Adsorption of Copper Ions and Methylene Blue in a Single and Binary System on Wheat Straw

Yongjun Wu,[†,‡] Lijun Zhang,[†] Congli Gao,[†] Jiangyan Ma,[†] Xinghua Ma,[§,†] and Runping Han*[,†,§]

Department of Chemistry, Zhengzhou University, No 100 of Kexue Road, Zhengzhou, 450001 P. R. China, College of Public Health, Zhengzhou University, No 100 of Kexue Road, Zhengzhou, 450001 P. R. China, and China Petroleum & Chemical Cooperation Luoyang Company, Jili District, Luoyang, 471012 P. R. China

A natural wheat straw was used as adsorbent for removal of copper and methylene blue (MB) from aqueous solution. A batch system was applied to study the behavior of Cu^{2+} and MB adsorption in single and binary systems on wheat straw. In the single systems, there was no significant difference in the quantity of MB adsorbed onto wheat straw within a pH range of 4.0 to 10.0. But for Cu^{2+}, the optimal pH is about 5. Kinetic studies indicate that Cu^{2+} and MB adsorption on the wheat straw follows the Elovich equation. The Cu^{2+} adsorption isotherm follows the Langmuir and Redlich−Peterson models, while MB adsorption follows the Redlich−Peterson isotherm. The adsorption capacities of Cu^{2+} and MB at 273 K and pH 5 are (7.05 and 60.66) $mg \cdot g^{-1}$, respectively. In the binary system, Cu^{2+} and MB exhibited competitive adsorption. The adsorption of Cu^{2+} or MB is considerably reduced with an increasing concentration of the other. The quantity of Cu^{2+} adsorbed is more strongly influenced by MB due to the higher affinity of wheat straw for the latter. As wheat straw is easily obtained and cheap, it will be promising for removal of metal ions and dyes.

1. Introduction

Dyes and heavy metal ions are important pollutants, causing environmental and health problems to human beings and aquatic animals. Wastewater from the textile and dyeing industries contains dye stuffs, suspended solids, other soluble organic substances, and heavy metals. Removal of heavy metals and dyes from wastewater can be achieved by several techniques, such as precipitation, flocculation, adsorption, ion exchange, etc.[1] Adsorption techniques have proved to be effective and attractive processes for the treatment of these dyes and heavy metal-bearing wastewaters.[2,3]

In heavy metals, the copper ion is widely used in electroplating, the light industry, the mechanical manufacturing industry, and architecture. Additionally, copper is an indispensable micronutrient element to humans and other life forms. However, it is one of the toxic metals to human beings as excessive copper causes serious lesions in the central nervous system and even permanent damage particularly for children.[4] Methylene blue (MB) is selected as a model compound to evaluate the capacity of adsorbents for the removal of basic dyes from aqueous solutions. MB has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, and coating for paper stock. The presence of dyes in water, even at very low concentrations, is highly visible and undesirable. Therefore these materials have to be removed from wastewater before discharging to diminish environmental effects.

Wheat straw contains abundant floristic fiber, protein, and some functional groups such as carboxyl, hydroxy, and amidogen, etc., which make the adsorption processes possible.[5] Furthermore, the yield of wheat straw obtained from agriculture as waste is vast. Hence wheat straw has a low cost and can be easily obtained. Wheat straw is an abundant resource available all over the north of China. In the past years, natural or modified wheat straw has been explored as an effective adsorbent for removal of various heavy metals and dyes.[6−8] However, in the previous studies, only single component systems were investigated, and a few investigations on binary systems (dye and metal ion) have been reported to consider competitive adsorption.[9]

Understanding of multicomponent interaction with wheat straw would be very helpful for its use in wastewater treatment. Moreover, removal kinetics and equilibrium are highly needed to optimize the design of adsorption reactors. In this paper, an investigation of coadsorption of Cu^{2+} and MB is presented. We compare their adsorption in single and binary systems to investigate simultaneous adsorption processes and determine the adsorption kinetics and equilibrium in single systems.

2. Materials and Methods

2.1. Materials. The wheat straw used in the present investigation was obtained from the local countryside. The collected materials were washed with distilled water several times to remove all the dirt particles. The washed material was dried in an oven at 373 K for a period of 24 h and then ground and screened through a set of sieves to get the geometrical sizes (20 to 40) mesh. This produced a uniform material for the complete set of adsorption tests which was stored in an airtight plastic container for all investigations.

The wheat straw is mainly composed of carbohydrates, lignin, cellulose, and volatile substances which are 91 % of the total weight.[5] The morphology of wheat straw is rough and has been shown to facilitate the adsorption of metals and dyes by SEM analysis (Figure not shown). The BET surface of wheat straw is 3.5 $m^2 \cdot g^{-1}$.

All chemicals were obtained from the Luoyang Chemical Corporation in China. Stock solutions of 500 $mg \cdot L^{-1}$ of Cu(II)

* Correspondening author. Telephone: +86 371 67781757. Fax: +86 371 67781556. E-mail: rphan67@zzu.edu.cn.
[†] Department of Chemistry, Zhengzhou University.
[‡] College of Public Health, Zhengzhou University.
[§] China Petroleum & Chemical Cooperation Luoyang Company.

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were prepared from $CuCl_2$ in distilled, deionized water containing a few drops of concentrated HCl to prevent the precipitation of Cu^{2+} by hydrolysis. The stock solutions of MB were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration. The initial pH of the working solution was adjusted by addition of HCl or NaOH solution.

2.2. Adsorption Tests. The adsorption tests were performed by the batch technique at 293 K. For kinetic and isothermal studies in single adsorbate systems, a series of 125 mL flasks were used, and each flask was filled with wheat straw at mass loadings of 2 $g \cdot L^{-1}$ for Cu^{2+} solutions and 1 $g \cdot L^{-1}$ for MB solutions at different initial concentrations (10 mL), respectively. The conical flasks were then agitated in an orbital shaker at 100 rpm, and liquid samples were taken out at a given time interval for Cu^{2+} or MB analyses. Cu^{2+} was measured using atomic absorption spectrometry at 234.8 nm (AAanalyst300, Perkin-Elmer). MB was analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at the wavelength of maximum absorbance (668 nm).

For coadsorption in binary systems, wheat straw at loadings of 2 $g \cdot L^{-1}$ were mixed with Cu^{2+} and MB mixture solutions at various initial concentrations. The procedure for testing and analysis was also the same as described above. The contact time was 6 h.

The data obtained in batch mode studies were used to calculate the equilibrium metal adsorptive quantity. It was calculated for each sample of Cu^{2+} or MB by using the following expression

$$q_e = \frac{V(c_0 - c_e)}{1000m} \quad (1)$$

where q_e is the equilibrium uptake value (the amount of Cu^{2+} or MB adsorbed per unit mass of dry wheat straw) in $mg \cdot g^{-1}$; V is the sample volume in mL; c_0 is the initial Cu^{2+} or MB concentration in $mg \cdot L^{-1}$; c_e is the equilibrium Cu^{2+} or MB concentration in $mg \cdot L^{-1}$; and m is the dry weight of wheat straw in grams.

3. Results and Discussion

3.1. Effect of Solution pH on Cu^{2+} and MB Adsorption. It is well-known that the pH of the system is an important variable in the adsorption process. The charge of the adsorbate and the adsorbent often depends on the pH of the solution. Figure 1 shows the variation of Cu^{2+} and MB adsorption on wheat straw at varying solution pH. For Cu^{2+}, adsorption increases with increasing pH from 2 to 5. For MB, adsorption also increases as pH is increased before pH 4 and then keeps nearly constant between 4 and 10.

At low pH, Cu^{2+} removal is inhibited possibly as a result of a competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions. As the pH increases, the negative charge density on the wheat straw surface increases due to deprotonation of the metal binding sites, and thus the adsorption of metal ions increases. The increase in adsorption with the decrease in H^+ ion concentration (high pH) indicates that ion exchange is one major adsorption process. Above pH 5, adsorption decreases. The reason is that when above this pH value copper ions in solution were in two forms: Cu^{2+} and $CuOH^+$. Since in the latter state copper in solution would present a larger size, it would be adsorbed less easily, and therefore a diminution in the adsorption capacity would be expected. Furthermore, if the pH value was over 7.0, the ions of copper would deposit. For MB, a basic dye, it will be

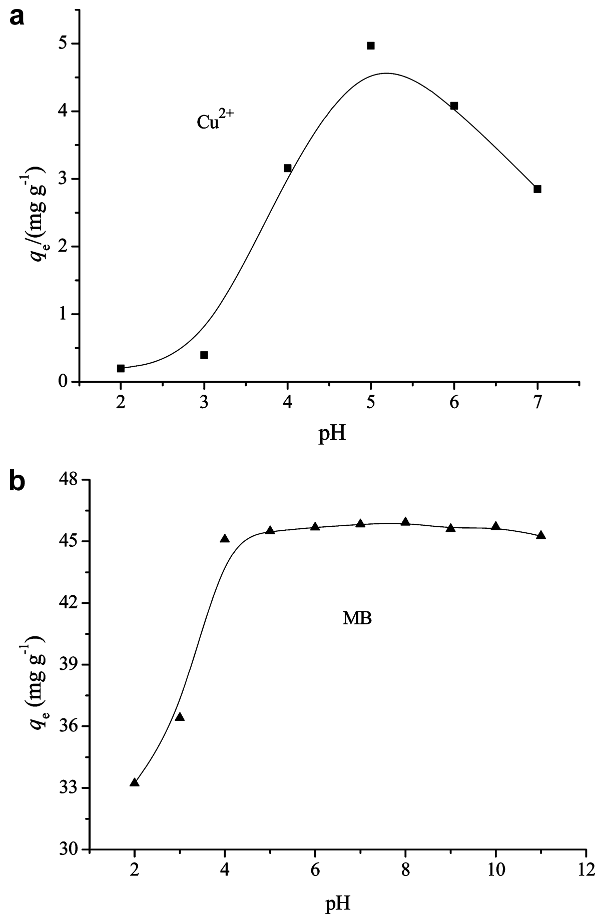


Figure 1. Effect of solution pH on Cu^{2+} (c_0 = 20 $mg \cdot L^{-1}$) and MB (c_0 = 50 $mg \cdot L^{-1}$) adsorption on wheat straw.

positively charged in solution. As the pH of the dye solution becomes higher, the association of dye cations on solid will take place more easily, resulting in an increase in adsorption. Some previous reports have shown similar results for Cu^{2+} and MB.[6,10−15]

The structure of wheat straw is cellulose based, and the surface of cellulose in contact with water is negatively charged.[5] Dissolved Cu^{2+} and MB ions are positively charged and will undergo attraction on approaching the anionic wheat straw structure. On this basis, it is expected that Cu^{2+} and MB will have a strong sorption affinity for wheat straw.

3.2. Dynamic Adsorption in Single-Component Solution. Figure 2 illustrates the dynamic adsorption process of Cu^{2+} and MB on wheat straw.

From Figure 2, it is found that the adsorptive quantity of both Cu^{2+} and MB on wheat straw increases with increasing contact time. A two-stage kinetic behavior is evident: an initial rapid stage where adsorption is fast and contributes significantly to equilibrium uptake and a slower second stage whose contribution to the total MB adsorption is relatively small. The first stage is the instantaneous adsorption stage or external surface adsorption. The second stage is the gradual adsorption stage (where the intraparticle diffusion is rate-controlled), and finally the Cu^{2+} and MB uptake reach equilibrium.[9,16] This suggests that the adsorption should include two diffusion processes, external and internal diffusion.

For Cu^{2+}, the adsorption can achieve near equilibrium at 1.5 h, faster than MB adsorption (near equilibrium at 5 h). The difference in diffusion processes of Cu^{2+} and MB is probably due to molecular size. MB is an organic compound having a

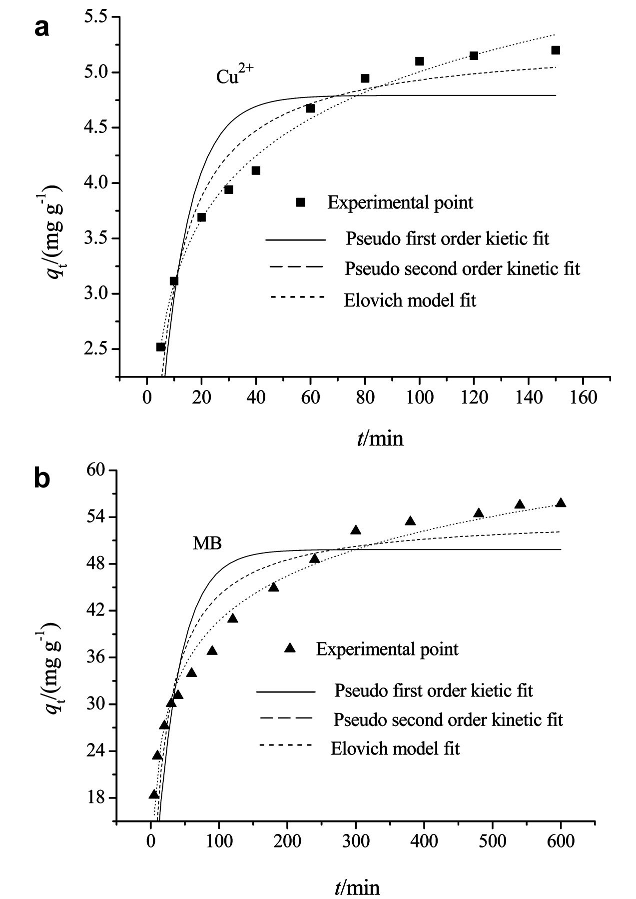


Figure 2. Dynamic adsorption of Cu^{2+} (c_0 = 20 mg·L^{-1}) and MB (c_0 = 100 mg·L^{-1}) on wheat straw in single systems.

larger molecular size, thus making it difficult to diffuse into pores of wheat straw.

To investigate the adsorption kinetics of Cu^{2+} and MB on wheat straw, three simple kinetic models are used, which are pseudo-first-order, pseudo-second-order, and the Elovich equation. The pseudo-second-order equation is expressed as[17]

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

where q_e and q_t are the amount of solute adsorbed (mg·g^{-1}) at equilibrium and time t (min), respectively, and k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}).

The pseudo-second-order equation is given by eq 3[18]

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where k_2 is the rate constant of the pseudo-second-order adsorption (mg·g^{-1}·min^{-1}).

The Elovich equation is used to describe the kinetics of chemisorption of gas on solids. The application of the Elovich equation in liquid phase sorption is now gaining in popularity.[19] The Elovich equation is expressed as

$$q_t = A + B \ln t \quad (4)$$

where A and B are the Elovich constant.

Nonlinear regressive analysis was conducted using the Origin 7.0 software. The relative kinetic parameters obtained from model simulations are given in Table 1.

From Table 1, the values of R^2 of the Elovich equation for Cu^{2+} and MB are high (> 0.980) and followed by those of the pseudo-second-order kinetic equation and pseudo-first-order

Table 1. Parameters of Three Kinetic Models for Cu^{2+} and MB Adsorption

first-order kinetic model	k_1 (min^{-1})	q_e (mg·g^{-1})	R^2	SS[a]
Cu^{2+}	0.0969 ± 0.0191	4.79 ± 0.19	0.774	0.220
MB	0.0288 ± 0.0061	49.84 ± 2.46	0.727	47.3
second-order kinetic model	**k_2 (g·mg^{-1}·min^{-1})**	**q_e (mg·g^{-1})**	**R^2**	**SS**
Cu^{2+}	0.0259 ± 0.0046	5.29 ± 0.15	0.936	0.0618
MB	0.00080 ± 0.00019	54.11 ± 2.18	0.876	21.5
Elovich model	**A**	**B**	**R^2**	**SS**
Cu^{2+}	1.19 ± 0.11	0.829 ± 0.029	0.990	0.0095
MB	2.45 ± 1.52	8.31 ± 0.32	0.982	3.20

[a] SS = $\Sigma(q_t - q_c)^2$; q_t and q_c are the experimental value and calculated value according the model, respectively.

equation, respectively, while the values of SS for the three models are of opposite order. From comparison of the experimental points and fitted curves with values of SS and R^2, the Elovich equation is best to predict the dynamic adsorption of Cu^{2+} and MB adsorption on wheat straw. As the Elovich equation is successfully used to describe the adsorption kinetics of ion exchange systems, it can be concluded from Table 1 that the adsorption system is a chemical process, especially an ion exchange process.[19]

The calculated values of equilibrium adsorption capacity (q_e, for Cu^{2+} 5.29 mg·g^{-1} and for MB 54.11 mg·g^{-1}, respectively) obtained from the pseudo-second-order model agree better with the experimental q_e values (Cu^{2+} 5.25 mg·g^{-1}, MB 56.0 mg·g^{-1}) than those from the pseudo-first-order model. The results with values of R^2 and SS show that the pseudo-second-order model is better for predicting the kinetic process in the experimental conditions than the pseudo-first-order model. This also implies that the adsorption process may be a chemical process.[18]

A comparison of fitted curves from three kinetic equations and experimental results for Cu^{2+} and MB adsorption is also shown in Figure 2. The Elovich equation provides the best correlation for both of the adsorption processes, whereas the pseudo-second-order equation also fits the experimental data well. The pseudo-first-order does not give a good fit to the experimental data for the adsorption of Cu^{2+} or MB.

3.3. Adsorption Isotherm. Figure 3 illustrates the adsorption isotherm of Cu^{2+} and MB on wheat straw in single systems. The equilibrium adsorption q_e increases with an increase in Cu^{2+} and MB concentrations.

Three adsorption isotherms, Langmuir, Freundlich, and Redlich−Peterson isotherms, were employed to calculate the adsorption capacity. The Langmuir adsorption isotherm has been successfully applied to many pollutant adsorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution.[20] The common form of the Langmuir isotherm is

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (5)$$

where q_m is the q_e for a complete monolayer (mg·g^{-1}), a constant related to adsorption capacity; and K_L is a constant related to the affinity of the binding sites and energy of adsorption (L·mg^{-1}).

The Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface. The Freundlich isotherm is commonly presented as[21]

$$q_e = K_F c^{1/n} \quad (6)$$

where K_F and $1/n$ are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively.

The three-parameter Redlich−Peterson equation which has a linear dependence on concentration in the numerator and an exponential function in the denominator has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by eq 7[22]

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (7)$$

where A, B, and g are the Redlich−Peterson parameters, and g lies between 0 and 1. For $g = 1$, eq 7 converts to the Langmuir form.

The parameters of the three isotherms based on eqs 5, 6, and 7 are presented in Table 2 using nonlinear regression analysis.

One can see that regression coefficients obtained from the Langmuir and Redlich−Peterson isotherms are higher than the Freundlich isotherm for Cu^{2+}, while the relative value of SS is lower, which suggests the applicablility of the Langmuir isotherm for Cu^{2+}. On the contrary, the Langmuir model will be better in describing MB adsorption isotherm from values of R^2 and SS.

The maximum adsorption of Cu^{2+} and MB is 7.05 (0.112 mmol·g^{-1}) and 60.66 mg·g^{-1} (0.162 mmol·g^{-1}), respectively, based on the Langmuir isotherm. This result shows that the wheat straw has more ability to bind MB than Cu^{2+}.

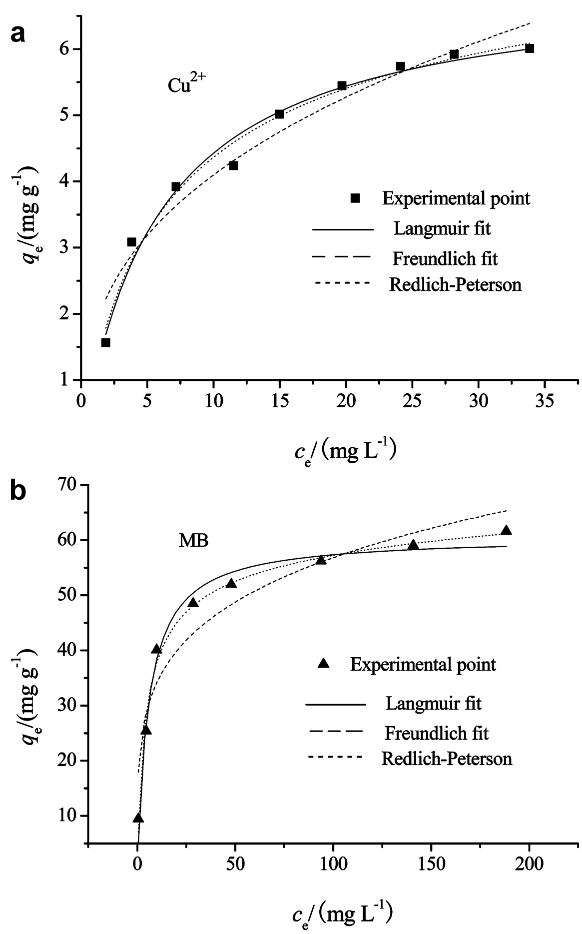


Figure 3. Adsorption isotherms of Cu^{2+} and MB on wheat straw in single systems.

Table 2. Parameters for Adsorption Isotherm of Cu^{2+} and MB in a Single System

Langmuir isotherm	K_L (L·mg^{-1})	q_m (mg·g^{-1})	R^2	SS
Cu^{2+}	0.169 ± 0.020	7.05 ± 0.24 (0.112 mmol·g^{-1})	0.983	0.0447
MB	0.172 ± 0.026	60.66 ± 1.61 (0.162 mmol·g^{-1})	0.982	6.89

Freundlich isotherm	K_F	$1/n$	R^2	SS
Cu^{2+}	1.77 ± 0.19	0.364 ± 0.037	0.953	0.120
MB	20.57 ± 3.03	0.221 ± 0.034	0.922	30.1

Redlich−Peterson isotherm	A	B	g	R^2	SS
Cu^{2+}	1.41 ± 0.37	0.269 ± 0.17	0.919 ± 0.099	0.984	0.0466
MB	16.1 ± 4.15	0.391 ± 0.16	0.921 ± 0.033	0.991	4.38

Table 3. Cu^{2+} and MB Adsorption by Plant-Derived Materials: q_m Obtained from the Langmuir Constant

q_m/(mg·g^{-1})	adsorbent	refs
	Cu^{2+}	
4.46	cereal chaff	11
8.3	wheat shell	24
4.45	wheat straw	25
5.40	soybean straw	25
3.75	corn stalk	25
2.16	corn cob	25
1.85	rice shell	26
7.39	wheat shell	26
8.98	lentil shell	26
8.45	sawdust	27
7.05	wheat straw	this study
	MB	
40.6	rice husk	13
20.3	cereal chaff	14
80.9	phoenix tree leaves	15
32.3	modified sawdust	28
16.56	wheat shell	29
76.9	hazelnut shell	30
60.66	wheat straw	this study

As shown in Table 2, all measured values of K_F show easy adsorption of Cu^{2+} and MB with a high adsorptive capacity of wheat straw. The obtained values of $1/n$ ($0.1 < 1/n < 1$) indicated favorable adsorption of Cu^{2+} and MB at all temperatures studied.[23]

From Table 2, the value of g from the Redlich−Peterson isotherm is near 1, and both Langmuir and Redlich−Peterson isotherms can better predict the data.

A comparison of fitted curves from three isotherms and experimental results for Cu^{2+} and MB adsorption is also shown in Figure 3. It is observed that the fitted curve is well represented by the Redlich−Peterson and Langmuir isotherm equations when compared to the Freundlich isotherm, with an SS value of 0.466, 0.0477, and 0.120 for Cu^{2+} adsorption and 4.38, 6.89, and 30.1, respectively (Table 2). There is a good agreement between the experimental data and the fitted curves from the Redlich−Peterson isotherm.

The q_m value shows that the adsorption capacity of wheat straw is highly comparable to that of some other low-cost adsorbent materials for Cu^{2+} and MB. The values q_m of some plant-derived materials binding Cu^{2+} or MB from the Langmuir constant are listed in Table 3. Compared to other materials listed in Table 3, the value of q_m of Cu^{2+} and MB adsorption onto wheat straw is higher. As waste, it is so cheap, so wheat straw can be used to remove Cu^{2+} and MB from solution.

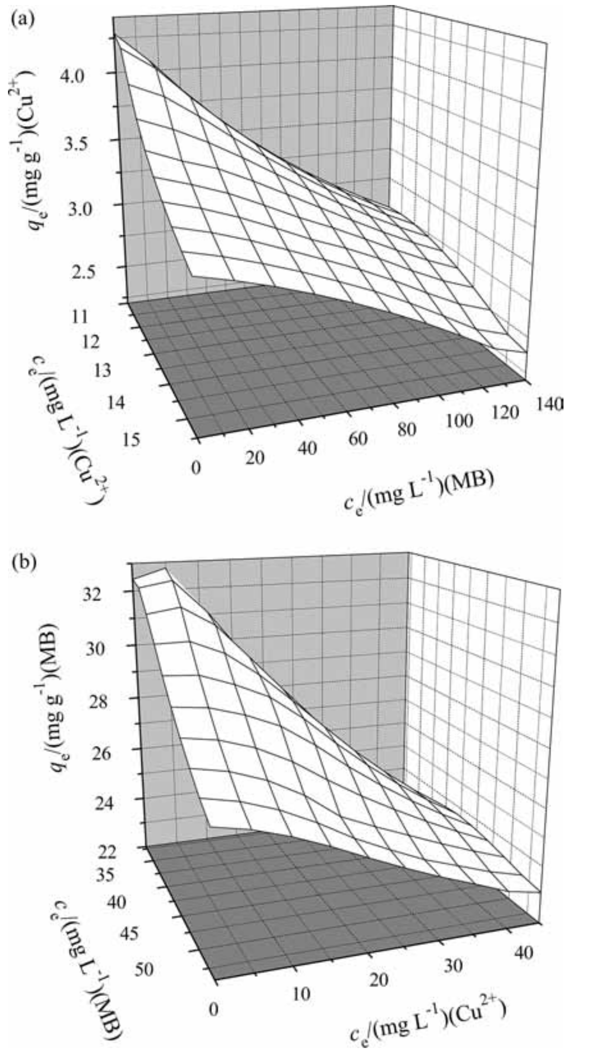


Figure 4. Binary adsorption isotherm. (a) The adsorption capacity of Cu^{2+} is plotted as a function of the equilibrium concentrations of Cu^{2+} and MB. (b) The adsorption capacity of MB is plotted as a function of the equilibrium concentrations of Cu^{2+}.

3.4. Competitive Adsorption of Cu^{2+} and MB in Equilibrium. The experiments of competitive adsorption of Cu^{2+} and MB include two parts: (i) the effect on Cu^{2+} adsorption with the presence of MB in the solution and the effect on MB adsorption with the presence of Cu^{2+} in the solution; (ii) the competitive adsorption of Cu(II) and MB in the total concentration did not change.

3.4.1. Effect on Adsorption of Cu^{2+} or MB with the Presence of MB or Cu^{2+} in the Solution. In a series of two binary systems, the initial concentration of Cu^{2+} is fixed to 20 $mg \cdot L^{-1}$ (0.315 $mmol \cdot L^{-1}$), whereas the concentration of MB is varied from (0 to 200) $mg \cdot L^{-1}$ ((0 to 0.535) $mmol \cdot L^{-1}$). In another binary system, the initial concentration of MB is constant at 100 $mg \cdot L^{-1}$ (0.267 $mmol \cdot L^{-1}$), and the concentration of Cu^{2+} is varied from (0 to 45) $mg \cdot L^{-1}$ ((0 to 0.709) $mmol \cdot L^{-1}$). The two (equilibrium) adsorbate concentrations were plotted against the Cu^{2+} or MB uptakes in Figure 4(a) and (b), respectively.

As shown in Figure 4, when both Cu^{2+} and MB are present in solution, some reduction of the Cu^{2+} or MB adsorption can be observed with increasing MB or Cu^{2+} concentration. From Figure 4(a), the interference of MB with the Cu^{2+} adsorption is much more pronounced. The adsorption capacities q_e (for Cu) decrease from (4.42 to 2.37) $mg \cdot g^{-1}$ (reduction of 46.2 %) in the presence of MB with the concentration from (0 to 200) $mg \cdot L^{-1}$, while the values of q_e (for MB) decrease from (33.97 to 23.22) $mg \cdot g^{-1}$ (reduction of 31.65 %) in the presence of Cu^{2+} with the concentration from (0 to 45) $mg \cdot L^{-1}$. From the extent of quantity reduction, the effect of MB in solution on Cu^{2+} adsorption is stronger. So MB has a better affinity for wheat straw than Cu^{2+}. This result is consistent with the single systems.

Wang and Ariyanto have studied the competition of malachite green (cation dye) and Pb ions on natural zeolite in a binary system, and the result is similar to this study; however, Pb^{2+} has a better affinity to natural zeolite than malachite green.[9] Aksu and Isoglu have studied the adsorption of Cu^{2+} and reactive dye (anion dye) onto dried sugar beet pulp in a binary system.[31] The presence of increasing concentrations of Cu^{2+} increases the equilibrium uptake of dye anions, while the adding of increasing concentrations of dye diminishes Cu^{2+} uptake. Wang et al. studied the coadsorption of heavy metal ions and humic acid on different adsorbents.[32−34] The results were that lead ions presented in the system would compete with the adsorption of humic acid on the adsorbent, thus resulting in a decrease in humic acid adsorption and lead adsorption in single systems, respectively.

3.4.2. Competitive Adsorption of Cu(II) and MB at a Fixed Total Concentration. The objective of this part of the work is to study the effect of Cu^{2+} and MB ion coexistence on the total adsorptive capacity of wheat straw. The experiment is carried out keeping the total concentration fixed (120 $mg \cdot L^{-1}$) and changing each ion concentration. The result is shown in Figure 5.

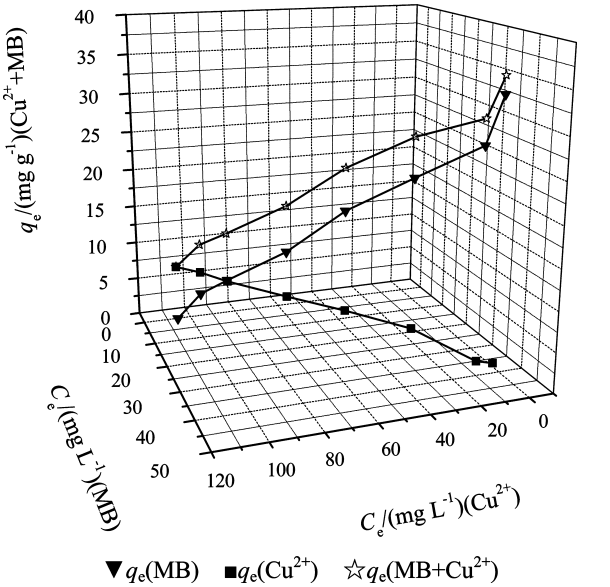


Figure 5. Effect of the fixed total initial concentration of Cu^{2+} and MB on the adsorption capacity of each adsorbate.

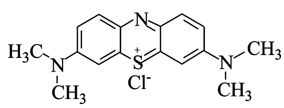
As shown in Figure 5, values of the adsorption capacities q_e obtained from the experiment results for the binary component system at described conditions are less than those for the single-component solutions. This indicates that the dye in solution can inhibit Cu^{2+} adsorption yield while Cu^{2+} inhibits MB adsorption yield. The data also show that the equilibrium concentration of one adsorbate will be significantly different when the concentration of another adsorbate in solution changes. However, the total adsorption capacity for these two ions in the binary system exceeded the capacity of Cu^{2+} but was less than that of MB in the single systems. One type of ion presented in solution interferes with the uptake of another in the same system, and the total adsorbate uptake is lower. In the binary system, there is competitive adsorption between copper ions and MB ions.

4. Conclusion

Natural wheat straw exhibits effective adsorption for Cu^{2+} and MB ions in aqueous solution, giving higher adsorption capacity for MB than Cu^{2+}. However, Cu^{2+} and MB in binary systems show competitive adsorption. The adsorption kinetics in single systems will best follow the Elovich equation. The adsorption capacities of Cu^{2+} and MB in single systems are (7.05 and 60.66) $mg \cdot g^{-1}$, respectively. The adsorption capacity of Cu^{2+} or MB will be decreased in the binary system. The result shows that MB may exhibit higher affinity and selectivity to wheat straw.

Appendix

Methylene blue (MB, C.I. no 52015) has a molecular weight of 373.9 $g \cdot mol^{-1}$, which corresponds to methylene blue hydrochloride with three molecules of water. The structure of MB is the following



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