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MODELLING OF COPPER AND ZINC ADSORPTION ONTO ZEOLITE

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Preliminary Note – Prethodno priopćenje

Adsorption of Cu(II) and Zn(II) ions from metallurgical solutions has been studied and the adsorption capacity of zeolite (Nižný Hrabovec, SK) has been determined. Zeolites are characterized by relatively high sorption capacity, i.e. Cu(II) and Zn(II) can be removed even at relatively low concentrations. The experiments were realised in a batch system and evaluated using isotherms. According to the results of the experiments the adsorption equilibrium of Cu(II) and Zn(II) on zeolite was best described by Freundlich isotherm. The maximum sorption capacity was 1,48 and 1,49 mg/g for Cu(II) and Zn(II), respectively. The experimental results of this study demonstrate that zeolite is suitable for adsorption of copper and zinc from aqueous solutions at low concentrations.

Key words: copper, zinc, adsorption, zeolite, removal

INTRODUCTION

Multifunctional application of heavy metals and their compounds in various industries results in their subsequent accumulation in the natural environment in the form of hazardous and non-degradable waste. The main sources of this form of waste are mainly anthropogenic activities (mining and metallurgical production), amortized products containing heavy metals, fossil fuel combustion, traffic fumes, excessive and improper application of pesticides and fertilizers in agriculture and the like. Heavy metals are getting different exposure routes (leachate of subsoil, the washing and the like) and their presence is considered to be dangerous as it causes serious disease and damage to the body.

Removal of heavy metals is now constantly studied because some technologies are proving to be highly inefficient or costly. Primarily it is these reasons that increasingly put emphasis on heavy metal removal technologies for the use of various natural, less financially demanding materials or industrial wastes.

Metal ions in low quantities are difficult to remove from aqueous solutions. One of the possible solutions for such situations is adsorption. Nowadays, a number of low cost adsorbent materials are available to remove metal ions. These adsorbents include various materials [1 - 3].

Adsorption is a process of metal ions binding on the surface of the adsorbent. It is therefore possible to use adsorbents to remove heavy metals from wastewater from different industrial applications [4, 5]. Zeolites are hydrated alumino-silicate minerals and have a microporous structure.

The zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. In order to be a zeolite the ratio (Si + Al)/O must equal 1/2. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Zeolites have large vacant spaces in their structures that allow space for large cations such as sodium, potassium, barium and calcium and even relatively large molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions [6].

Zeolites have basically three different structural variations:

- There are chain-like structures where minerals form acicular or needle-like prismatic crystals.
- Sheet-like structures where the crystals are flattened platy or tabular with usually good basal cleavages.
- And framework structures where the crystals are more equate in dimensions.

Isotherms

Generally, adsorption isotherms provide vital information in optimizing for the use of adsorbents. Descriptions on affinity between sorbates and sorbents, bond energy and adsorption capacity, to mention a few, can be extracted from isotherm equilibrium models applicable to adsorption processes. Isotherm models provide an adequate description of metal adsorption equilibria on wide range of adsorbent materials.

Equilibrium data, used for designing adsorption isotherms, are used for estimation of adsorption system. There are several adsorption models that can be used to describe the equilibrium between adsorbed ions on the

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adsorbents (q_e) and ions in solution (c_e) at a constant temperature and pH.

The Freundlich equation [7], based on sorption onto a heterogeneous surface, is an exponential equation and, therefore, assumes that the concentration of adsorbate on the adsorbent surface increases with the adsorbate concentration [2, 3, 8 - 10]. It is originally an empirical equation, but later it was interpreted for sorption on heterogeneous surfaces or surfaces with active areas of different affinity. Active areas are filled up prior due to strong binding force which decreases with increasing degree of occupation of the active areas [11].

The Langmuir equation [12] is valid for monolayer sorption onto a surface [2, 3, 8 - 10]. It was originally developed to describe the adsorption process at the interface of gas and solid phases of activated carbon. The theory assumes that physical strength takes effect at the adsorbent surface and the active sites have the same affinity for the absorbed substance. The application of this isotherm was later extended to use for liquid – solid interphase [11]. The active areas of the adsorbent equally adsorb one molecule therefore a monolayer is created. The thickness of the monolayer is equal to the thickness of the molecule [13]. The maximum adsorption capacity is reached when the adsorption energy is constant and there is no longer a transition of the adsorbed substance from the solution to the surface of the adsorbent.

The Redlich-Peterson equation [14] represents the equilibrium adsorption over a wide concentration range [15 - 17]. The isotherm is characterized by fusion of 12 and Freundlich isotherms into a simple equation.

MATERIAL AND METHODS

Adsorbents and reagents

Zeolite used for the experiments is from the Nižný Hrabovec (SK). The zeolite from the Nižný Hrabovec localization is a natural rock, which principal part is composed of crystalline hydrated aluminosilicate of alkaline metals and metals of alkaline soils (Ca, K, Na, Mg) so-called klinoptilolite. The structure of the klinoptilolite is based on the three dimensional skeleton consisting of $(SiO_4)^{4-}$ tetrahedrites interconnected via oxygen atoms, while a part of silicon atoms is replaced with $(AlO_4)^{5-}$ aluminum atoms. The particle size distribution of the adsorbent is presented in Figure 1.

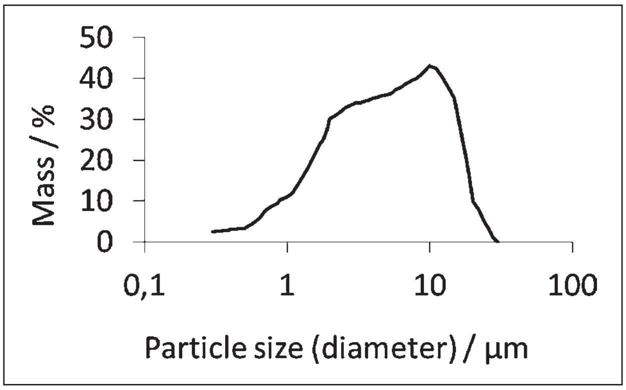

Figure 1 Particle size distribution of the adsorbent- Zeolite

The stock solutions of certain concentrations were prepared by dissolving analytical grade $Cu(NO_3)_2{\cdot}3H_2O$ or $Zn(NO_3)_2{\cdot}6H_2O$ in distilled water.

Apparatus

Thermo SCIENTIFIC model iCE 3000 SERIES atomic absorption spectrometer (AAS) operating with air-acetylene flame was used to analyse the concentration of Cu(II) in solutions.

Adsorption experiments

A desired amount of sorbent – zeolite (1 g) was weighed and added into an Erlenmeyer flask (100 mL), in which a desired volume of distilled water was added. Then a required amount of standard solution of Cu(II) or Zn(II) was put to the flask. The experiments were carried out by varying concentrations of initial Cu(II) or Zn(II) solution (10 - 3 000 mg/L). In all experiments, the flasks were shaken on orbital shaker at 200 rpm and at 25 ˚C for 6 hours to ensure ion-exchange equilibrium. The suspensions were then filtered through a micro filter of pore size 0,8 μm and filtrates were analysed using flame AAS in order to determine the final Cu(II) or Zn(II) concentration in solution.

The Cu(II) or Zn(II) concentration retained in the adsorbent phase, q_e (mg/g) was calculated according to following relation:

$$q_e = \frac{(C_e - C_0)\,V}{m} \quad (1)$$

where q_e / mg/g is the equilibrium adsorption capacity, C_0 and C_e / mg/L are the initial and equilibrium concentration of metal ions in solution, respectively, V / L is the volume, and m / g is the amount of the resin. Using this formula q_e values for different metal concentrations were calculated [18].

All the experiments were performed in twice and the result was taken as the average value of each experiment.

RESULTS AND DISCUSSION

The adsorption isotherms for copper on zeolite are presented in Figure 2.

The adsorption isotherms for zinc on zeolite are presented in Figure 3.

According to the results of the experiments the adsorption equilibrium of Cu(II) and Zn(II) on zeolite was best described by Freundlich isotherm. The maximum sorption capacity was 1,48 and 1,49 mg/g for Cu(II) and Zn(II), respectively. The experimental results of this study demonstrate that zeolite is suitable for adsorption of copper and zinc from aqueous solutions at low concentrations.

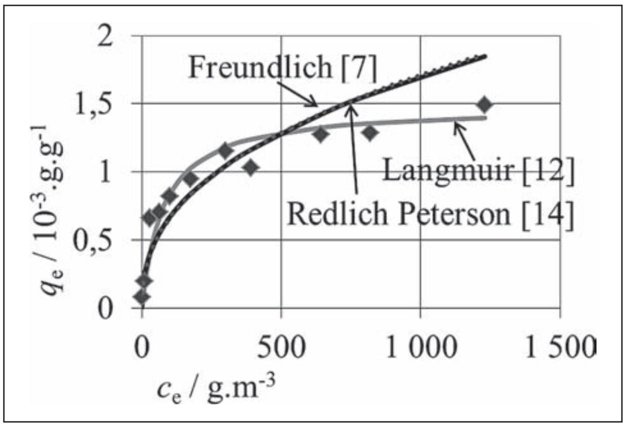

Figure 2 Cu(II) ions adsorption on Zeolite

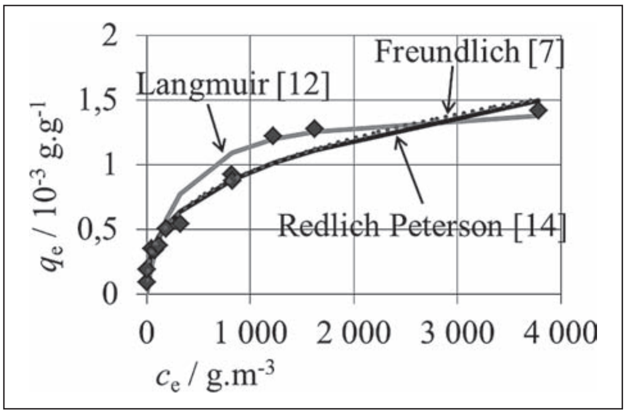

Figure 3 Zn(II) ions adsorption on Zeolite

CONCLUSION

Removal of heavy metal ions from wastewater after various metallurgical processes is currently highly topical. There is a quite broad spectrum of sorbents, which are suitable for the decontamination; the zeolites are sorbents with a strong affinity to metal cations, as demonstrated by the results of the above experiments. Zeolites are characterized by relatively high sorption capacity, i.e. Cu(II) and Zn(II) removal even at relatively low concentrations, indicating significant positives in their application in the field and in practice.

Acknowledgements

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