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Investigation of antagonistic and synergistic interactions on simultaneous adsorption of crystal violet and Cu(II) using chitin and chitosan

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ABSTRACT

The simultaneous adsorption of crystal violet (CV), a cationic dye, and Cu(II) ions on chitin and chitosan from multi-component systems was investigated in batch stirred reactors and compared to single-component systems. Both components, Cu(II) ions and CV dye, have cationic properties, so that their dual adsorption systems by chitin and chitosan are competitive. CV was adsorbed selectively by chitin, while Cu(II) was retained preferentially by chitosan in the media containing equal quantities of the components (100 and 200 mg/L). For the multi-component adsorption equilibria, competitive adsorption isotherms were developed. The multi-component three-parameter Redlich Peterson model was used successfully to characterize competitive adsorption of CV and Cu(II) ions on chitin and chitosan.

Keywords: Wastewater treatment; Adsorption; Crystal violet; Cu(II); Chitin; Chitosan

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1. Introduction

Pollution of the environment from various activities of the heavy metal and dye using or producing industries has become an increasingly serious problem in recent years. Moreover, dyes and heavy metals are hazardous pollutants often found together in wastewaters of several industries. In many industries (mining, energy and fuel production, fertilizer and pesticide industry, leather tanning, metallurgy and iron–steel industries, leather processing, and photography) heavy-metal-containing wastewaters are discharged directly or indirectly to the nature. Among these, copper is especially used in paper industry, fertilizer industry, iron–steel industries, and power generation in thermal power plants. Being a trace element, copper has important role in human metabolism. It is used in synthesis of enzymes and development of soft and hard tissues [1,2]. However, Cu(II) is critically toxic. This kind of pollution damages the ecosystem and with the help of the food pyramid, excessive amount of copper can be taken by any kind of living organisms [3,4].

Wastewaters coming from several branches of the textile industry, leather tanning, paper industry, food technologies, agricultural activities, pharmaceutical industries, hair coloring and cosmetic fields contain high concentrations of dyes [5,6]. Crystal violet (CV) is a member of the triphenylmethane group and cationic dye. This purple colored dye is a widely used in different sectors such as a protein dye or biological stain in biochemical studies and in medicine, textile dye in

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various commercial textile operations [7,8]. CV is toxic, carcinogenic and nonbiodegradable as being poorly metabolized by micro-organisms [9,10].

Conventional methods for removing heavy-metal ions from aqueous solution are chemical precipitation, filtration, ion-exchange, reverse osmosis, coagulation, electrochemical treatment, membrane technologies, adsorption–biosorption on sorbents and biosorbents, evaporation, etc. All of these heavy-metal removal techniques have some advantages and disadvantages in terms of operational costs, efficiency, and applicability. Considering these techniques, biosorption which utilizes various certain natural materials of biological origin seems to be a very feasible method [11–15]. On the other hand, many physical and chemical treatment methods including membrane filtration, ion exchange, oxidative degradation, photodegradation, chemical oxidation, biochemical degradation, ozonation, electrochemical destruction, electroflotation, irradiation, coagulation, flocculation with Fe(II)/Ca(OH)$_2$, and physical–chemical flocculation combined with flotation, adsorption–biosorption have been used for the treatment of dye-containing effluents [16,17]. Many of these techniques have several disadvantages such as lack of effective color reduction, excess amount of chemical usage, accumulation of concentrated sludge, and formation of hazardous by-products, high plant, energy requirements, and operating cost. However, the removal and recovery of these pollutants in multi-component mixtures of dyes and heavy metals are especially difficult and ineffective using some conventional treatment processes. Until now, activated carbons, natural and synthetic polymers, clays, zeolites, micro-organisms, agricultural, and industrial by-products have been used to remove dyes and heavy metals from single-component solutions [18–26]. In all of them, the effectiveness and operational costs vary. However, there is still a need for adsorbents with feasible prices and efficiencies.

Poly (N-acetyl-1,4-β-D-glucopyranosamine) also named as chitin $(C_8H_{13}NO_5)_n$ is a natural polysaccharide which is a derivative of glucose and the second most synthesized polymer after cellulose [27]. Chitin is mostly found on the cell walls of fungi and in the exoskeletons of arthropods and internal shells of some water organisms. Chitosan [2-amino-2-deoxy-(1→4)-β-D-glucopyranan; (poly1,4-β-D-glucopyranosamine)] is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin. In fact, chitin cannot be sharply distinguished from chitosan, because fully acetylated and fully deacetylated chitins do not normally occur in nature and are difficult to prepare.

Several mechanisms have been proposed for the sorption of heavy-metal ions and dyes by chitin or chitosan, such as precipitation, deposition of metal aggregate, ion exchange, complexation, physical adsorption due to electrostatic forces, and weak van der Waals forces. Metal ions can mainly bind to the amino groups of chitin (R$_2$-NH) and chitosan (R-NH$_2$). Chitin and its associated proteins contain many carboxylate groups. Aspartate, glutamate, and cysteine play an important role in metal chelation. The formation of a coordination complex between the metal and the chitin nitrogen or oxygen has been suggested. Chitosan also collects metal ions and dyes through chelation, due to the presence of an amino group of the 2-amino-2-deoxy-D-glucose (glocosamine) unit. The hydroxyl groups of chitosan can also serve as the active sites [28]. Amino groups of chitosan can be cationized, after which they adsorb anionic dyes strongly by electrostatic attraction in the acidic media. Chitosan is polycationic and positively charged at lower pH degrees than 6. The reason for this is the amino group dispersions on the protonated structure of the polymer. For that reason, the efficiency of chitosan as an adsorbent to remove acid (anionic) dyes has been generally investigated in literature. Only a limited number of studies have been performed on the use of chitin and chitosan as an adsorbent for cationic (basic) dye removal.

The Langmuir and Freundlich adsorption isotherm models to define single-component adsorption equilibrium are frequently used. A further empirical isotherm has been developed by Redlich and Peterson, incorporating three parameters [29]:

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

where the exponent β, lies between 0 and 1. When $\beta = 1$, the Redlich–Peterson equation reduces to the Langmuir equation. When $\beta = 0$, the Henry's Law form results. If $a_R C_{\mathrm{eq}}^{\beta}$s much greater than 1, then it becomes the Freundlich equation. If $a_R C_{\mathrm{eq}}^{\beta}$s much less than 1, which occurs at low concentrations, then it becomes a linear isotherm equation. Competitive isotherms, describing multi-component sorption, are classified according to the relationship they have with single-component isotherms. Better accuracy may be achieved by extracting additional coefficients from experimental competitive isotherms. The three parameter isotherm of Redlich–Peterson that has been empirically developed for multi-component mixtures is given as:

$$q_{j,\mathrm{eq}} = \frac{K_{R,j} C_{j,\mathrm{eq}}}{1 + \sum_{k=1}^{N} a_{R,k} \cdot C_{\mathrm{k,eq}}^{\beta_{\mathrm{k}}}}$$

The aim of this paper is to investigate the results of a feasibility study using chitin and chitosan as adsorbent for both heavy metals and dyes either in mixed- or single-component media. Till date, the removal of heavy metals and water decolorization by various biosorbents has been investigated individually in single-component systems and a limited importance has been given to the study of multi-component systems. However, to determine the competitive effects of heavy metals and anionic or cationic dyes on chitin–chitosan, multi-component adsorption studies should be performed. Multi-component synthetic adsorption media reflect better the characteristics of real wastewaters; these studies play an important role for the proper design, scale-up and operation of water purification processes. When two or more pollutants are present in solution together, the adsorption of each component in the mixture may be greater than that of in the single-system (synergism), less than that of in the single-system (antagonism), or equivalent to the individual adsorption in the single-system (noninteraction) [30,31]. The evaluation of multi-component adsorption equilibrium data is also different from the mono-component data. Multi-component adsorption equilibrium models have been rarely used in the literature to represent multi-component adsorption equilibria [32,33]. So, in this research, the competitive adsorption equilibrium capacities and efficiencies of Cu(II) and CV have been investigated by terms of multi-component adsoption equilibrium models.

2. Materials and methods

Chitin prepared from shrimp shells (CAS1398-61, practical grade, powder (SIGMA)) was used for Cu(II) and CV removal. Chitosan (CAS9012-76-4, (ALDRICH)) with low molecular weight has a degree of deacetylation 75–85%. It is a linear amino polysaccharid composed of approximately 20% β 1,4-linked N-acetyl-D-glucosamine (GlcNAc) and approximately 80% β 1,4-linked D-glucosamine (GlcN) that is prepared by the partial deacetylation of chitin in hot alkali. The molecular weight is 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)- $400 < d_p < 550$. The simultaneous adsorption of Cu(II) ions and CV, a cationic dye, by chitin and chitosan was investigated in batch stirred reactors at 25℃. The batch adsorption experiments were performed in an orbital agitated incubator operated at 150 rpm, while the volume of batches was 150 mL. All the experiments were continued for 24 h. In order to estimate the optimum pH and sorbent quantity for the adsorption of Cu(II) ions and CV dye from the aqueous solution by chitin and chitosan, preliminary experiments were set. In the single-component systems, the maximum adsorption for both the Cu(II) and crystal violet was obtained at pH 5.0 and when a amount of chitin and chitosan of 0.8 g was used. The dual-component experiments were also performed at pH 5.0 and using 0.8 g of the adsorbent. Cu(II) solutions were prepared to required concentrations by diluting 1 g/L stock solution of Cu(II) dissolving $Cu(NO_3)_2.3H_2O$ in distilled water. The range of concentrations of prepared Cu(II) solutions varied from 25 to 200 mg/L, while the concentrations of dye 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. Samples (1 mL) were taken from the adsorption media at time periods of 0, 5, 15, 30, 60, 120, 180, and 1,440 min and then centrifuged at 19,000 g for 5 min. The concentration of free Cu(II) ions in the supernatant liquid was determined using an atomic absorption spectrophotometer (Thermo Scientific ICE 300 AA) with an air-acetylene flame. CV concentration which is not adsorbed was analyzed via spectrophotometer (Spectronic 20 Genesys) at 586 nm.

3. Results and discussion

For the competitive adsorption of Cu(II) and CV from binary mixtures on chitin and chitosan, the results were evaluated in terms of initial adsorption rates, $r_{j,i}$ (mg/g-min), amount of sorbed components per unit weight of adsorbent at equilibrium, $q_{j,\mathrm{eq}}$ (mg/g) and adsorption efficiency, $\mathrm{Ads}_{j,\mathrm{eq}}$ (%).(%). Here, a series of experiments were carried out at different initial concentrations, $C_{j,i}$ (mg/L), and the initial rate of reaction, $r_{j,i}$ (mg/g-min), was determined for each run. The initial rate, $r_{j,i}$, can be found by differentiating the data and extrapolating to zero time. The derivative at time $t = 0$ was found from the slope of the plot of amount of sorbed component per unit weight of adsorbent, q_j (mg/g), vs. time evaluated at $t = 0$. The amount of sorbed component per unit weight of adsorbent, q_j, is the ratio of concentration of sorbed component, $C_{\mathrm{ads},j}$, to concentration of adsorbent. In addition, $q_{j,\mathrm{eq}}$, is the amount of solutes sorbed per unit weight of sorbent at equilibrium concentration, $C_{i,\mathrm{eq}}$. The adsorption efficiency, $\mathrm{Ads}_{j,\mathrm{eq}}$ (%), is the ratio of concentration of sorbed component, $C_{\mathrm{ads},j}$, at equilibrium to initial concentration of solute, $C_{j,i}$, and multiplied by 100.

3.1. Competitive adsorption of Cu(II) and CV from binary mixtures on chitin

The change of initial Cu(II) adsorption rate with increasing initial Cu(II) concentration from binary mixtures of Cu(II) and CV by chitin was given in Fig. 1(a). While the initial Cu(II) concentration was varied between 25 and 150 mg/L, the initial Cu(II) adsorption rate in the presence of CV increased with respect to CV free-medium. When the initial Cu(II) concentration reached to 200 mg/L, increasing dye concentration in the medium caused a reduction in the initial Cu(II) adsorption rate with respect to CV free-medium. The initial adsorption rates of Cu(II) decreased with increasing dye concentration. This interesting phenomena can be explained by saturation kinetics. Since chitin offers a finite number of binding sites, the initial uptake, being physical adsorption, and the subsequent slow uptake, being chemical adsorption, would be expected to show saturation kinetics in binary mixtures containing Cu(II) ions and CV at increasing concentrations. Increasing the concentrations of Cu(II) ions did not lead correspondingly to higher initial uptake of Cu(II) ions. In other words, a fixed number of Cu(II) ions bound to the adsorptive sites of chitin owing to the preferential adsorption of CV at high concentrations of CV. It is important to notice that this nonlinearity does not result only from the saturation of the active sites, but is also mainly related to the interferences between concentrated components that compete for the adsorption sites. It is also seen in Fig. 1(b) that the Cu(II) adsorption efficiency decreased with increasing initial Cu(II) concentration. Similar to the effect of initial Cu(II) concentration, increasing concentrations of CV also decreased the adsorption efficiency of Cu(II) on chitin.

It is observed surprisingly in Fig. 2(a) that the initial adsorption rates of crystal violet on chitin was increased with increasing dye concentration in the media containing 0 to 200 mg/L Cu(II) concentration, compared with the Cu(II)-free media. The initial

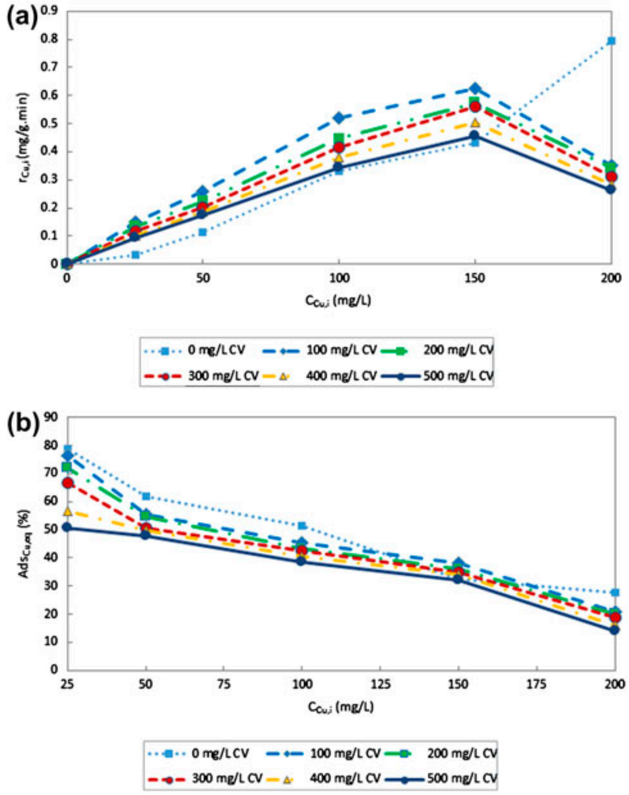

Fig. 1. (a) Change of the initial adsorption rates of Cu(II) with the initial Cu(II) concentrations on chitin; (b) Change of the adsorption efficiencies of Cu(II) with the initial Cu(II) concentrations on chitin in the presence of increasing concentrations of CV and comparison with the Cu(II) present as the single metal.

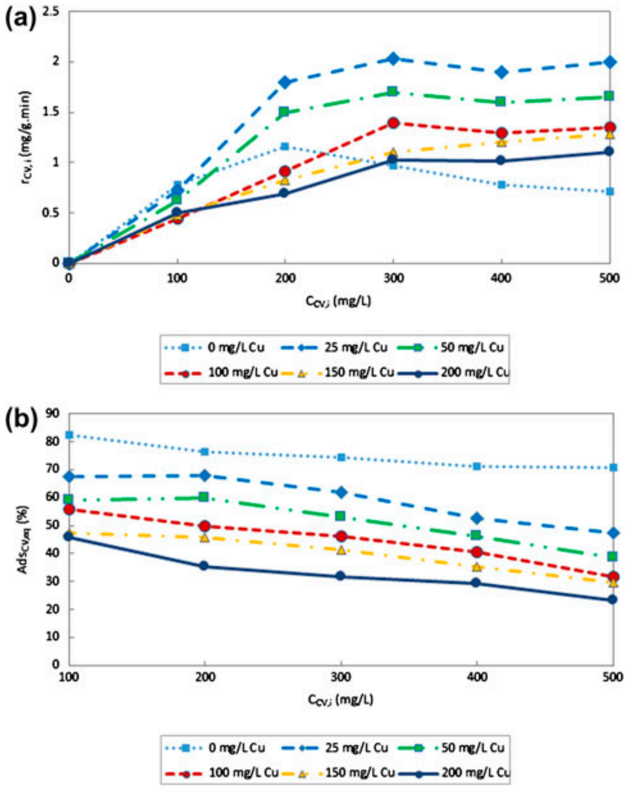

Fig. 2. (a) Change of the initial adsorption rates of CV with the initial CV concentrations on chitin; (b) Change of the adsorption efficiencies of CV with the initial CV concentrations on chitin in the presence of increasing concentrations of Cu and comparison with the CV present as the single dye.

adsorption rates of CV on chitin from the mono-component media containing 100–200 mg/L dye concentration were higher than the initial adsorption rates of CV in the media containing of 100–200 mg/L Cu(II). Because of the strong driving force, initial adsorption rates of the dye increased with increasing total concentration. Increasing Cu(II) concentration and/or the ratio of Cu(II) concentration to the dye concentration, the initial adsorption rates of the dye decreased with respect to the single-component dye system. As also seen in Fig. 2(b), the adsorption efficiency of CV in the presence of increasing concentrations of Cu(II) ions decreased regularly comparing with the single-component system of the dye.

For the simultaneous adsorption of Cu(II) and CV from binary mixtures using chitin, adsorbed concentrations of the components, total adsorbed concentrations, and total adsorption efficiencies are given in Table 1 as comparative with the single-component systems. Total adsorbed concentrations of dual systems were higher than the adsorbed concentrations of single-component Cu(II) system, and lower than the adsorbed concentration of single-component dye system. A similar trend was also observed in the case of the total sorbed quantities per unit weight of chitin at equilibrium. The combined action of Cu(II) and CV on the sorption capacity of chitin caused a synergistic effect compared to the single-component Cu(II) system. This can be attributed to the fact that increases in the total concentration in the dual systems result in a strong driving force or a large difference in concentration between adsorbent surface and solution, and further uptake of the competing component. The screening effect of the presence of the second component in the adsorption medium can also give rise to mixed synergism and antagonism toward adsorption. Thus, the screening effect of the presence of the second component can induce synergism mutually ameliorating their individual repulsive forces and masking the antagonism. Another possible explanation of this observed synergism is that Cu(II) and CV each bind to different types of sites on the chitin/chitosan surface because of the different affinities of the ligands for CV and Cu(II) on the chitin/chitosan. For polyionic sorbents such as chitosan, the components can bind to the different sites on the sorbent with various mechanisms, such as complexation, chelating, and ion exchange. Even if the individual sorbed amounts as in the case CV adsorption on chitin decrease with respect to single-component dye system, the total adsorbed amounts increase and the surface of the adsorbent is used more effectively. Although CV dominated the competitive binding, the total effect of Cu(II) and CV on the CV sorption capacity of chitin showed an antagonistic effect. The most logical reason for the antagonistic action is claimed to be the competition for the same adsorption sites on chitin, and/or a screening effect by the second component. The increasing concentrations of one component that are not selectively adsorbed can mask preferentially adsorbed component.

3.2. Competitive adsorption of Cu(II) and CV from binary mixtures on chitosan

The initial adsorption rates and efficiencies of Cu (II) on chitosan with the addition of increasing concentrations of CV to the media decreased significantly compared to the mono-component Cu(II) systems (Fig. 3(a) and (b)). The observed decrease in initial adsorption rates and efficiencies of Cu(II) on chitosan increased properly with increasing concentrations of CV. A nonlinear kinetics was also observed due to saturation of the binding sites of chitosan with Cu(II) ions. Above a certain Cu(II) concentration (150 mg/L) at the adsorption site, a further increase in the adsorption of Cu(II) ions was not observed. The initial rates of Cu(II) ions reached a maximum plateau value, then decreased with doses leading to concentrations at the adsorption site above the maximal adsorption capacity. Another reason of this observed decrease in initial adsorption rates of Cu(II) could be that the inhibition or antagonistic effect caused by CV adsorbed other binding sites of chitosan.

The presence of increasing concentrations of Cu(II) in the media caused a reduction in the initial adsorption rates of CV dye by chitosan compared to the single-component dye system (Fig. 4(a)). The adsorption efficiencies of CV on chitosan decreased regularly with increasing concentrations of Cu(II) ions (Fig. 4(b)). If the data are examined in detail, it is seen that the adsorption efficiencies of CV on chitosan in the media containing lower concentrations of the dye (100 and 200 mg/L) in the presence of Cu(II) increased compared to the single-component dye system. Even the dye adsorption efficiency obtained at 300 mg/L CV concentration and at the Cu(II) concentrations changing from 25 to 50 mg/L was higher than that of the single-component dye system. At higher concentrations of CV (400 and 500 mg/L), the presence of Cu (II) in the media reduced the adsorption efficiency of CV with respect to the mono-component system. Increase in total concentration in the dual component systems caused an enhancement on the driving force. For that reason, the adsorption of CV at relatively low CV concentrations increased compared to single-component systems, and a selectivity for CV with respect to Cu(II) was obtained.

Table 1
Comparison of the adsorbed Cu(II) and CV concentrations on chitin, the total adsorbed concentrations, and the total adsorption efficiencies at equilibrium obtained in the adsorption media containing fixed concentrations of CV in the range 100–500 mg/L, but increasing concentrations of Cu(II) in the range 25–200 mg/L

$C_{\mathrm{Cu},i}$ (mg/L)	$C_{\mathrm{Cv},i}$ (mg/L)	$C_{\mathrm{ads,Cu}}$ (mg/L)	$C_{\mathrm{ads,CV}}$ (mg/L)	$C_{\mathrm{ads,total}}$ (mg/L)	q_{total} (mg/g)	$\%\mathrm{Ads}_{\mathrm{total}}$
25	0	19.73	0.00	19.73	3.70	78.93
50.5	0	31.31	0.00	31.31	5.87	62.00
100.8	0	51.71	0.00	51.71	9.70	51.30
150.4	0	48.99	0.00	65.91	12.35	43.82
203.7	0	56.57	0.00	56.57	10.61	27.77
0	101.4	0.00	93.59	93.59	17.55	92.30
0	200.8	0.00	163.05	163.05	30.57	81.20
0	302.6	0.00	230.88	230.88	43.29	76.30
0	400.7	0.00	260.05	260.05	48.76	64.90
0	501.3	0.00	223.08	223.08	41.83	44.50
26.5	100.8	20.20	68.00	88.20	16.54	69.28
52.4	101.3	29.02	59.71	88.73	16.64	57.73
102.6	103.4	46.67	57.91	104.59	19.61	50.77
150.4	102.6	57.26	48.44	105.69	19.82	41.78
201.3	100.9	42.09	46.40	88.50	16.59	29.28
25.9	201.5	18.68	136.50	155.17	29.09	68.24
50.6	200.7	27.67	120.06	147.73	27.70	58.79
103.5	204.6	45.03	96.59	141.62	26.55	45.97
151.7	203.2	54.75	92.96	147.71	27.70	41.62
203.1	201.8	40.46	71.01	111.47	20.90	27.53
24.9	301.4	16.59	186.51	203.09	38.08	62.24
51.3	303.2	26.02	160.94	186.96	35.06	52.74
102.7	300.8	43.67	138.46	182.13	34.15	45.14
152.6	303.5	53.56	125.50	179.06	33.57	39.26
201.4	301.9	38.13	95.61	133.74	25.08	26.57
26.7	400.9	15.11	210.39	225.50	42.28	52.74
50.8	401.8	25.27	186.15	211.42	39.64	46.71
102.7	400.6	41.63	183.27	224.91	42.17	44.69
152.4	403.2	51.98	141.89	193.87	36.35	34.89
203.6	402.5	32.51	118.05	150.57	28.23	24.84
25.2	500.6	12.76	236.33	249.09	46.71	47.37
53.6	501.7	25.60	192.75	218.35	40.94	39.32
101.8	503.8	39.25	159.55	198.81	37.28	32.83
152.5	501.5	49.00	148.54	197.54	37.04	30.21
201.7	502.6	28.24	116.45	144.69	27.13	20.54

The total adsorbed concentrations, total amount of sorbed components per unit weight of chitosan at equilibrium, and total adsorption efficiency for the simultaneous adsorption of CV and Cu(II) are compared with the single-component systems in Table 2. The equilibrium uptake and efficiency of Cu(II) and CV singly on chitosan seems to be very close to each other. In the dual systems of Cu(II) and CV, the total adsorbed concentrations and total amount of sorbed components per unit weight of chitosan at equilibrium were higher than those of each single-component systems. In the presence of Cu(II) in the media, the individual adsorption equilibrium removal (mg/g) and efficiency of CV at lower concentrations of CV such as 100 and 200 mg/L also increased compared to the single-component system. The combined effect of Cu(II) and CV on the sorption capacity of chitosan can be considered to be synergistic.

Both components, Cu(II) ions and CV 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. Another important result of this study is that CV was adsorbed selectively by chitin, while Cu(II) was retained preferentially by chitosan in the media

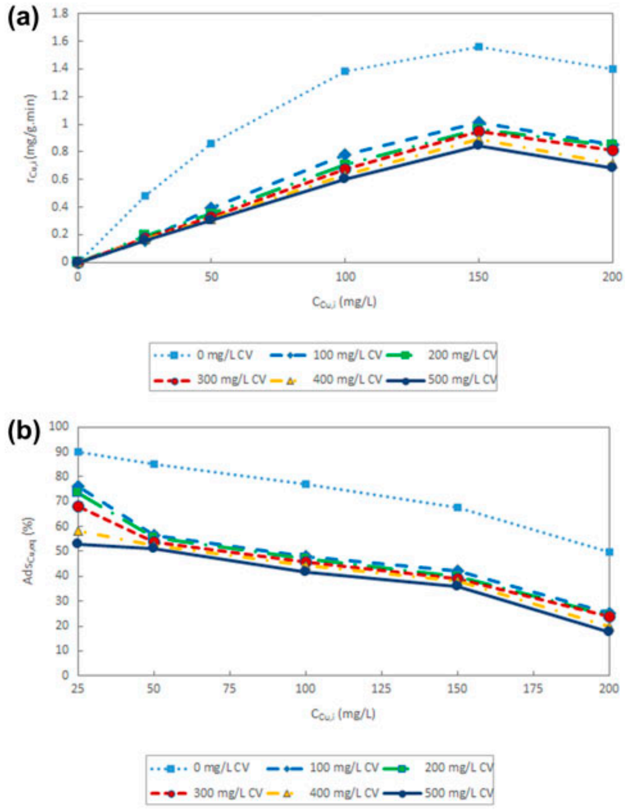

Fig. 3. (a) Change of the initial adsorption rates of Cu(II) with the initial Cu(II) concentrations on chitosan; (b) Change of the adsorption efficiencies of Cu(II) with the initial Cu(II) concentrations on chitosan in the presence of increasing concentrations of CV and comparison with the Cu(II) present as the single metal.

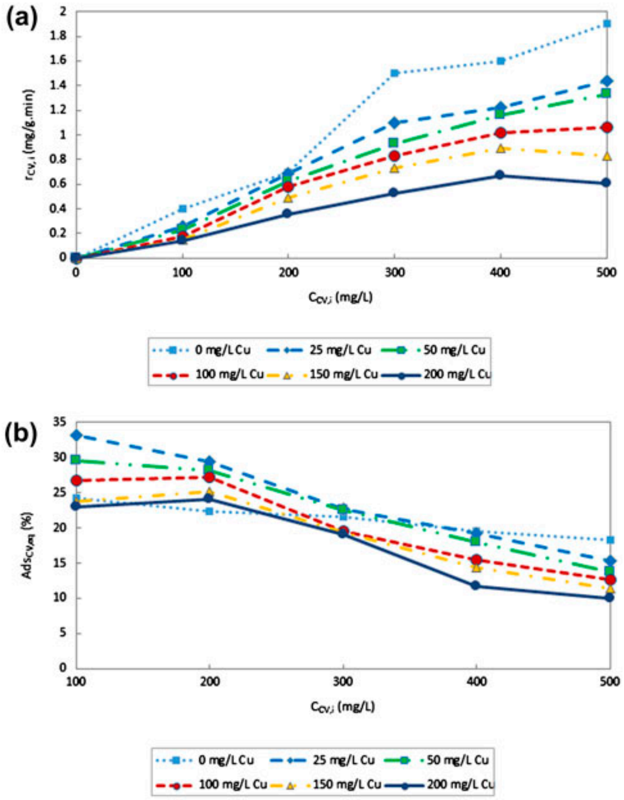

Fig. 4. (a) Change of the initial adsorption rates of CV with the initial CV concentrations on chitosan; (b) Change of the adsorption efficiencies of CV with the initial CV concentrations on chitosan in the presence of increasing concentrations of Cu and comparison with the CV present as the single dye.

containing equal quantities of the components (100 and 200 mg/L). In chitin and chitosan sorbents, degree of the deacetylation, a proportion between amine, and acetylamino groups, could be a key parameter in controlling sorption of sorbates. Interactions of chitosan with metals are always much more important compared to those of chitin due to the higher number of free amine groups in the chitosan molecule. However, an increment in concentration of CV in the binary mixtures causes enhancement in the selectiveness of CV to chitosan. The sorbed quantities of Cu(II) and CV per unit weight of chitosan in the dual systems are close to each other. However, the adsorption of CV on chitin especially at high concentrations are significantly higher than that of Cu(II).

Chitin is a Cu(II)-chelating agent that binds the metal by amine and hydroxyl groups. However, chitin has been little studied as biosorbent compared to chitosan, due to the concentration of primary amine groups in chitosan. Such chemical groups are the main responsible for adsorption either of cations (by chelation), or anions (by electrostatic attraction) or polar molecules (by interactions as ion-dipole, dipole-dipole, van der Waals forces, etc.). The chitosan contains amine group, $–NH_2$, which is easily protonated to form $–NH^{3+}$ in acidic solutions. The high adsorption capacity of chitosan is due to the strong electrostatic interaction between the $–NH^{3+}$ of chitosan and the dye anions. On the other hand, the 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 [34,35]. 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

Table 2
Comparison of the adsorbed Cu(II) and CV concentrations on chitosan, the total adsorbed concentrations, and the total adsorption efficiencies at equilibrium obtained in the adsorption media containing fixed concentrations of CV in the range 100–500 mg/L, but increasing concentrations of Cu(II) in the range 25–200 mg/L

$C_{\mathrm{Cu},i}$ (mg/L)	$C_{\mathrm{Cv},i}$ (mg/L)	$C_{\mathrm{ads,Cu}}$ (mg/L)	$C_{\mathrm{ads,CV}}$ (mg/L)	$C_{\mathrm{ads,total}}$ (mg/L)	q_{total} (mg/g)	$\%\mathrm{Ads}_{\mathrm{total}}$
25.06	0	22.60	0.00	22.60	4.24	90.17
50.3	0	42.76	0.00	42.76	8.02	85.00
100.6	0	77.33	0.00	77.33	14.50	76.87
151.1	0	102.48	0.00	102.48	19.21	67.82
201.3	0	100.13	0.00	100.13	18.77	49.74
0	103.8	0.00	25.12	25.12	4.71	24.20
0	199.3	0.00	44.64	44.64	8.37	22.40
0	300.5	0.00	64.61	64.61	12.11	21.50
0	405.7	0.00	79.52	79.52	14.91	19.60
0	499	0.00	91.32	91.32	17.12	18.30
26.1	100.8	19.85	33.36	53.22	9.98	41.94
50.6	103.5	28.58	30.66	59.24	11.11	38.44
101.5	102.6	48.86	27.38	76.25	14.30	37.36
152.4	101.7	64.05	24.15	88.20	16.54	34.71
203.1	100.6	50.78	46.27	97.04	18.20	31.95
25.8	201.5	18.97	59.10	78.07	14.64	34.34
51.3	203.6	28.50	57.31	85.81	16.09	33.66
102.6	202.5	48.35	57.00	105.35	19.75	34.53
151.7	200.8	60.39	50.64	111.03	20.82	31.50
201.8	201.4	48.57	44.89	93.47	17.52	23.18
25.3	300.6	17.24	68.36	85.60	16.05	26.26
50.9	301.2	27.42	67.62	95.04	17.82	26.99
101.4	300.8	46.19	58.75	104.93	19.68	26.09
152.2	303.7	59.74	58.61	118.35	22.19	25.96
202.1	302.1	48.42	57.58	106.00	19.88	21.02
26.7	402.1	15.57	77.36	92.94	17.43	21.67
52.3	401.3	27.36	71.79	99.15	18.59	21.86
102.4	400.8	45.40	62.28	107.69	20.19	21.40
151.6	403.5	58.09	57.98	116.08	21.76	20.91
203.4	401.7	39.93	47.24	87.17	16.34	14.41
26.1	502.3	13.78	76.60	90.38	16.95	17.10
51.7	503.1	26.42	69.33	95.75	17.95	17.26
103.4	500.4	43.08	63.10	106.18	19.91	17.58
152.7	501.7	55.14	57.54	112.68	21.13	17.22
202.4	500.6	35.95	50.06	86.01	16.13	12.23

advantages compared to chitosan as a lower solubility in acid medium and lower cost [27,35,36].

One of the most important characteristics that affect the adsorption capacity of chitosan is the degree of deacetylation. Although the hydroxyl groups also attract the dye molecules, the main active groups which impress the adsorption efficiency of chitosan are the amine groups. The degree of deacetylation of chitosan is directly related to the number of available amine groups. Thus, an increment in the degree of deacetylation ordinarily causes an increase in sorption capacity for anionic dyes due to the availability of protonated amine groups [37,38]. As ionic bonding between the amino groups and the dye anions is formed, the higher adsorption capacity of chitosan as compared to chitin is attributed to the presence of protonated amino groups in chitosan [39]. For example, positively charged amine groups of chitosan were reported to attract the negative charge of the sulfonate groups found in methyl blue, an anionic dye, via electrostatic interaction [40,41].

On the other hand, the variation in adsorption properties was reported to be not proportional to the degree of deacetylation [42]. For basic dyes such as CV, the adsorption capacity was generally recorded to be low in comparison to acidic dyes. This was due to the positive charge of basic dye that creates strong coulombic repulsions between chitosan and basic dye [43]. However, the hydroxyl group (–OH) in chitosan could adsorb the basic dye via covalent and hydrogen bonding. The interaction of CV with chitosan occurs mainly through hydrogen bonding and van der Waals forces [44]. A similar adsorption mechanism was observed in the adsorption of reactive dyes with cellulose polymers [45]. The deprotonation of the hydroxyl group occurs by the following mechanism:

$$CH_2OH + OH^- \rightarrow CH_2O^- + H_2O$$

Not only are covalent linkages involved in the adsorption mechanism of CV and Cu(II), but also van der Waals forces, the ionic forces and hydrogen bonds occur. Chitosan also connects Cu(II) ions via chelation, due to the presence of an amino group of the 2-amino-2-deoxy-D-glucose (glocosamine) unit. Better chelation is obtained for greater degrees of deacetylation of chitin. Thus, chelation is related to the $-NH_2$ content as well as to the $-NH_2$ distribution. The proposed two forms are given as follows [27]:

$$[Cu(-NH_2)]^{2+}, 2OH^-, H_2O \text{ and}$$

$$[Cu(-NH_2)_2]^{2+}, 2OH^-,$$

The first complex is reported to form at pH between 5.0 and 5.8, while the second forms above 5.8. However, there is a disagreement in the literature regarding the coordination modes for the chitosan-Cu complex. Using the technique of electrospray mass spectrometry, it has been lately proved that the Cu(II) is coordinated to the C(1)-alkoxide, the four amine nitrogens of chitosan, tetrasaccharide, and an anion. Considering the possible mechanisms described above, the competition of both cationic species (dye and metal) by the chitosan can be associated by the competition of both cationic species (CV and Cu(II) by the surface hydroxyl groups of chitosan. As a matter of fact, significant amounts of both Cu(II) and CV were removed from the binary mixtures by chitosan in this study.

3.3. Application of multi-component Redlich–Peterson model on the competitive adsorption of Cu(II) and CV from binary mixtures on chitin and chitosan

The multi-component adsorption equilibria of Cu (II) and CV from dual-systems by chitin and chitosan at pH 5.0 and 25˚C were investigated to describe by competitive adsorption models. The previously mentioned approaches deduce competitive isotherms only from single-component isotherms, using the individual isotherm parameters only. However, in the present approach, better accuracy has been achieved by extracting additional comparative coefficients from experimental competitive isotherms. Application of multi-component Langmuir, Freundlich, and Redlich–Peterson models to the multi-component adsorption equilibria of Cu(II) and CV was tested. Among the tested models, the multi-component three-parameter Redlich–Peterson model showed the best fit for the competitive Cu(II)-CV adsorption equilibrium data both on chitin and chitosan. The three parameters given by the Redlich–Peterson adsorption model were estimated from the multi-component adsorption data of Cu(II) and CV by using a Microsoft Office 2013 Excel software. The constants calculated from the multi-component Redlich–Peterson isotherm model are given in Table 3. To quantify the agreement between the model predictions and experimental observations, three different statistical methods were used: the relative percentage error (RPE), the variance (MSR), and the objective function (E_i). Comparison of the values of statistical parameters using to test the accuracy of the multi-component Redlich Peterson model shows clearly that this model provided a good correlation for the comperative adsorption of Cu(II) and CV by chitin and chitosan. The highest Redlich–Peterson constants which are a measure of the adsorption capacity and affinity, K_{R1} and a_{R1}, respectively, were obtained in the adsorption of Cu(II) by chitosan in the presence of increasing concentrations of CV in the media. If the Redlich–Peterson coefficients of Cu (II) and CV are compared, it is seen clearly that Cu(II) was adsorbed selectively by chitosan in the binary mixtures.

In addition, Redlich–Peterson isotherms for the competitive adsorption of Cu(II)—CV by chitin and chitosan are given in Figs. 5(a) and (b), 6(a) and (b) as comparative with the model curves and experimental values. The amount of sorbed Cu(II) per unit weight of chitin at equilibrium with increasing concentration of the dye decreased comparing with the single-component Cu(II) system (Fig. 5(a)). The amount of sorbed Cu(II) per unit weight of chitin at equilibrium in the medium containing 100 mg/L CV was only higher than that of the single-component Cu(II) system due to the higher concentration difference between the adsorbent surface and the solution.

As also seen in Fig. 5(b), the amount of sorbed CV per unit weight of chitin at equilibrium in the presence of increasing concentrations of Cu(II) ions decreased regularly comparing with the single-component system of the dye. In the single-component CV

Table 3
Multi-component Redlich–Peterson constants of Cu(II) and CV

	Cu						Crystal Violet					
Sorbent	a_{R1} (mg$^{\beta+1}$/g l$^{\beta}$)	K_{R1} (l g^{-1})	β_1	RPE (%)[a]	MSR[b]	E_i[c]	a_{R1} (mg$^{\beta+1}$/g l$^{\beta}$)	K_{R1} (l g^{-1})	β_1	RPE (%)[a]	MSR[b]	E_i[c]
Chitin	0.085	1.201	0.899	19.1	3.2	2.02	0.055	1.318	0.812	18.0	20.8	1.21
Chitosan	5.700	15.586	0.639	19.7	6.9	2.48	0.128	3.866	0.871	26.8	8.8	1.67

[a] Relative percent error:

$$\mathrm{RPE}(\%) = \frac{\sum\left[\left|(q_{i,\mathrm{eq}})_{\mathrm{predicted}} - (q_{i,\mathrm{eq}})_{\mathrm{experimental}}\right|/(q_{i,\mathrm{eq}})_{\mathrm{experimental}}\right] \times 100}{N}$$

where N is the number of experimental data.

[b] Mean square of residuals:

$$\mathrm{MSR} = \frac{\sum\left[(q_{i,\mathrm{eq}})_{\mathrm{predicted}} - (q_{i,\mathrm{eq}})_{\mathrm{experimental}}\right]^2}{N}$$

[c] Objective function:

$$E_\mathrm{i} = \sum_{j=i}^{N}\left[\frac{(q_{i,\mathrm{eq}})_{\mathrm{experimental}} - (q_{i,\mathrm{eq}})_{\mathrm{predicted}}}{(q_{i,\mathrm{eq}})_{\mathrm{experimental}}}\right]^2$$

system, the amount of sorbed CV per unit weight of chitin at equilibrium increased to 49.4 mg/g ($C_{\mathrm{ads.}}$ = 263.49 mg/L) with increasing CV concentration up to 407.22 mg/L, then the saturation of chitin surface with CV began. In the binary mixture containing 152.4 mg/L Cu(II) and 403.2 mg/L CV, the amount of sorbed CV per unit weight of chitin at equilibrium increased to 26.66 mg/g ($C_{\mathrm{ads.}}$ = 141.89 mg/L), then the saturation of chitin surface both the Cu(II) and CV was observed. For that reason in the presence of increasing concentrations of Cu(II) ions, although the amount of sorbed CV per unit weight of chitin at equilibrium decreased with respect to single-component system, the rising trend of the competitive adsorption isotherms continued without saturation.

The amount of sorbed Cu(II) per unit weight of chitosan at equilibrium in the presence of increasing concentrations of CV decreased significantly comparing with the single-component system of the Cu(II) (Fig. 6(a)). On the other hand, the amount of sorbed CV per unit weight of chitosan at equilibrium in the media containing 50 mg/L Cu(II) was higher than that of the single-component CV system (Fig. 6(b)). When the concentration of Cu(II) was increased from 100 to 200 mg/L, the amount of sorbed CV per unit weight of chitosan decreased compared with the single-component system. However, at increasing concentrations of Cu(II) (100–200 mg/L), the amounts of sorbed CV per unit weight of chitosan at equilibrium was generally higher than those of the proposed by the model. This was observed especially at lower concentrations of CV. Since the expected increases in the inhibitory effects caused by the presence of Cu(II) at increasing concentrations were not observed, the predicted equilibrium uptake values for CV were lower than the experimental equilibrium uptake values.

To define multi-component adsorption equilibria of one metal and one dye, multi-component adsorption models have been rarely used. However, multi-component adsorption of dyes or metals separately has been generally defined by modified Freundlich and Langmuir models extended for competitive adsorption and characterizing antagonistic interaction between components. Ideal adsorbed solution theory (IAST) is assumed to be the most thermodynamically adopted base for physical adsorption of dyes in multi-component systems. The IAST models based on the three isotherms, Langmuir, Sips, and Redlich–Peterson models

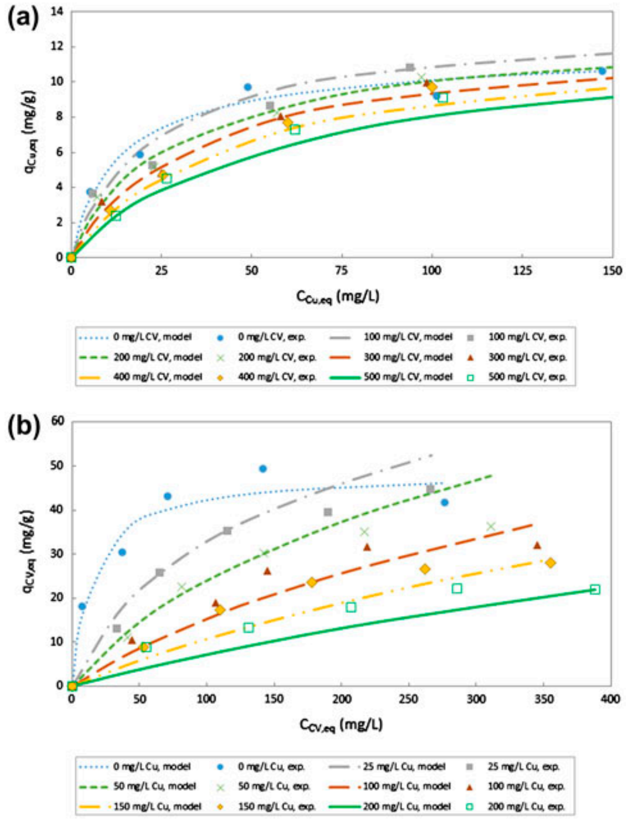

Fig. 5. Comparison of the single- and multi-component Redlich-Peterson adsorption isotherms (a) for Cu(II) adsorption on chitin with the Cu(II) present as the single metal and in the presence of increasing concentrations of CV; (b) for CV adsorption on chitin with the CV present as the single dye and in the presence of increasing concentrations of Cu(II).

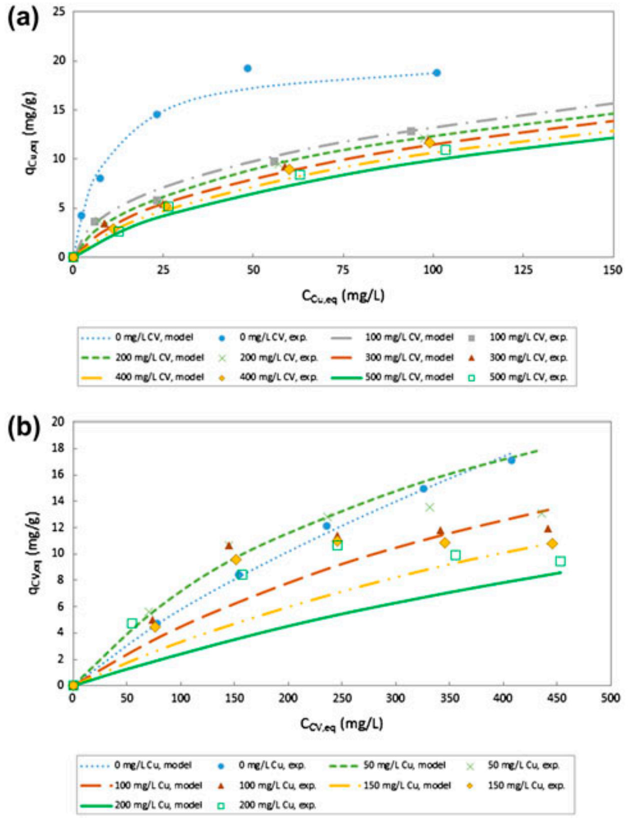

Fig. 6. Comparison of the single- and multi-component Redlich-Peterson adsorption isotherms (a) for Cu(II) adsorption on chitosan with the Cu(II) present as the single metal and in the presence of increasing concentrations of CV; (b) for CV adsorption on chitosan with the CV present as the single dye and in the presence of increasing concentrations of Cu(II).

have been shown to produce a good fit for the multi-component equilibrium data of dyes [33]. Considering this point, the representation of competitive adsorption data of CV and Cu(II) on chitin/chitosan is consistent with the literature.

3.4. Analysis of reaction kinetic data

To design a wastewater treatment system, it is extremely important to known values of kinetic parameters. The pseudo-first-order and pseudo-second-order kinetic models are commonly used to calculate the values of adsorption kinetic parameters. In order to explore the kinetic mechanism of Cu(II) and CV adsorption on chitin and chitosan, two kinetic models, the pseudo-first-order model of Lagergren [46], and pseudo-second-order reaction model of Ho and McKay [47] based on the solid-phase sorption were applied. The linearized forms of pseudo-first and second-order models are given below:

$$\text{Pseudo-first-order}: \ln(q_{\text{eq}} - q_{\text{t}}) = \ln q_{\text{eq}} - k_{\text{s1}} t$$

$$\text{Pseudo-second-order}: \frac{t}{q_t} = \frac{1}{k_{\text{s2}} q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}} t$$

where q_t is the amount of solute adsorbed per unit weight of adsorbent at any time t, q_{eq} the amount of solute adsorbed per unit weight of adsorbent at equilibrium, k_{s1} the pseudo-first-order reaction rate constant, and k_{s2} is the pseudo-second-order reaction rate constant.

The experimental adsorption kinetic data of Cu(II) and CV on chitin and chitosan were tested using the above two kinetic models and a comparison of the best fit adsorption mechanism was given below. The pseudo-first-order reaction rate constant, k_{s1}, and the pseudo-second-order reaction rate constant, k_{s2}, were evaluated; the linearized equations for these models along with the correlation coefficients are presented in

Table 4
Comparison of kinetic models and correlation coefficients for Cu(II) and CV adsorption on chitin and chitosan

Adsorbent	Adsorbate	Pseudo-first-order rate equation	R^2
Chitin	Cu(II)	$\ln(q_{\mathrm{eq}} - q_t) = 2.280 - 0.009t$	973
Chitin	CV	$\ln(q_{\mathrm{eq}} - q_t) = 2.399 - 0.028t$	800
Chitosan	Cu(II)	$\ln(q_{\mathrm{eq}} - q_t) = 2.431 - 0.007t$	869
Chitosan	CV	$\ln(q_{\mathrm{eq}} - q_t) = 1.391 - 0.0041t$	888
Adsorbent	Adsorbate	Pseudo second order rate equation	R^2
Chitin	Cu(II)	$\frac{t}{q_t} = 2.209 + 0.094t$	954
Chitin	CV	$\frac{t}{q_t} = 0.292 + 0.054t$	997
Chitosan	Cu(II)	$\frac{t}{q_t} = 0.661 + 0.068t$	988
Chitosan	CV	$\frac{t}{q_t} = 1.213 + 0.209t$	997

Table 4. The pseudo-second-order rate model provided the best correlation of the kinetic data for both Cu(II) and CV adsorption on chitin and chitosan with higher correlation coefficients. The pseudo-first-order rate model is the one-site model. This model propose that the reaction rate is limited by only one process or mechanism on a single class of sorbing sites, and that all sites are of the time-dependent type. For that reason, it is not appropriate for most heterogeneous systems, as multiple sorption sites exist in chitin and chitosan, having polycationic property. The second-order models are the two-site or bicontinuum models and are used to define chemical and physical nonequilibrium. 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. The pseudo-second-order kinetic model is specifically based on the assumption that the rate-limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate.

4. Conclusion

In the two-component adsorption of Cu(II) and CV on chitin, the amount of sorbed Cu(II) per unit weight of chitin was decreased generally with increasing concentration of CV In addition at all Cu(II) concentrations studied, the sorption efficiency of Cu(II) also decreased with increasing concentrations of CV In the presence of increasing concentrations of Cu(II) in the media, the initial adsorption rates of CV on chitin increased generally, on the other hand, adsorption equilibrium removal and efficiency of CV decreased with respect to single-component systems. Additionally, total adsorbed concentrations of Cu(II) and CV together was higher than those of single-component Cu(II) system, lower than those of single-component CV system. The same trend was also observed in the total amounts of sorbed Cu and CV per unit weight of chitin. Consequently, the combined action of Cu(II) and CV caused a synergistic impact on adsorption capacity of chitin compared to the single-component Cu(II) system, and an antogonistic effect compared to the single-component CV system.

In case of chitosan, in the competitive adsorption of Cu(II) and CV, increasing concentrations of CV reduced the initial adsorption rate's efficiency of Cu (II) compared to the single-component system. In the binary mixtures, total adsorbed concentrations and the total amounts of sorbed Cu(II) and CV per unit weight of chitosan, $q_{\mathrm{tot.}}$(mg/g), were higher than those of each single-component systems. In this case, the combined action of Cu(II) and CV on the adsorption capacity of chitosan is remarked to be synergistic. The competitive Redlich–Peterson model was employed successfully to describe complex adsorption behavior of Cu(II) and CV in aqueous media. The multi-component Redlich-Peterson model physically provided a more realistic description of metal-dye adsorption by biological material because it accounts for different binding sites. As a consequence, understanding of multi-component interaction of Cu(II) and CV would be very helpful to optimize the design of chitin–chitosan-based wastewater treatment units.

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