freundlich-type isotherm indicating multilayer adsorption with interaction between adsorbed molecules was observed to the best fit for the sorption of MR by both chitin and chitosan. The values of the Redlich-Peterson constant β for the sorption of MR by both chitin and chitosan were found to be zero, and the Redlich-Peterson equation resulted the Henry's law form (Table 4). The adsorption capacity parameter, K_F, of Freundlich isotherm for the adsorption of MR by chitosan was found to be higher than that of chitin. The isotherm non-linearity factor, n, representing adsorption intensity for the adsorption of MR by chitosan was also higher than that of chitin.

The variation of MR adsorption rate constants on chitin and chitosan with initial concentration of MR was calculated by both the pseudo first order kinetic model of Lagergren and the pseudo-second order model. The pseudo-second order rate model was shown to provide the best correlation of the kinetic data for MR adsorption on both chitin and chitosan (Tables 5, 6). Fig. 4a and 4b shows contact time curves for sorption of MR onto chitosan and the linearized form of the pseudo-second order model at various initial MR concentrations, respectively. The values of kinetic parameters decreased markedly with increasing initial dye adsorption. The pseudo-second order rate constants for the MR adsorption by chitin and chitosan decreased in the range of 0.01–0.002 g/mg-min and 0.009–0.001 g/mg-min, respectively

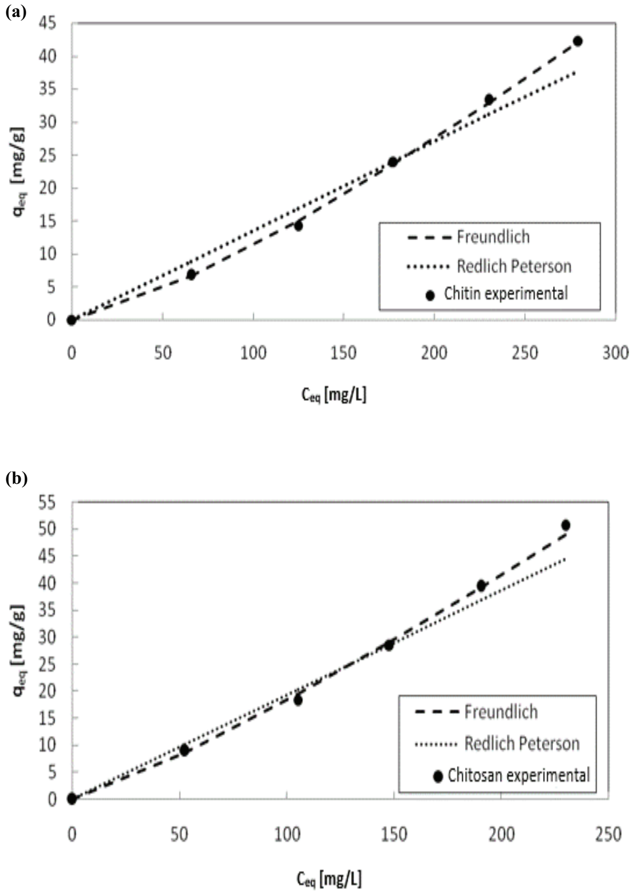

Fig. 3. The adsorption isotherms for MR adsorption on a) chitin and b) chitosan, respectively. The Freundlich and Redlich-Peterson model profiles are presented in dushed and dot lines, respectively, whereas the symbols denote experimentally obtained values.

Table 4

The Freundlich and Redlich-Peterson adsorption constants for the MR adsorption by chitin and chitosan

Freundlich Model	K_F ($mg^{(1-1/n)}$ g^{-1} L^{-n})	$1/n$	n	R^2	RPE (%)
Chitin	0.032	1.277	0.783	0.998	2.21
Chitosan	0.105	1.199	0.834	0.999	2.87
Redlich-Peterson model	a_R ($mg^{\beta+1}$·g^{-1}·$L^{-\beta}$)	K_R (L·g^{-1})	β	R^2	RPE (%)
Chitin	0.151	0.155	0	0.995	13.22
Chitosan	2.943	0.842	0	0.994	8.78

Table 5

Change of the pseudo-first order rate constants with concentration for MR adsorption on chitin and chitosan

	Chitin				Chitosan		
C_i (mg/L)	k_1 (1/min)	R^2	RPE (%)	C_i (mg/L)	k_1 (1/min)	R^2	RPE (%)
101.8	0.023	0.978	12.31	103.44	0.021	0.912	22.14
201.17	0.009	0.771	33.58	203.05	0.014	0.896	30.26
305.41	0.016	0.959	19.97	305.41	0.014	0.852	35.13
407.22	0.018	0.843	41.59	407.22	0.016	0.973	32.32
504.92	0.016	0.922	41.96	509.03	0.016	0.970	31.87

Table 6

Change of the pseudo-second order rate constants with concentration for MR adsorption on chitin and chitosan

	Chitin				Chitosan		
C_i (mg/L)	k_2 (g/mg-min)	R^2	RPE (%)	C_i (mg/L)	k_2 (g/mg-min)	R^2	RPE (%)
101.80	0.010	0.987	5.51	103.44	0.009	0.990	3.78
201.17	0.006	0.980	0.27	203.05	0.004	0.985	2.04
305.41	0.002	0.981	6.76	305.41	0.003	0.989	2.52
407.22	0.004	0.998	3.69	407.22	0.002	0.992	3.82
504.92	0.003	0.997	2.69	509.03	0.001	0.992	9.18

with increasing initial concentration of MR in the range of 100–500 mg/L. It is a mostly known fact related to the interpretation of k_2 as a time-scaling factor. When the initial dye concentrations are increased, the longer time is required to reach an adsorption equilibrium. The adsorption of dye probably takes place via surface exchange reactions until the surface functional sites are fully occupied; then multi layer adsorption begins. Dye molecules can also diffuse into the polymer network for further interactions and/or reactions. The second order models are the two-site or bicontinuum models. In these models, two reactions are assumed to occur either in series or in parallel. One reaction is rapid and reaches equilibrium quickly, and other is a slower reaction that can continue for long time periods.

3.3. Influence of Cu(II) ions on AB113 adsorption by chitin and chitosan

The amounts of AB113 sorbed per unit weight of chitin at equilibrium in case of AB113 present as the single dye and in the presence of increasing concentrations of Cu(II) ions in the range 25–200 mg/L are given in Fig. 5. A comparison of the initial adsorption rates of Cu(II) and AB113 on chitosan, $r_{j'i}$(mg/g·min), the amounts of adsorbed Cu(II) and AB113 per unit weight of chitosan, $q_{j,eq}$ (mg/g) and the individual adsorption efficiencies, Y_j (%) at equilibrium obtained in the adsorption media containing fixed concentrations of AB113 in the range 100–500 mg/L, but increasing concentrations of Cu(II) in the range 25–200 mg/L is given in Table 7. The adsorption equilibrium removal and efficiency of AB113 on both chitin and chitosan decreased in the presence of Cu(II) ions with respect to single-component systems. When the concentration or ratio of AB113 to Cu(II) ions was increased, a increasing selectivity for AB113 with respect to Cu(II) ions by chitin and chitosan was obtained. For example, in the binary systems contain-

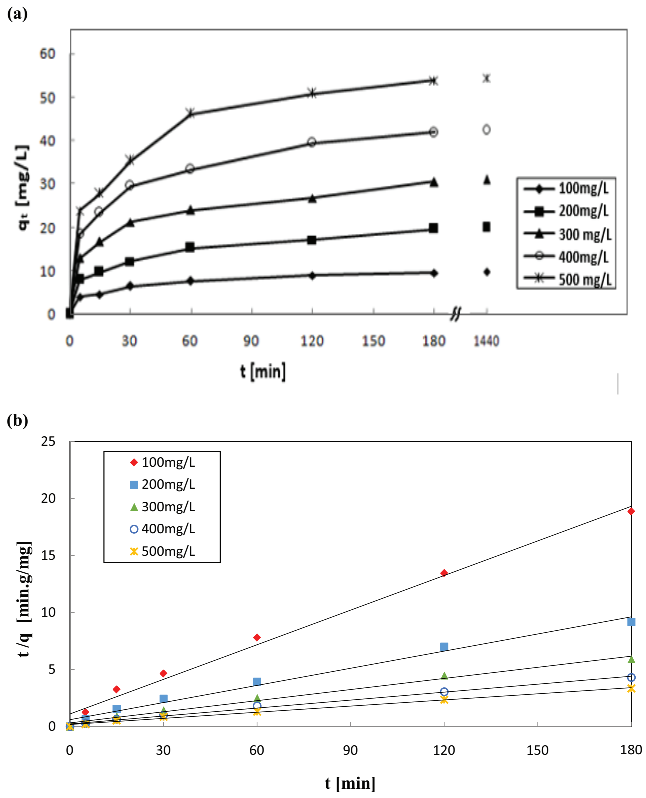

Fig. 4. a) The adsorption curves and b) the linearized form of the pseudo-second order model for adsorption of MR onto chitosan at various initial MR concentrations.

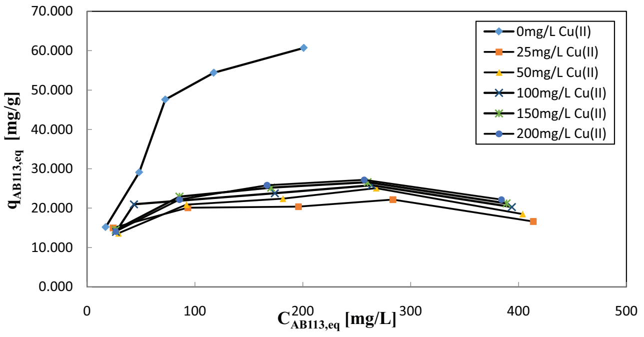

Fig. 5. Comparison of the single- and multi-component adsorption isotherms for AB113 adsorption on chitin with the AB113 present as the single dye and in the presence of increasing concentrations of Cu(II).

ing 400.9 mg/L AB113 and 200.9 mg/L Cu(II) concentrations, the individual initial adsorption rates, equilibrium removal and efficiency of AB113 and Cu(II) on chitin were 2.7 mg/g-min, 27.2 mg/g, 36.1% for AB113; 0.37 mg/g-min, 7.57 mg/g, 19.9% for Cu(II) ions, respectively. The total adsorption capacity and efficiency of Cu(II) ions and AB113 by chitin and chitosan in the binary systems were higher than those of single-component Cu(II) ions, lower than those of single-component AB113 sytems. For that reason, the presence of Cu(II) and AB113 together showed an antagonistic effect on the adsorption of AB113.

3.4. Influence of Cu(II) ions on MR adsorption by chitin and chitosan

The amounts of MR adsorbed per unit weight of chitin at equilibrium in case of MR present as the single dye and in the presence of increasing concentrations of Cu(II) ions in the range 25–200 mg/L are given in Fig. 6. A comparison of the initial adsorption rates of Cu(II) and MR on chitosan, the amounts of adsorbed Cu(II) and MR per unit weight of chitosan and the individual adsorption efficiencies at equilibrium obtained in the adsorption media containing fixed concentrations of MR in the range 100–500 mg/L, but increasing concentrations of Cu(II) in the range 25–200 mg/L is given in Table 8. The adsorption equilibrium removal and efficiency of MR by chitin and chitosan increased with increasing MR and Cu(II) ion concentrations with respect to single-component systems. In the adsorption of two component system of Cu(II)-MR onto chitin and chitosan, a synergistic effect was observed for MR. In the binary systems containing equal concentrations of MR (100 mg/L) and Cu(II) (100 mg/L), the initial adsorption rates, the individual equilibrium removal and efficiency of MR and Cu(II) on chitin were found to be 0.43 mg/g-min, 7.54 mg/g, 39.5% for MR; 0.42 mg/g-min, 8.06 mg/g, 42.5% for Cu(II) ions. The initial adsorption rates, the individual adsorption equilibrium removal and efficiency of MR increased with increasing MR concentration, for example the adsorption rate, equilibrium removal and efficiency of MR and Cu(II) on chitin was determined as 3.69 mg/g-min, 60.04 mg/g, 63.9% at 500 mg/L initial MR concentration; 0.23 mg/g-min, 6.37 mg/g, 33.6% at 100 mg/L initial Cu(II) concentration, respectively. As also seen in Table 4, a similar competitive adsorption pattern for MR and Cu(II) ions was also observed for chitosan.

3.5. Application of multi-component Redlich-Peterson model on the binary adsorption of AB113-Cu(II) and MR-Cu(II) on chitin and chitosan

The multi-component adsorption of AB113, MR and Cu(II) ions on chitin and chitosan was described by multi-component Redlich-Peterson model and three-parameters of the model were calculated for each component. The three parameters given by the Redlich–Peterson adsorption model were estimated from the multi-component adsorption data of Cu(II)-AB113 and Cu(II)-MR by using a Microsoft Office 2013 Excel software. The constants calculated from the multi-component Redlich–Peterson isotherm model are given in Table 9. The total adsorbed Cu(II) and AB113 concentrations on chitin and chitosan, the total adsorbed amount of Cu(II) and AB113 per unit weight of adsorbent and the total adsorption efficiencies at equilibrium were higher than those of Cu(II) and MR system. As AB113 is an anionic dye, the surface binding sides of chitin and chitosan in the presence of Cu(II) ions are used more effectively comparing two competitive cationic component MR and Cu(II). Although individual effects of AB113 and Cu(II) are antagonistic with respect to single-component

Table 7
Comparison of the initial adsorption rates of Cu(II) and AB113, the amounts of adsorbed Cu(II) and AB113 per unit weight of chitosan and the individual adsorption efficiencies at equilibrium obtained in the adsorption media containing fixed concentrations of AB113 in the range 100–500 mg/L, but increasing concentrations of Cu(II) in the range 25–200 mg/L

$C_{Cu,i}$ (mg/L)	$C_{AB113,i}$ (mg/L)	$r_{Cu,i}$ (mg/g.min)	$q_{Cu,eq}$ (mg/g)	Y_{Cu} (%)	$r_{AB113,i}$ (mg/g.min)	$q_{AB113,eq}$ (mg/g)	Y_{AB113} (%)
25.6	0	0.48	4.23	90.2	0	0	0
50.3	0	0.86	8.02	85.0	0	0	0
100.6	0	1.38	14.50	76.9	0	0	0
150.9	0	1.56	19.19	67.8	0	0	0
201.2	0	1.40	18.77	49.7	0	0	0
0	100.2	0	0	0	1.04	16.20	86.2
0	200.3	0	0	0	1.04	31.10	82.8
0	300.5	0	0	0	1.55	43.70	77.6
0	407.5	0	0	0	1.81	55.70	72.9
0	500.8	0	0	0	1.94	66.40	70.7
26.3	100.6	0.19	4.16	87.1	0.20	15.90	77.8
51.2	102.4	0.29	5.60	58.6	0.50	15.00	73.3
102.3	103.8	0.55	9.31	48.8	0.60	14.50	74.4
152.8	101.7	0.71	11.16	39.0	0.90	14.90	75.0
203.4	103.2	0.43	9.11	23.9	1.20	14.50	73.1
25.8	203.8	0.16	3.97	83.2	0.40	21.00	54.5
52.4	201.5	0.27	5.31	55.7	0.50	21.80	56.6
103.1	202.6	0.56	8.75	45.9	1.10	22.70	58.1
152.6	204.5	0.66	11.02	38.5	1.50	23.70	59.6
201.7	201.1	0.43	8.81	23.1	1.70	22.90	58.8
26.8	300.7	0.12	3.76	78.9	0.70	21.80	37.2
52.7	303.2	0.24	5.25	55.0	1.00	24.50	41.9
101.3	302.8	0.48	8.39	43.9	1.10	24.50	42.9
151.4	301.9	0.61	10.46	36.5	1.40	31.30	54.8
203.1	302.7	0.42	8.05	21.1	2.20	27.20	46.5
25.3	401.1	0.11	3.30	68.5	0.90	23.60	30.8
51.8	403.2	0.22	4.87	51.1	1.20	26.60	34.6
103.2	402.5	0.44	8.19	42.9	1.50	27.30	35.6
152.3	401.9	0.61	10.20	35.6	2.10	28.10	36.5
201.3	403.5	0.40	7.68	20.2	3.00	28.60	37.3
25.6	503.4	0.11	2.80	58.6	0.70	18.50	19.2
53.6	502.7	0.20	4.79	50.3	1.10	20.30	21.2
102.8	503.1	0.41	7.81	40.9	1.50	22.20	23.1
150.9	500.8	0.55	9.89	34.6	2.20	23.10	24.0
202.5	501.8	0.38	7.31	19.2	3.00	24.00	25.0

systems, the cumulative effects of being together shows a synergistic effect on the total adsorption capacity of chitin and chitosan. Both components, Cu(II) ions and MR dye have cationic properties, so that their dual adsorption systems by chitin and chitosan are competitive. They compete with each other to be attached partially with same active sites or same charged sites of chitin and chitosan.

In acid conditions, the protonation of amine groups gives to the polymer a cationic behavior that leads to electrostatic attraction of anions. Chitosan is characterized by the deacetylation degree of the biopolymer; increasing the deacethylation degree involves an increase in the relative proportion of amine groups, which can be protonated. The sorption of dyes onto chitin followed the same trend as that of chitosan, but the sorption level was generally lower. The presence of acetyl groups limited the accessibility to protonated-amine sites and then reduced the sorption capacities. Depending on the pH and the dye, the reduction in sorption capacity can be by two to threefold. The sorption is not solely due to protonated amine sites.

The variation in sorption properties is not proportional to deacetylation degree, and it changes with the type of dye. Amide and hydroxyl groups can also be involved in dye fixation. The intrinsic pKa of chitosan has been shown to range between 6.4 and 7.1. Consequently, below pH 6.4, chitosan can be considered as a cationic support. This property will influence the sorption procedure, depending on the charge (and functions) of the dye under the corresponding

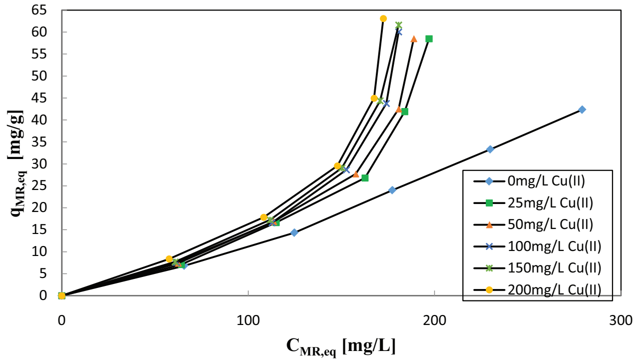

Fig. 6. Comparison of the single- and multi-component adsorption isotherms for MR adsorption on chitin with the MR present as the single dye and in the presence of increasing concentrations of Cu(II).

experimental conditions (pH). Dye sorption also occur via hydrogen bonding with dyes and/or electrostatic interactions with acetamide groups on chitin. The influence of the pH on anionic dye sorption confirms the electrostatic interaction between chitosan and anionic dyes. In acid solutions, amine functions on chitosan are protonated and subjected to electrostatic attraction of dye anions, mainly on sulfonic acid groups. However, sorption performance cannot be directly correlated to the sulfonic acid content of the dye. The differences between the dyes may be due to different pKa values or, alternatively, to the contribution of other sorption mechanisms, including hydrophilic and hydrophobic interactions. For example, increasing the size of the aromatic portion of dye molecules was reported to increase the adsorption efficiency [37].

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the dye solution influences not only the surface charge of the adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry. Chitosan is polycationic and positively charged at lower pH degrees than 6: the free amino groups are protonated and this facilitates electrostatic interaction between chitosan and the negatively charged anionic dyes. The free amine groups in chitosan are much more reactive and effective for chelating pollutants than the acetyl groups in chitin. Amine sites are the main reactive groups for (anionic) dye adsorption, though hydroxyl groups (especially in the C-3 position) may also contribute to adsorption. On the other hand, chitin include amide group, –CO–NH–, which cannot be readily protonated in acidic solutions. Amide is a much weaker base than amine. As electrons are less available for sharing with a hydrogen ion, the electron withdrawal by carbonyl group makes the nitrogen of the amide group a much weaker source of electrons than that of the amine group [38,39]. However, chitin can also have a considerable density of primary amine groups even at high deacetylation values; such density can be enough to make chitin a competitive biosorbent compared to other materials. Besides, chitin has advantages compared to chitosan as a lower solubility in acid medium and lower cost.

Two mechanisms are clearly established for the interpretation of metal adsorption on chitosan materials, i.e. electrostatic interactions in acid media (ion-exchange) and metal chelation (coordination). Metal ion adsorption is assumed to occur through single or mixed mechanisms including coordination on amino groups in a pendant fashion or in combination with vicinal hydroxyl groups, and ion-exchange with protonated amino groups through proton exchange or anion exchange, the counter ion being exchanged with the metal anion [40].

On the contrary, the adsorption mechanisms for dye molecules onto chitosan occurs with surface adsorption, chemisorption, diffusion and adsorption-complexation being the prevalent theories. Different kinds of interactions such as chemical bonding, ion-exchange, hydrogen bonds, hydrophobic attractions, van der Waals force, physical adsorption, aggregation mechanisms, dye–dye interactions, etc., can act simultaneously [19,41].

It is now recognized that chemisorption (ion-exchange, electrostatic attractions) is the most prevalent mechanism with the pH as the main factor affecting adsorption. Chemisorption is a strong type of adsorption in which molecules are not exchanged but electrons may be exchanged. Chemisorption is especially cited as the main mechanism for the adsorption of anionic dyes in acidic conditions. The adsorption mechanism of anionic dyes by chitosan is described by the following mechanism: in the presence of H^+, the amino groups of chitosan become protonated; also, in aqueous solution, the anionic dye is first dissolved and the sulfonate groups in the case of acid or reactive dyes dissociate and are converted to anionic dye ions; the adsorption process then proceeds due to the electrostatic attraction between these two counter ions [37]. In general, as the initial dye concentration increases, the equilibrium pH decreases. This is consistent with the principles of ion-exchange since as more dye molecules are adsorbed onto material, more hydrogen ions are released, thereby decreasing the pH. For cationic dyes such as MR, the adsorption capacity was generally recorded to be low in comparison to acidic dyes. This was due to the positive charge of dye that creates strong coulombic repulsions between chitosan and dye [41]. However, the hydroxyl group (–OH) in chitosan could adsorb the basic dye via covalent and hydrogen bonding. The interaction of MR with chitosan occurs mainly through hydrogen bonding and van der Waals forces [42]. Competitive adsorption occurs where the adsorption of a mixture of adsorbates is carried out on one surface. Some of the components in the effluent may induce the adsorption of others or may coadsorb along with another components. However, only very limited information is available on the competitive adsorption of cationic dye molecules with chitosan-based materials. Those having the greatest ionic potential would be removed first, and if the sites were still undersaturated, then those having lower ionic potential would be removed in sequence. The more electronegative molecules are attracted to the surface more strongly. Although the presence of more than one dye or component such as metal ions in a solution creates competition for adsorption sites, the total adsorption capacity has been found to increase. Addition of other cation species generally decreased color removal. This was attributed to chelation between cations and chitosan chains, which decreased

Table 8
Comparison of the initial adsorption rates of Cu(II) and MR, the amounts of adsorbed Cu(II) and MR per unit weight of chitosan and the individual adsorption efficiencies at equilibrium obtained in the adsorption media containing fixed concentrations of MR in the range 100–500 mg/L, but increasing concentrations of Cu(II) in the range 25–200 mg/L

$C_{Cu,i}$ (mg/L)	$C_{MR,i}$ (mg/L)	$r_{Cu,i}$ (mg/g·min)	$q_{Cu,eq}$ (mg/g)	Y_{Cu} (%)	$r_{MR,i}$ (mg/g·min)	$q_{MR,eq}$ (mg/g)	Y_{MR} (%)
25.06	0	0.48	4.23	90.2	0	0	0
50.3	0	0.86	8.02	85.0	0	0	0
100.6	0	1.38	14.50	76.9	0	0	0
151.1	0	1.56	19.20	67.8	0	0	0
201.3	0	1.40	18.80	49.7	0	0	0
0	100.1	0	0	0	0.70	8.90	47.5
0	203.0	0	0	0	1.60	18.40	48.2
0	300.4	0	0	0	2.40	28.60	50.8
0	400.6	0	0	0	3.00	39.40	52.5
0	500.8	0	0	0	4.00	50.80	54.1
26.4	100.3	0.26	3.92	79.8	0.42	8.15	42.9
51.3	101.5	0.33	5.73	56.6	0.68	8.31	43.6
102.4	103.4	0.71	9.91	48.5	0.80	8.47	44.4
152.6	102.3	1.01	12.76	41.6	0.74	8.77	46.0
203.7	100.8	0.93	8.21	20.2	0.84	8.90	46.0
25.3	200.6	0.22	3.66	74.4	1.48	19.70	51.6
51.7	203.8	0.31	5.36	52.9	1.60	19.83	51.9
101.8	201.6	0.66	9.54	46.7	1.63	20.32	54.1
150.9	200.7	0.95	11.92	38.9	1.72	20.94	54.8
203.5	201.5	0.91	7.83	19.4	1.85	21.60	56.6
26.3	300.5	0.19	3.65	72.2	1.85	31.40	54.8
52.4	300.9	0.30	5.17	51.1	2.03	32.30	55.5
102.8	302.5	0.63	9.18	44.9	2.07	32.33	56.5
153.6	301.4	0.90	11.64	38.0	2.27	32.79	56.8
201.8	300.9	0.83	7.16	17.8	2.29	34.17	59.2
25.6	400.8	0.17	3.00	59.3	2.41	46.55	60.0
50.9	401.6	0.30	5.16	51.0	2.46	46.80	61.3
102.7	403.5	0.58	8.60	42.1	2.71	48.52	63.6
153.1	402.8	0.84	11.36	37.1	2.96	48.89	64.0
203.4	401.6	0.76	6.71	16.9	3.02	48.30	64.0
26.7	501.6	0.16	2.77	54.6	4.00	64.66	67.7
53.1	502.8	0.30	4.98	48.8	4.16	66.20	69.4
100.9	501.3	0.53	8.22	40.3	4.31	68.50	71.8
151.2	503.7	0.76	10.51	34.3	4.46	69.27	72.6
201.5	500.4	0.66	6.00	15.2	4.62	71.58	75.0

Table 9
Multi-component Redlich-Peterson constants of AB113-Cu(II) and MR-Cu(II)

Sorbent	Copper(II)				AB113			
	a_{R1} ($mg^{\beta+1}/g·L^{\beta}$)	K_{R1} ($L·g^{-1}$)	β_1	RPE (%)	a_{R2} ($mg^{\beta+1}/g·L^{\beta}$)	K_{R2} ($L·g^{-1}$)	β_2	RPE (%)
Chitin	0.075	1.251	0.873	18.3	0.091	1.927	0.846	20.1
Chitosan	1.415	12.792	0.783	18.6	1.569	24.80	0.892	19.6
Sorbent	Copper(II)				MR			
	a_{R1} ($mg^{\beta+1}/g·L^{\beta}$)	K_{R1} ($L·g^{-1}$)	β_1	RPE (%)	a_{R2} ($mg^{\beta+1}/g·L^{\beta}$)	K_{R2} ($L·g^{-1}$)	β_2	RPE (%)
Chitin	0.044	0.510	0.981	19.9	1.027	0.565	0	26.4
Chitosan	16.27	0.921	0.05	19.4	2.797	4.613	0	25.7

the electrostatic interaction between MR and chitosan. Both components, Cu(II) ions and MR dye have cationic properties, so that their dual adsorption systems by chitin and chitosan are competitive. They compete with each other to be attached partially with same active sites or same charged sites of chitin and chitosan.

4. Conclusion

In the binary mixtures containing the equal concentrations of Cu(II) (100 mg/L) and dye stuff (100 mg/L), total adsorption efficiency order was: Cu(II)-AB113 on chitosan (62.3%) > Cu(II)-AB113 on chitin (59.8%) > Cu(II)-MR on chitosan (46.4%) > Cu(II)-MR on chitin (41.0%). In the same systems, total adsorption capacity order was: Cu(II)-AB113 on chitosan (23.80 mg/g) > Cu(II)-AB113 on chitin (23.11 mg/g) > Cu(II)-MR on chitosan (17.90 mg/g) > Cu(II)-MR on chitin (15.64 mg/g).

The individual adsorption capacity and efficiency of Cu(II) ions and AB113 by chitin and chitosan in the binary systems were higher than those of single-component Cu(II) ions, lower than those of single-component AB113 systems. On the other hand, as Cu(II) and AB113 bind to different active sites or opposite charged sites of chitin and chitosan, active surface area of the sorbents is effectively used and the total adsorption capacity and efficiency increased.

The adsorption equilibrium removal and efficiency of MR by chitin and chitosan increased with increasing MR and Cu(II) ion concentrations with respect to single-component systems.

The multi-component three-parameter Redlich-Peterson adsorption model was used to characterize mutual interactions of AB113-Cu(II) ions and MR-Cu(II) ions on chitin and chitosan.

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