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Adsorption of copper by canola meal

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Abstract

In this work canola meal (CM) was used for adsorption of copper. Adsorption of copper per unit of CM decreased with an increase in the concentation of the adsorbent. The pH did not affect the process very much. Increasing the initial copper concentration in the solution resulted in an increase of its uptake per unit of CM. A linear relationship between the final copper ion concentrations in solution and the uptake of the ions was observed for lower copper cocentrations while leveling off was noticed at higher concentrations; a Langmuir isotherm type model fits these experimental data. The uptake of copper ions was enhanced with decreasing canola meal particle sizes. The copper adsorption capacity of CM decreased with its phytic acid content reduction. Adsorption of zinc and cadmium by canola meal was higher than that of copper.

Keywords: Canola meal; Adsorption; Copper; Nickel; Cadmium

1. Introduction

Various types of processes such as carbon adsorption, ion exchange, membrane separation, precipitation, solvent extraction are available for reducing the level of toxic metals in industrial solutions. However, most of these methods are complex, sophisticated, and the processes are usually either non-selective or expensive for the removal of very dilute highly toxic heavy metals from various industrial solutions and wastewater. One of the most recent methods that have been developed for adsorption of metals is the utilization of microbial biomass as an adsorbent. Various microorganisms were tested for their ability to adsorb metals. Table 1 reviews some microorganisms used with the amount of metals uptaken by them. Moreover, Hutchins et al. [1] reviewd some microorganisms used in metal recovery, and recognized that active organisms, e.g. *Pseudomonas maltophilia*, *Staphylococcus aureus*, and a coryneform

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Table 1
Review of some microorganisms used for metal removal

Microorganism	Metal	Uptake (μg/mg)	Conditions				Reference
			pH	T (°C)	C_{A_0} (ppm)	Biomass (mg/ml)	
Z. ramigera	Cr^{6+}	27.5	2.0	25	125	1.0	[20]
S. cerevesiae	Cd^{2+}	9.0	6.5	25	22.5	0.41	[18]
	Co^{+}	4.1			5.8		
C. vulgaris	Cd^{2+}	1.4		25	1.0	0.575	[3]
M. miehei	UO_2^{+2}	180	5.0	20	100.0	0.50	[21]
E. coli	Zn^{2+}	1.65	5.0	20	50.0	0.40	[22]
C. vulgaris	Pb^{2+}	83.0	5.0	25	100.0	0.75	[4]
P. stutzeri	Cr^{6+}	0.75	7.5	22	5.0	2.0	[23]
Thiothrix strain	Ni^{2+}	7.6			3.1	0.197	[24]
A1	Zn^{2+}	7.8			2.9		
R. arrhizos	Cu^{2+}	9.5	5.5	25	22.8	1.07	[17]
C. resinae		16.5			22.3	1.16	
P. italicum		6.67			26.7	0.96	
A. niger	Ag^{+}	22.4	4.0	5	107.8	3.0	[25]
	Cu^{2+}	1.78			63.5		
	La^{3+}	7.5			138.8		
M. rouxiir	Ag^{+}	17.4			107.8		
	Cu^{2+}	2.6			63.5		
	La^{3+}	5.7			138.8		
S. iongwoodensis	UO_2^{+2}	380.0	3.0		200.0	0.3	[26]
	Pb^{2+}	92.0			170.0		
S. noursei	Cd^{2+}	3.4	5-6	30	112.4	3.53	[16]
	Cr^{3+}	10.6			52.0		
	Cu^{2+}	9.0			63.5		
	Ni^{2+}	0.8			58.8		
	Zn^{2+}	1.6			65.38		

organism which accumulated over 300 mg Ag^{+}/g biomass, and passive organisms, e.g. copper and cadmium, are readily sorbed by *Zoogloea* polymer/biomass to levels of nearly 0.3 and 0.1 g metal per g dry wt, respectively. Siegel et al. [2] reported, in their review paper, that *Pencillium* can solubilize metals and metalloids accumulating as such as (in mmol/kg dry wt): 1270 for Cu^{2+}; 154 for Zn^{2+}; 45 for Cd^{2+}; and even remove Fe^{2+} from stainless Fe–Ni–Cr alloys.

Taking into account that proteins, in addition to polysaccharides, lipids and some other compounds of microbial cells, are considered an important component responsible for metal adsorption by microorganisms [3–7], it is also possible to imagine the utilization of CM for metal adsorption because it contains 37–40% protein, and 4–6% phytic acid that possesses a high metal-binding capability [8]. CM is a by-product from canola oil production from canola seeds. Canada produced 1.097×10^6 t of CM in the year 1991/1992 [9]. Because of its high nutritional value, the meal would be suitable as feedstuff for animals, but the presence of phytic acid, phenolic compounds and glucosinolates limits its utilization for animals [8]. This is one of the reasons why a large amount of the meal is used as a fertilizer [8]. It can also be used in fermentations as a medium component for the production of enzymes, e.g. phytase [10]. The protein and phytic acid contents in CM makes this commodity a good candidate for metal recovery from wastewaters.

The purpose of this work is to study the possibility of the utilization of CM for the reduction of copper, or zinc or cadmium concentrations in their solutions, since this material has not been considered previously for this purpose. The effects of parameters such as the CM and copper concentrations, particle size of CM, its phytic acid content, and pH of the meal–metal suspensions on the metal adsorption were studied and the results are presented in this paper.

2. Material and methods

Canola meal was used to study the adsorption of Cu^{2+}, Zn^{2+} and Cd^{2+} from its water solutions. The moisture content of the meal was 8% but its dry basis was used for the calculation of the amount of copper adsorbed per unit of meal. Dry weight of CM was obtained by weighing after its drying at 105 °C for 48 h.

A required amount of the CM was weighed and transferred into a 250 ml Erlenmeyer flask containing 49 ml of 5 m*M* 2{*N*-morpholino}-ethano sulphonic acid (MES) buffer, adjusted to pH 6 (unless otherwise specified) with 1 *N* NaOH. This buffer has negligible metal complexing properties [11].

One ml of 5000 ppm Cu^{2+} (in the form of $CuSO_4 \cdot 5H_2O$) solution was added to the CM suspension in the buffer to make the final metal concentration 100 ppm (unless otherwise stated). The mixture was agitated on a shaker at a temperature of 25 °C and samples were taken at specific times. CM from the samples was separated by vacuum filtration using 45 μm filter paper and the filtrate was analyzed for Cu^{2+} using atomic absorption spectrophotometer (Varian AA-1475 series), which produces the readings of an acceptable reproducibility. Each experiment was carried out in duplicate and the average results are presented in this work. The results of a duplicate test were discarded if they differed by more than 7%.

3. Results and discussion

The copper uptake from its solution is influenced by the canola meal concentration (Fig. 1). It was noted that the Cu^{2+} uptake per unit of the meal increased with a decrease in the CM concentration. The maximum removal of about 70% of the initial copper amount was achieved in the system with the meal concentration of 3.5 mg/ml, while about 60% of the initial copper was removed in 1 h when concentrations of the meal were 2.3 mg/ml and 4.6 mg/ml. When the tests were extended to 24 h,

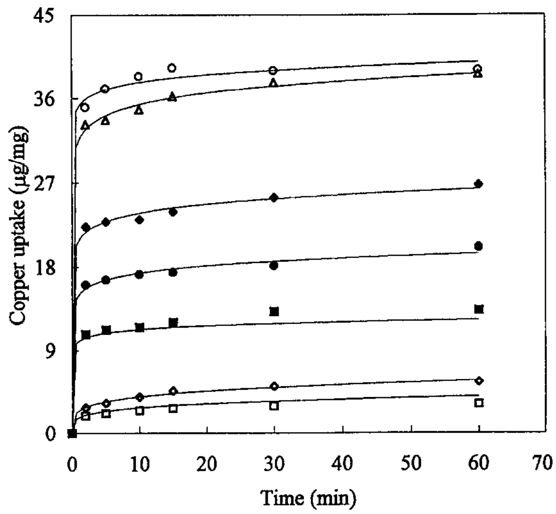

Fig. 1. Effect of CM concentration on copper uptake at pH 6 of a 100 ppm copper solution. Symbols are experimental and solid lines are predicted data using Eq. (1). CM concentration (mg/ml); (○) 1.15, (△) 1.75, (◆) 2.3, (●) 3.5, (■) 4.6, (◇) 9.2, (□) 18.4.

the amount of Cu^{2+} adsorbed stayed at the 1 h level. Gadd and White [12] also noticed that the uptake of thorium per unit of biomass was higher in the tests with lower concentrations of *S. cerevisiae*. The amount of metal adsorbed by CM is comparable to those mentioned in Table 1 for microbial sorbents. The results from this work showed a steep initial slope of copper adsorption. It indicates a high metal binding power of CM chemical functional groups which sequestered copper ions from its dilute solution. In general, the biosorbents with this characteristic have a high affinity for metal ions [5]. The results from Fig. 1 can very well be represented by the following expression:

$$q = at^m, \tag{1}$$

where q is the copper uptake, t is the contact time, and a and m are empirical constants. The constants a and m (Table 2) were evaluated for each CM concentration by fitting Eq. (1) to the experimental data using the program Scientist (Micromath Scientist Software).

A study of the effect of the initial copper concentration on its uptake by CM (Table 3) showed an increase in the metal uptake with an increase in its concentration but the percentage of the copper removal from the solutions decreased. Using the experimental data, the first-order reaction rate in terms of the metal consumed from the solution, k, was calculated (Table 3) from the following relationship:

$$k = (1/t)\ln(C_{A_0}/C_{A_f}), \tag{2}$$

where C_{A_0} and C_{A_f} are the initial and final concentrations of Cu^{2+}, respectively, and t is the contact time (1 h). The values of k are proportional to percentage of the

Table 2
Parameters a and m of Eq. (1) for different CM concentration

CM (mg/ml)	a	m
1.15	35.17	0.0307
1.75	31.58	0.0491
2.3	20.88	0.0561
3.5	15.05	0.0616
4.6	10.08	0.0711
9.2	2.452	0.20652
18.4	1.706	0.20652

Table 3
Effect of Cu^{2+} concentration on its uptake by CM at pH 6 and 1.75 mg/ml of CM suspension

C_{A_0} (ppm)	C_{A_f} (ppm)	Cu^{2+} uptake (μg/mg)	Cu^{2+} removal (%)	k (h^{-1})
25	7.75	9.85	69.0	1.17
50	18.5	18.0	63.0	0.99
100	33.45	38.0	66.5	1.09
200	100	57.1	50.0	0.69
400	256.2	82.2	35.9	0.44

removal of Cu^{2+} ions. Deshkar et al. [13] obtained k values similar to these shown in Table 3 in a study of the adsorption of mercury (II) by *Hardwickia binata* bark.

When the relationship between the initial copper concentration and CM concentration, and the uptake of copper was studied, it was noticed that for the initial copper concentrations approximately up to 200 ppm, the uptake of copper per unit of CM tended to fairly comparable values for the same meal: initial copper concentration ratios (Fig. 2). The results also showed higher copper uptakes per unit of CM in the systems with the lower meal concentrations regardless of the initial copper concentration. Luef et al. [14] studied the same relationship for the adsorption of zinc by *Claviceps paspali*, *Aspergillus niger* and *Pencillium chrysogenum*, and obtained results similar to those in Fig. 2.

When the saturation of CM with copper was examined, the initial concentration of the meal was 9.2 mg/ml, while that of copper varied between 25 ppm and 2000 ppm. The tests were carried out at pH 6 for 15 min. The experimental results indicate (Fig. 3) that up to a residual Cu^{2+} concentration in solution of about 180 ppm there was a linear relationship between the copper ion residual concentrations and the uptake of the ions but the linearity was lost above this concentration. The following Langmuir isotherm model was used to fit the experimental data shown in Fig. 3:

$$q_f = \frac{KC_{A_f}}{1 + bC_{A_f}} \tag{3}$$

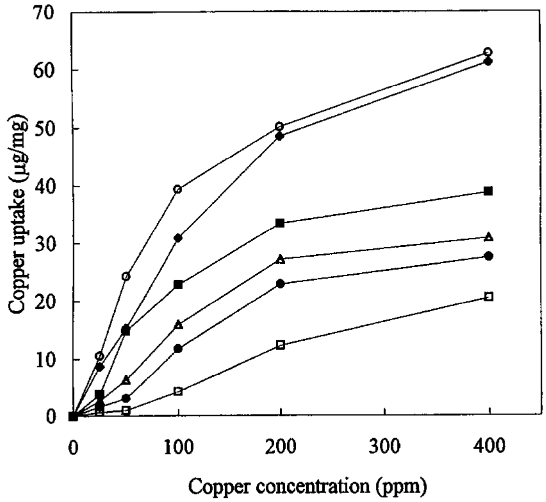

Fig. 2. Relationship between copper and CM concentrations and copper uptake at pH 6. CM concentration (mg/ml); (○) 1.38, (◆) 1.61, (■) 2.3, (△) 3.22, (●) 4.6, (□) 9.2.

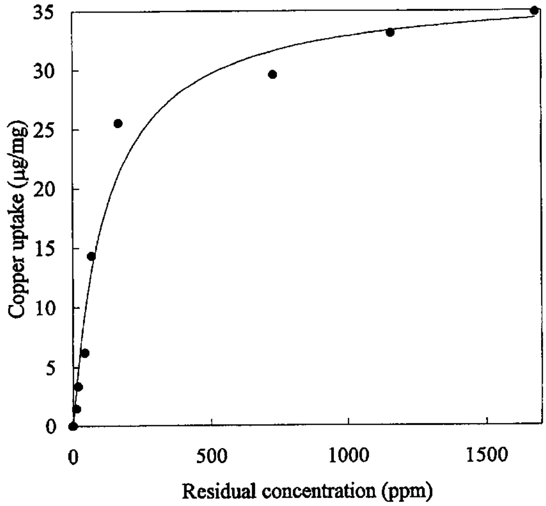

Fig. 3. Relationship between residual copper concentration and its uptake at pH 6 of a 9.2 mg/ml meal suspension. Symbols are experimental and solid line represents predicted data using Eq. (3).

where q_f is the Cu^{2+} uptake at the final concentration C_{A_f}, K and b are the Langmuir constants. The constants K and b are 0.305 ml/mg and 0.0083 ml/μg, respectively; they are evaluated by fitting Eq. (3) to the experimental data using the program Scientist. The Langmuir model represents the experimental data fairly well (Fig. 3). We also tried to apply a Freundlich type model to these data but it showed larger deviation than the Langmuir model. Similar isotherm curves for Cu^{2+} uptake were also obtained by other authors using various microorganisms such as *Rhizopus arrhizus* [15], *Streptomyces noursei* [16], *Cladosporium resinae* and *Penicillium italicum* [17].

The particle size of CM is expected to play a role in the adsorption process because adsorption is a surface phenomenon. As the particle size decreases, the surface area per unit weight increases and so does the adsorption capacity of the adsorbent. To investigate this, CM was screened through sieves and the following size distribution fractions were obtained: one smaller than 0.18 mm, four fractions with sizes between 0.18 and 1.4 mm, and one fraction with particle size bigger than 1.4 mm. In these tests, the initial Cu^{2+} and CM concentrations were 100 ppm and 9.2 mg/ml, respectively, and pH was 6. As it was expected, very fine particles showed maximum Cu^{2+} uptake (Fig. 4).

The pH of metal solutions affects biosorption as well. For example, Luef et al. [14] noticed an increase in Zn^{2+} uptake by *Aspergillus niger* with an increase in pH from 2 to 4 for various biomass and metal concentrations. The copper uptake from its solution by activated sludge bacteria was very low at pH 2 but when the pH value increased to 5, the uptake of the metal ions increased as well [4]. Our results with CM also showed an increase in copper uptake with an increase in pH up to 7 (Fig. 5).

The CM used in this study contained 34% proteins and 4.7% phytic acid. It can be supposed that the adsorption of metal by this material was largely influenced by these components. To test the effect of phytic acid on the adsorption process, the meal was treated with 2.4% HCl for various times in order to extract various amounts of phytic acid. After the treatment, the meal was dried and used for Cu^{2+} uptake. The results indicate (Fig. 6) a substantial decrease in the copper adsorption capability of the meal

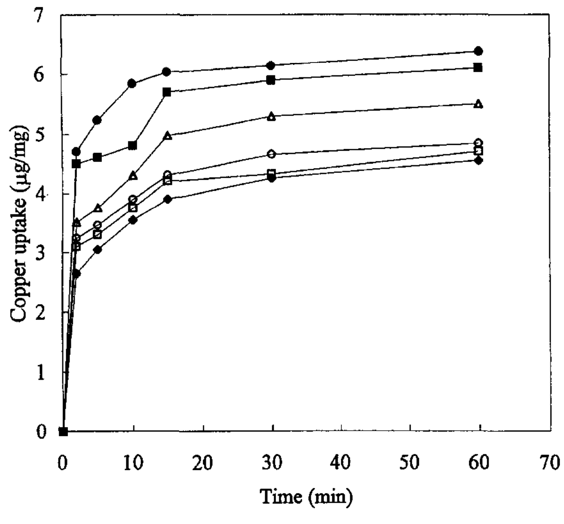

Fig. 4. Effect of particle size of CM on its uptake at pH 6 of 100 ppm copper and a 9.2 mg/ml meal suspension. Particle size (mm); (●) smaller than 0.18, (■) between 0.18 and 0.425, (△) between 0.425 and 0.71, (○) between 0.71 and 1.0, (□) between 1.0 and 1.4, (◆) bigger than 1.4.

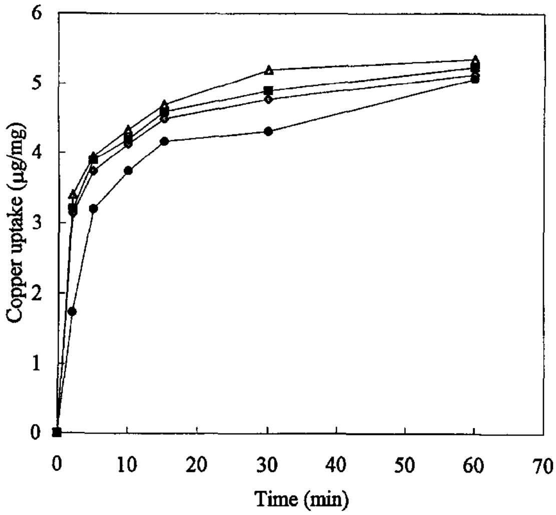

Fig. 5. Effect of pH on copper uptake by CM at 100 ppm copper and a 9.2 mg/ml meal suspension. pH; (●) 4, (◇) 5, (■) 6, (△) 7.

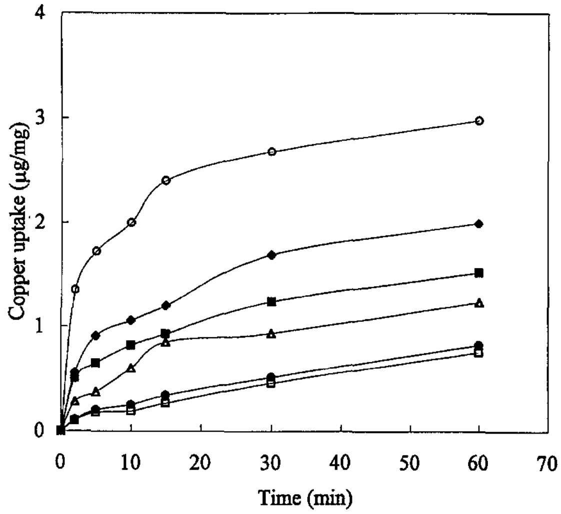

Fig. 6. Effect of phytic acid and protein removal from CM, using 2.4% HCl, on copper uptake from a 100 ppm copper and a 18.4 mg/ml meal suspension at pH 6. Phytic acid and protein removal (%); (○) 0.0 and 0.0, (◆) 76.5 and 15.4, (■) 81.5 and 16.0, (△) 87.2 and 16.5, (●) 93.6 and 17.3, (□) 100.0 and 17.7.

with the extraction of phytic acid. But some proteins were also extracted and, therefore, the loss of copper adsorption capability should be ascribed to them as well because our additional test indicated that the adsorption of Cu^{2+} by the meal was negligible when the total amount of proteins was extracted with 1 *N* NaOH. Since

CM contains larger amount of proteins than phytic acid, it can be assumed that the proteins are the major set of ligands responsible for binding of Cu^{2+}.

When the adsorption of Zn^{2+}, Cd^{2+} and Cu^{2+} was carried out separately for each of these ions, it was noticed that the meal adsorbed the largest amount of zinc ions and then cadmium and copper ions followed (Fig. 7). Unlike the other results in this work, the results of Fig. 7 are expressed in molar bases for the purpose of comparison. When a mixture of these three ions was used in a concentration of 100 ppm each, the order of preference of the meal for them was the same as that which has been just mentioned. But the results also showed that the absolute amount of adsorbed copper was greater, and zinc and cadmium smaller in this case than when the adsorption process was carried out in the presence of the individual solutions of these ions. It could be assumed that certain adsorption sites are reserved only for certain metals while various metals can compete to other sites. The overall amount of the metal uptake by the meal is larger in the mixture of the three types of ions because of a higher total concentration of ions (300 ppm) than when the individual solutions of each of them were tested. Norris and Kelly [18] studied adsorption of Zn^{2+}, Ni^{2+} and Co^{+} by *S. cerevisiae*, and noticed inhibitory effect of Zn^{2+} and Mg^{2+} on Ni^{2+} uptake, while Co^{+} uptake was inhibited more by Zn^{+2} than by Ni^{2+} or Mg^{2+}. Ting et al. [19] observed a higher Zn^{2+} uptake by the alga *Chlorella vulgaris* in the presence of Cd^{2+} than when Zn^{2+} was alone in the solution.

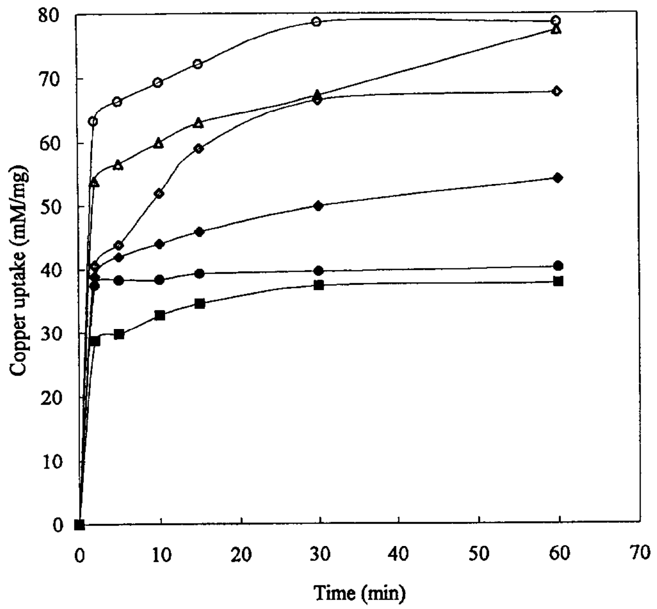

Fig. 7. Adsorption of zinc, cadmium and copper from their individual solutions by a 18.4 mg/ml meal containing 100 ppm of each of these metals or from their mixtures with 100 ppm each of the three metals at pH. (◆) Cu^{2+} only, (◇) Cu^{2+} from a mixture of Cu^{2+}, Zn^{2+} and Cd^{2+}, (○) Zn^{2+} only, (△) Zn^{2+} from a mixture of Cu^{2+}, Zn^{2+} and Cd^{2+}, (●) Cd^{2+} only, (■) Cd^{2+} from a mixture of Cu^{2+}, Zn^{2+} and Cd^{2+}.

Once CM being saturated with the Cu^{2+} ions, these ions can be recovered by elution and used.

4. Conclusions

Canola meal has a significant adsorption capacity for copper ions from their solutions. The protein and phytic acid contents of the meal play an important role in this respect. More copper was adsorbed per unit of meal in the adsorption systems with lower concentrations of canola meal than in those with higher levels of the adsorbent. A loading of the meal with copper increased with an increase in the initial concentrations of copper in the solution. A linear relationship between the final copper ion concentrations in solution and the uptake of the ions was observed for lower copper ion concentrations. A Langmuir type isotherm model was proposed to fit these data. Adsorption capacity of the metal increased with a decrease of the particle size of the meal. The pH of the copper solutions influenced the adsorption process. The results also indicate that the meal can adsorb higher amounts of zinc and cadmium than copper.

5. Notation

C_{A_0}	initial copper concentration, μg/ml (ppm)
C_{A_f}	final copper concentration, μg/ml (ppm)
K	Langmuir constant, ml/mg
T	temperature, °C
a	empirical constant, μg/(mg min^m)
b	Lungmuir constant, ml/μg
k	first-order reaction rate constant, h^{-1}
m	empirical constant, dimensionless
q	metal uptake, μg/mg
q_f	metal uptake at the final metal concentration, μg/mg
t	contact time, min

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