Adsorption Kinetics and Isotherm Study of Cu(II) Ion Sorption from Acidic Solutions by Peat

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Summary

Acid mine drainage (AMD) is one of the most significant environmental problem resulting from the oxidation of pyrite in presence of water, air and microorganisms, providing an acidic solution that contains heavy metal ions. Copper ions are an essential part of AMD, which is characteristic by low value of pH. This fact has a significant effect on research of the sorption properties of Cu(II).

Aim of this paper is to report batch adsorption study of divalent copper, Cu(II) onto peat. Kinetics of Cu(II) adsorption and adsorption isotherms were determined by varying operating parameters such as pH, initial concentration and contact time. The equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption isotherms models. Langmuir model with r2 = 0.9923 best fits the adsorption data. The kinetics of adsorption was found to follow the second order reaction.

Keywords: sorption, peat, copper, kinetics, isotherm

Introduction

Acid mine drainage (AMD) is a serious current environmental problem. The occurrence of AMD is usually associated with mining activities, particularly after closure and abandonment of mining works. This situation also occurred in Slovak Republic, where the mining activities had a long tradition and now there are some localities with existing AMD generation conditions. The main characteristic of such waters is their low pH and high content of heavy metals as a result of weathering of remnant sulfide minerals, e.g. pyrite, chalcopyrite, tetrahedrite, tennantite or gersdorffite (Samesova et al., 2009). These heavy metals are non – biodegradable, tend to accumulate in living organisms bodies and causing various disorders (Zheng et al., 2008).

There are different ways of the removal of toxic metals from these waters, including chemical precipitation (Macingova and Luptakova, 2012), neutralization (Doya et al., 2003), ion – exchange (Feng et al., 2000), reverse osmosis, hydrolysis (Chartrand et al., 2003) and sorption (Mohan et al., 2006). Among above listed various water treatment techniques, sorption is generally preferred due its high efficiency, easy handling, availability of various sorbents and low cost.

In presented work, the study of using of natural peat as a sorbent for copper removal from model acidic solutions is presented. The experiments were carried out for the purpose of the follow parameters investigation: kinetics and isotherm modeling, removal efficiency and adsorption capacity of peat in dependence on initial concentration. To simulate AMD conditions experiments were realized with acidic solutions (pH ≈ 4).

Materials and methods

As a sorptive material in experiments a commercial peat "PEATSORB" (REO AMOS Slovakia) was used. The sorbent was not modified; finer fraction prepared by sieving through a 2 mm sieve was applied. After sieving, the separated fraction of peat was dried at 105 °C for 2 h and then allowed to cool in the desiccators.

For the purpose of determination of changes in concentrations and pH following apparatus have been used:

- A Colorimeter DR890 (HACH LANGE, Germany) with appropriate reagent was used to determine concentration of dissolved Cu(II),
- pH were determined by pH meter FiveGO – FG2 (METTLER TOLEDO, Switzerland) which was standardized using buffer solutions of different pH values (4.01, 7.00).

Model solutions were prepared by dilution to the desired initial concentration from concentrated stock solution of copper, which was prepared by dissolution of copper (II) sulfate pentahydrate in deionized water. The initial pH of each solution was adjusted to the required value (pH=4.1 – 4.2) by adding 0.001M H_2SO_4.

Batch experiments were carried out at room temperature (23±0.2°C) in beakers by adding of a constant mass of peat (1.0 g) in 100mL of solution with Cu(II).

Kinetics sorption studies were carried out using 100 mL of Cu(II) ions solution of initial concentration 50 mg/L. The metal ion solutions were measured into different labeled beakers containing 1.0 g of adsorbent. The mixture was agitated at a speed of 500 rpm for 1, 3, 5, 7, 10, 30 and 60 minutes, respectively. Also kinetic affinity sorption was also carried out for 24 hours. At the end of each contact time, the solid was removed by filtration through a laboratory filter paper for qualitative analysis.

In order to obtain data for isotherms study, the various solutions with initial Cu(II) concentrations ranging from 10 to 90 mg/L (10, 20, 30, 50, 70 and 90) were prepared. Adsorbates were mixed with 1 g of adsorbent for the time required to establish equilibrium. After that adsorbents were removed by filtration and equilibrium concentrations were determined. In all experiments, measurement of pH at the beginning and at the end of sorption was also done.

The copper adsorption capacities were calculated by the following equation:

$$q = \frac{(c_0 - c_e)}{m} \times V \qquad (1)$$

where q, adsorption capacity per unit mass of adsorbent (mg/g), c_0 is the initial concentration of metal ions (mg/L); c_e, equilibrium concentration of metal ions (mg/L); V, the volume of the aqueous phase (L) and m, mass of adsorbent (g).

The % heavy metal removal was calculated using the following equation:

$$\% \ metal \ ion \ removal = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (2)$$

The kinetics of Cu(II) ion sorption was analyzed using two kinetic models: the pseudo – first order and pseudo – second order.

The pseudo – first order equation is generally expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (3)$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo – first order sorption (L/min).

The pseudo – second order kinetic equation is expressed as eqn (4):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (4)$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_2 is the rate constant of pseudo – second order sorption (L/min).

For the purpose of isotherm study two different isotherm theories have been adopted in this paper, namely, the Freundlich and Langmuir equilibrium isotherm theories.

The Freundlich equation has been widely used for isothermal adsorption. This is a special case for heterogeneous surface and her form can be represented by the following equation (Freundlich, 1926):

$$q_e = k c_e^{1/n}, \qquad (5)$$

where k represents the sorption capacity when metal equilibrium concentration equals to 1; c_e, the equilibrium concentration of remaining metal in the solution (mg/L); q_e, the amount of adsorbed per unit weight (mg/g) and n, Freundlich constants related to adsorption intensity.

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. This model is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface (Zheng et al., 2008).

This model is represented as follows (Langmuir, 1918):

$$q_e = \frac{Q_{max} b c_e}{1 + b c_e} \qquad (6)$$

where q_e is the amount of a metal adsorbed per mass unit of sorbent at equilibrium (mg/g); Q_{max}, the amount of adsorbate at complete monolayer (mg/g) and b (L/mg) is the Langmuir constant that relates to the heat of adsorption.

Results and discussion

The results of the sorption experiments in dependence on the initial concentration are shown in Table 1. Removal efficiency decreases with increasing initial concentration. This fact is caused by limitation of peat sorption capacity. Further studying phenomenon was

Table 1. Results of sorption experiments (concentrations, pH and removal efficiency)

Tabela 1. Wyniki badań sorpcji (stężenia, pH oraz skuteczność usuwania)

Initial concentration	[mg/L]	9.92	19	29.4	49.9	69	89
Concentration after sorption	[mg/L]	1.79	4.12	6.68	12.44	22.8	36.16
pH after sorption (initial pH ≈ 4)		4.25	3.66	3.6	3.53	3.4	3.32
Removal efficiency	[%]	81.96	78.32	77.28	75.07	66.96	59.37

pH change. Resulting from Table 1, using of peat in conditions of higher concentrations of copper cations is connected with pH decrease. This fact is due to releasing of hydrogen ions from peat into solution (Ho et al., 2000). The higher the initial concentration, the stronger is pH decrease, because the ion exchange is more intensive. At lower concentrations the ion exchange isn't so dominant and can't cause decreasing of the pH value. In this range increasing of pH is caused by alkaline effect of peat, which was confirmed by control measurements with deionized water.

The kinetic sorption data were analyzed using program Matlab. Kinetic sorption data better correlated with pseudo – second model, which is also evident from the Figure 1. The fit was obtained with regression coefficient $r^2=0.8951$ and $k_2=0.392$ L/min.

The equilibrium sorption data were analyzed using program DataFit 9.0.59. Results of calculations are shown in the Table 2. The equilibrium adsorption data better correlated with Langmuir isotherm model. From the values in the table and also from the Figure 2 is clearly evident, that the sorption can be better described with Langmuir model. The fit was obtained with regression coefficient $r^2=0.9923$.

Conclusions

This study showed the possibility of peat utilization as a low cost sorbent for Cu(II) removal from
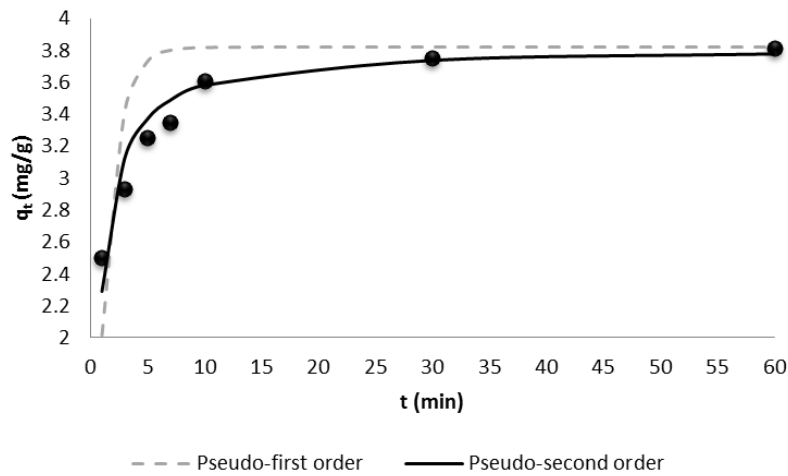

Fig. 1. Comparison of kinetic curves

Rys. 1 Porównanie krzywych kinetycznych

Table 2. Freundlich and Langmuir isotherm parameters

Tabela 2. Parametry izoterm Freundlicha i Langmuira

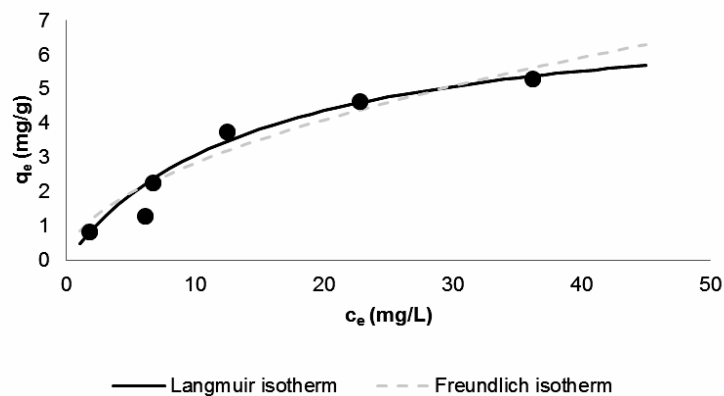|	Freundlich isotherm constants			Langmuir isotherm constants		
	k	1/n	r^2	Q_{max}	b	r^2
Cu(II)	0.841	0.529	0.9587	7.534	0,0688	0.9923

Fig. 2. Comparison of adsorption isotherms

Rys. 2. Porównanie izoterm adsorpcji

model acidic solutions. From kinetic data was found, that the equilibrium was reached during 4 hours and the kinetics of adsorption was found to follow the second order reaction.

The experimental equilibrium data better correlated to the Langmuir equation, but Freundlich model fits also well.

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Badanie kinetyki i izoterm adsorpcji jonów Cu (II) z roztworów kwaśnych za pomocą torfu

Kwaśny drenaż kopalń (AMD – Acid mine drainage) jest jednym z najbardziej znaczących problemów środowiskowych powstającym na skutek utleniania pirytu w obecności wody, powietrza I mikroorganizmów I dostarczania roztworu kwasowego zawierającego jony metali ciężkich. Jony miedzi są istotną częścią AMD, co jest charakterystyczne dla niskiej wartości pH. Fakt ten ma duży wpływ na badania właściwości sorpcyjnych Cu(II). Celem tego referatu jest przedstawienie badań adsorpcji miedzi dwuwartościowej Cu(II) na torfie. Kinetyka adsorpcji Cu(II) i izoterm adsorpcji została określona przez zmienianie parametrów operacyjnych takich jak pH, stężenie początkowe i czas kontaktu. Dane równowagi adsorpcji zostały dopasowane do modeli izoterm adsorpcji Langmuira i Freundlicha. Model Langmuira o $r^2 = 0,9923$ najlepiej pasuje do danych adsorpcji. Kinetyka adsorpcji odpowiadała reakcji drugiego rzędu.

Słowa kluczowe: sorpcja, torf, miedź, kinetyka, izoterma