Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.861362

53 (2015) 778–784
January

Taylor & Francis
Taylor & Francis Group

Equilibrium kinetics studies on the biosorption of Cu (II) from aqueous solutions by a new adsorbent from a *Eupatorium adenophorum* Spreng/ buckwheat straw mixture

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Received 6 March 2013; Accepted 8 September 2013

ABSTRACT

Adsorbent was prepared by mixing *Eupatorium adenophorum* Spreng and buckwheat straw. The optimum carbonization conditions for time, temperature, and mixture ratio were determined by orthogonal test and extreme difference analysis. The adsorption character was studied by varying conditions of contact time, initial metal ion concentration, adsorbent dose, and pH. The optimum adsorption conditions for Cu (II) biosorption occurred at a temperature of 298 K, a pH of 3, and an adsorbent dosage of 0.25 g. Equilibrium and kinetics studies indicated that the adsorption process followed the Freundlich isotherm ($R^2 = 0.9896$) adsorption model. The biosorption kinetics could be well described by the pseudo-second-order equation.

Keywords: *Eupatorium adenophorum* Spreng; Buckwheat; Adsorption; Cu (II); Kinetic equation

1. Introduction

Copper (II) is one of the ubiquitous toxic heavy metals in surface water. The potential sources of Cu^{2+} ions in the environment are essentially electroplating, fertilizer industries, wood pulp production, smelting, etc. [1]. Copper (II) has several toxic effects on humans; its accumulation in the human body leads to hepatic and renal damage, as well as central nervous system problems followed by depression and gastrointestinal irritation. Conventional methods for Cu ion removal from wastewater include ion exchange, chemical precipitation, ultrafiltration, electrochemical treatment, and solvent extraction [2–5]. However, the above methods have been found to be limited because of high cost, complicated operation, and secondary pollution. Adsorption has been considered as an economically efficient and promising technology in metal ion wastewater treatment. Many absorbents have been used to remove heavy metals from wastewater including activated carbon, chestnut inner shells, rice husk, and straw [6–12]. Low-cost biosorbents with high adsorption capacities have been given increasing attention as they can significantly reduce the cost of an adsorption system.

Eupatorium adenophorum Spreng (EaS) is an invasive perennial plant which is found worldwide. It can cause great damage to biodiversity and the structure and function of invaded ecosystems [13]. Physical, biological, and chemical methods have been used to attempt to control its spread; however, these have been largely ineffective. To treat EaS as a resource has been demonstrated as a practical method [14,15]. Buckwheat is an annual crop which is grown

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in many countries in Asia, Europe, North America, and South America [16,17]. Buckwheat straw, a by-product of buckwheat production, is mostly burned for the purpose of quick disposal and land clearing due to its lower heat value compared with other agricultural residues. The disposal of buckwheat straw by open-field burning frequently causes serious air pollution. Thus, new economical technologies for buckwheat straw disposal and resource utilization of (EaS) must be developed.

This study reports the use of a carbonized EaS and buckwheat straw mixture as an adsorbent to remove Copper (II) ions from aqueous solutions. In this study, the experimental parameters for the adsorption of Copper (II) ions from aqueous solutions under different equilibrium conditions were investigated in a batch study. The equilibrium isotherm data were described with the Langmuir, Freundlich model. The biosorption kinetics was also studied from the adsorption measurements.

2. Materials and methods

2.1. Materials

Cu^{2+} solutions were prepared using $Cu(NO_3)_2$ (analytical reagent grade) in distilled water. A stock solution (1,000 mg/L) was prepared and the solutions for adsorption tests were prepared from the stock solution to the various desired concentrations in distilled water. Sodium citrate, oxammonium hydrochloride, acetic acid, copper (I)-2, 9-dimethyl-1, 10-phenanthroline, and all other chemicals were of reagent grade. The pH of adsorbate solutions was adjusted to desired values with 0.1 mol/L HCl or 0.1 mol/L NaOH.

2.2. Preparation of the adsorbent

EaS and buckwheat straw were obtained from the southwestern part of China where EaS has caused serious ecological problems and buckwheat straw is a low-cost agricultural waste product. Both of the fresh materials were cut into pieces measuring less than 1 cm and then dried at 378 K until the weight was constant. The dried materials were sieved to 0.25–0.5 mm for carbonization.

The best carbonized parameters of the EaS and buckwheat straw mixture were determined by orthogonal tests of three factors at four different levels: carbonization time (15, 30, 45, and 60 min), carbonization temperature (673, 723, 773, and 823 K), and mass ratio (1:1, 1:2, 1:3, 2:1 for EaS: buckwheat straw) (M:M). The orthogonal experiment was divided into 16 groups and 100 mL adsorbate liquid was used in each group.

2.3. Batch adsorption experiment

A fixed dose of adsorbent was added to a 100 mL solution with a given Cu (II) ion concentration in a 150 mL stopper conical flask, and then shaken in the electrically thermostatic reciprocating shaker at 298 K at a frequency of 150 rpm. After the concentration of C and C_0 was measured, the percent removal of Cu (II) could be calculated.

Kinetic experiments were performed by adding a fixed dose of the adsorbent (2.5 g/L) to 100 mL of Cu^{2+} solution (26, 52, and 109 mg/L). The pH value of the solution was adjusted to 3. Samples were removed at 10, 20, 30, 40, 60, 90, and 120 min for analysis of Cu^{2+} concentration. Rate constants of kinetic models were also calculated from the conventional rate equations.

The adsorption isotherms experiment was carried out by adding 0.25 g of carbonized EaS and buckwheat straw mixture to 150 mL of the Cu^{2+} solution (15, 30, 45, 65, 100, 130, and 190 mg/L). The temperature was maintained at 298 K and the pH value of the solution was adjusted to 3. The solution was shaken for 120 min at a frequency of 150 rpm. At various intervals, the adsorbent and the solution were separated by filtration. The solution phase was diluted and the Cu^{2+} concentration in the solution was measured. The adsorption data were fitted in Langmuir and Freundlich adsorption isotherm.

2.4. Chemical analysis and data analysis

The copper-29-Dimethy-110-phenanthroline spectrophotometer method was used for the analysis of Cu^{2+} ions in the aqueous solutions (HJ 486-2009, China). Data analysis models and parameters used in this study are showed in Table 1.

3. Results and discussion

3.1. Physical and chemical characterization of the biosorbent

SEM was used to characterize the microstructure of the samples. SEM was performed with SEM (HITACHIS ~ 450, Japan), operating at an acceleration voltage of 5 kV. The surface composition of the GAC was analysis with the aid of EDX (Oxford Instruments 7200).

Table 1
Data analysis models and parameters

Data analysis models	Mathematical expressions
Calculation of the percent removal of copper (II)	$R = (1 - \frac{C_e}{C_0}) \times 100\%$
Lagergren pseudo-first-order kinetic equation	$q_e = \frac{V(C_0 - C_t)}{m} \log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$
Lagergren pseudo-second-order kinetic equation	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Langmuir model	$q_e = \frac{q_m b C_e}{1 + b C_e}$
Freundlich model	$q_e = k_f C_e^{\frac{1}{n}}$
Separation factors	$R_L \equiv \frac{1}{1 + b C_e}$

The scanning electron micrograph clearly revealed the granules' carbon surface texture and morphology (Fig. 1) at different magnifications. The coarse, porous nature of the biosorbent can be clearly seen. There are many small convex globular particles (diameter 1–2 μm) in the biosorbent, which increase the surface roughness and specific surface area.

The result of EDX analysis for the sample is shown in Fig. 2 and Table 2. The main element in the biosorbent is O, K, and C. There is no any harmful element in the biosorbent which indicated the biosorbent from mixed EaS, and Buckwheat straw is environment friendly.

3.2. Analysis of orthogonal experimental data

The orthogonal parameters on adsorption of Cu (II) by EaS and buckwheat straw are shown in Table 3.

From the Table 3, the degree of different factors affecting the adsorption capacity of carbonized EaS and buckwheat straw was carbonization temperature > mixing ratio > carbonization time. The corresponding range values are: 19.61, 13.16, and 9.57. The effect value of carbonization temperature increased in the order of 17.91 < 20.12 < 21.50 < 22.81. The Cu (II) removal percentage increased with the raising of carbonization temperature. The result of orthogonal test indicated that the adsorbability increased with the extension of carbonization time. On basis of the consideration for maximum absorption capacity, the optimized time was 60 min. All of above, the optimum carbonization parameters are a carbonization temperature of 823 K, a carbonization time of 60 min, and a mixing ratio of EaS to buckwheat straw of 2:1 (M: M).

3.3. Effect of pH on adsorption

The pH value is one of the most important parameters governing the adsorption behavior of transition metal ions on adsorbents; pH can affect the surface

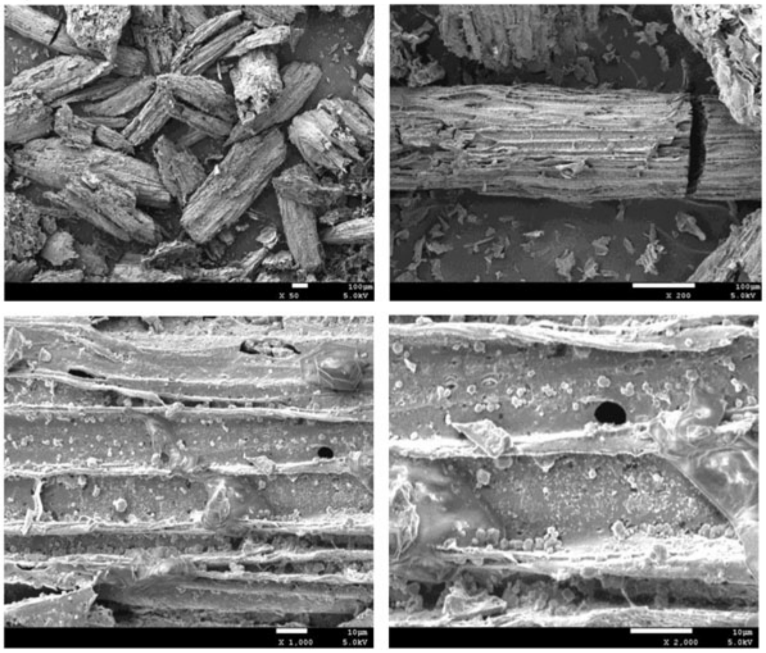

Fig. 1. SEM photo of the biosorbent sample at different magnifications.

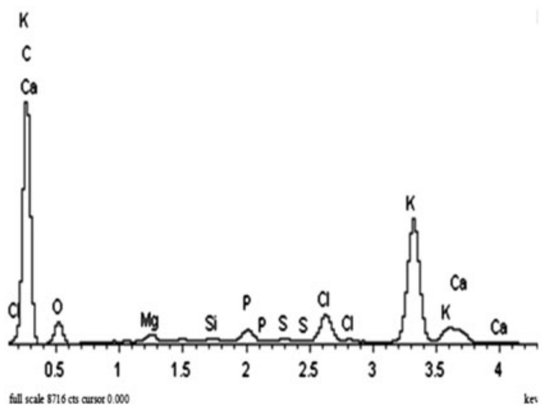

Fig. 2. EDX pattern of the biosorbent sample.

electrical properties and the formation of metal ions and may also influence the binding ability of coordinating groups on biomass surface [18].

The removal rate of Cu (II) from the solution increased significantly with the increase in solution pH from 2 to 3 (Fig. 3).

Table 2
The percentage of each element in the biosorbent

Element	Weight/percent	Atom/percent
C	9.85	17.31
O	41.87	55.23
Mg	1.82	1.58
Si	0.64	0.48
P	2.41	1.64
S	0.48	0.32
Cl	6.00	3.57
K	32.71	17.65
Ca	4.21	2.22

The highest adsorption capacity of the adsorbent for Cu (II) was 16.51 mg/g at pH 3. When the pH value increased to 5, the removal rate and the adsorption capacity of the adsorbent to Cu (II) decreased sharply. This may due to the fact that at pH values less than 2, a large number of H_30^+ exists in the solution. Most of functional groups on the adsorbent were protonated and because H_3O^+ competes with metal ions for adsorption sites, adsorption capacity was

Table 3
The orthogonal parameters on adsorption of Cu (II) by EaS and buckwheat straw

Serial number	Carbonization time (min)	Carbonization temperature (K)	Mixing ratio of EaS and buckwheat straw	Cu (II) removal percentage (%)
1	15	673	1:1	74.17
2	15	723	1:2	86.43
3	15	773	2:1	78.1
4	15	823	3:1	75.9
5	30	673	1:2	75.5
6	30	723	2:1	73.88
7	30	773	3:1	82.3
8	30	823	1:1	91.3
9	45	673	2:1	66.3
10	45	723	3:1	74.3
11	45	773	1:1	88.26
12	45	823	1:2	98.5
13	60	673	3:1	70.6
14	60	723	1:1	87.3
15	60	773	1:2	95.31
16	60	823	2:1	99.33
K_1	78.56	71.64	79.41	
K_2	80.74	80.47	88.93	
K_3	81.84	85.99	79.40	
K_4	88.13	91.25	75.77	
$K_{1/4}$	19.64	17.91	19.85	
$K_{2/4}$	20.19	20.12	22.23	
$K_{3/4}$	20.46	21.50	19.85	
$K_{4/4}$	22.03	22.81	18.94	
R	9.57	19.61	13.16	

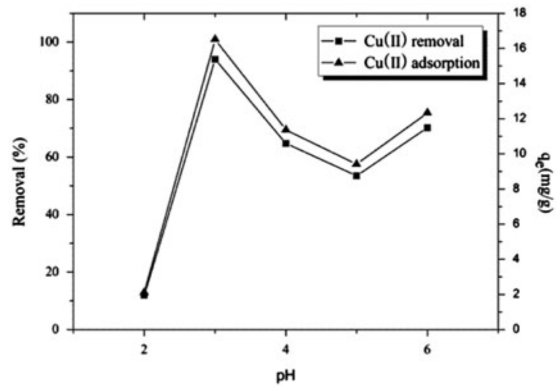

Fig. 3. Effect of pH on Cu (II) adsorption.

inhibited [19]. When the pH value of the solution increased to 3, the adsorption of the adsorbent to Cu (II), competitive adsorption between H^+ and Cu^{2+} was not evident and had no negative effect on the adsorption of Cu^{2+}. At a pH range of 3–5, the formation of Cu (II) is Cu^{2+} and $CuOH^+$ and an excess of hydrogen ions have greater negative influence on the adsorption of the adsorbent to $CuOH^+$ than Cu^{2+} [20]. At pH values of 6 or higher, the Cu^{2+} produced a flocculated precipitate, from which the adsorption data could not be measured.

3.4. Effect of adsorbent dose

A study of adsorbent dose is important for determination of the sorbent—sorbate equilibrium of the system and assessment of absorbability of adsorbents.

As shown in Fig. 4, carbonized EaS and buckwheat straw dosages varying from 0 to 0.4 g at 0.05 g intervals were studied using 100 mL Cu (II) solution (50 mg/L, pH 3). The solution was shaken at a frequency of 150 rpm at 298 K. As the adsorbent dose increased from 0.05 to 0.15 g, the percentage of Cu (II) removal increased rapidly. The Cu (II) removal rate was maximal (95.67%) when the adsorbent dose was 0.25 g and at higher doses plateaued. A possible reason for this is that after adsorption reached equilibrium, the added adsorbent provided excessive active groups beyond the capacity to be accepted by the metal ions [21,22]. The amount of metal ions adsorbed per unit weight of adsorbent (q_e) increased with the adsorbent dose between 0.05 and 0.10 g and decreases with the adsorbent dose between 0.10 and 0.40 g. This is due to the fact that after the q_e reached its maximum, the solution ion concentration drops to a lower value.

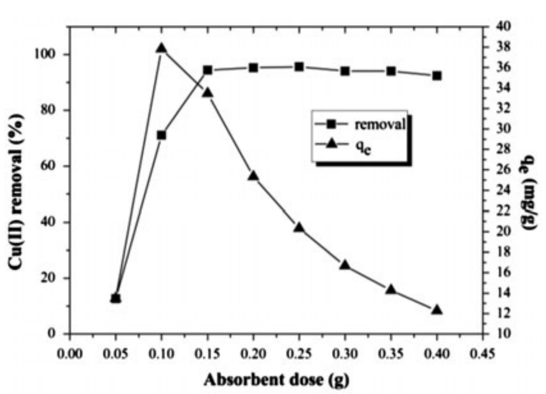

Fig. 4. Effect of sorbent dosage on Cu (II) adsorption.

3.5. Effect of initial Cu^{2+} concentration and adsorption isotherm

The initial Cu^{2+} concentration in the solution also had an influence on the adsorption capability of the adsorbent (Table 4).

The amount of metal adsorbed per unit weight of adsorbent, q_e, is higher at high concentrations. The equilibrium behavior of the adsorption of Cu (II) ions on carbonized EaS and buckwheat straw can be mathematically expressed via proper equations of adsorption isotherms. Two sorption isotherms models viz. Langmuir and Freundlich isotherms were tested for fitness. Isotherm parameters for Cu (II) adsorption on carbonized EaS and Buckwheat are shown in Table 5.

Table 4
Effect of concentration of Cu (II) on adsorption capacity

Initial concentration C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)
16.2	1.7	5.8
31.22	2.3	11.56
46.87	4.5	16.94
65.57	5.6	23.98
97.3	7.7	35.84
130.7	13.6	46.84
193.3	27.3	66.4

Table 5
Isotherm parameters for Cu (II) adsorption on carbonized EaS and Buckwheat straw

Langmuir model			Freundlich model		
q_m (mg/g)	b (L/mg)	R^2	k_f (L/mg)	n	R^2
56.62	0.0139	0.93118	2.515	1.835	0.9896

Table 6
Comparison of parameters for the pseudo-first- and pseudo-second-order reaction kinetics of removal of Cu (II) by carbonized EaS and buckwheat straw

		Pseudo first-order kinetic			Pseudo second-order kinetic		
C_0 (mg/L)	$q_{e,\exp}$ (mg/g)	$q_{e,cal1}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,cal2}$ (mg/g)	K_2 (min^{-1})	R^2
26	10.12	0.3369	−0.01006	0.4808	10.11	0.27443	0.9998
52	21.0	2.213	0.00942	0.8852	21.33	0.0149	0.998
109	42	1.124	0.00725	0.1314	42.11	0.02577	0.9998

As seen from Table 5, the correlation coefficients R^2 values for the Langmuir and Freundlich isotherm models were both above 0.90, suggesting that both isotherms can fit the data well. The Freundlich equation described Cu (II) onto carbonized EaS and buckwheat straw ($R^2 = 0.9896$) better than Langmuir model. The value for coefficient n is an empirical parameter that varies with the degree of heterogeneity, and it is related to the distribution of bonded ions on the sorbent surface. In general, $n > 1$ illustrates that adsorbate is favorably adsorbed on an adsorbent and a higher n value means stronger adsorption intensity [23]. Separation factor R_L is a measure of the favorability of the sorption process.

For a favorable reaction process, $0 < R_L < 1$; whereas $R_L = 0$ for the irreversible case, $R_L = 1$ for the linear case and $R > 1$ for unfavorable reaction [24]. For these experiments, the R_L was found to be between 0 and 1, which indicated that the adsorption of Cu (II) onto carbonized EaS and buckwheat straw is a favorable reaction process. R_L decreases with initial Cu^{2+} concentration, which indicated that a higher Cu^{2+} initial concentration increases adsorption.

3.6. Adsorption kinetics

Adsorption kinetics describe the solute uptake rate which in turn controls the residence time and is required for selecting optimum operating conditions for the full-scale batch process [25]. The adsorption kinetics was studied with respect to Lagergren's pseudo-first-order and pseudo-second-order kinetic models. The validity of these two models was tested by performing kinetics under three different initial metal concentrations. Comparison of the test results for the pseudo-first- and pseudo-second-order reaction kinetics of Cu (II) removal by carbonized EaS and Buckwheat straw adsorbent is shown in Table 6.

It was found that the pseudo-second-order model yielded the best results based on plotting t/q_t vs. t. Lagergren's pseudo-first-order model showed correlation coefficients (R^2) of 0.499 on average, where the second-order kinetic model showed a higher R value of 0.999 on average. All the quasi-second-order kinetic equations have R^2 values of above 0.998, with only a small difference. The results suggested that the pseudo-second-order adsorption mechanism was predominant for this adsorbent system [26,27].

4. Conclusions

In this study, an attempt has been made to evaluate the use of carbonized EaS and buckwheat straw as an adsorbent to remove Cu (II) in wastewater treatment. The results show that carbonized EaS and buckwheat straw are good adsorbent for the removal of Cu (II) from water. Removal of metal ions was highest at pH 3 and Cu^{2+} initial concentration and adsorbent dose also affect the Cu removal efficiency. A higher Cu^{2+} initial concentration is propitious to the adsorption and the optimum dosage of the adsorbent is 0.25 g. The Langmuir adsorption isotherm fits well with the adsorption equilibrium data. The maximum sorption calculated from the Langmuir isotherm was 56.62 mg/g. The adsorption kinetics fit a pseudo-second-order model, which is based on the assumption that the rate-limiting step is chemisorption. Low cost and high removal rate make carbonized EaS and buckwheat straw a potential alternative for adsorption of toxic Cu^{2+} from wastewater.

More technical and feasible data are required for a better understanding and effective application of the adsorbent for real industrial wastewater.

Acknowledgment

The authors give thanks to the Science and Technology department of Sichuan province for financial support from the basic and applied research Project (No.2013JY0131).

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