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Comparative study of cu^{2+} adsorption on a zeolite, a clay and a diatomite from Serbia

M. Šljivić [a,*], I. Smičiklas [a], S. Pejanović [b], I. Plećaš [a]

[a] The Institute of Nuclear Sciences "Vinča", P.O. Box 522, 11000 Belgrade, Serbia
[b] The Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia

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ABSTRACT

The adsorption of a zeolite, clay and diatomite from Serbia toward aqueous Cu^{2+} ions was studied, at different pH. The adsorbents were characterized with respect to phase composition, specific surface area and point of zero charge. The amounts of Cu^{2+} removed from the solution, increased with increasing initial pH, reaching nearly 100% at $pH>7$, regardless of the adsorbent type and metal concentration, due to precipitation of $Cu(OH)_2$. Relatively constant final pH values and less significant increase of Cu^{2+} uptake observed in the initial pH range 4–6 have pointed out the role of buffering properties of investigated adsorbent materials. The maximum adsorption capacities decreased in the order zeolite (0.128 mmol/g)>clay (0.096 mmol/g)>diatomite (0.047 mmol/g). The Langmuir equation was most suitable for data fitting. The proportion of Cu^{2+} desorbed in acidic media decreased with the increase of previously adsorbed amounts by zeolite and clay, while the opposite was true for diatomite. Ion exchange of exchangeable cations and protons were identified as main adsorption mechanisms, with latter being most apparent in the removal mechanism of diatomite. Considering low-cost, local availability and environmentally friendly materials, zeolite exhibited highest potential for environmental and health protection applications.

1. Introduction

Waste streams encountered in mining operations, and various chemical processing industries, contain heavy metals which are non-biodegradable, toxic priority pollutants. Due to their tendency to accumulate in living organisms, causing various diseases and disorders, the treatment methods for metal-bearing effluents are essential for environmental and human health protection. Among numerous commonly used techniques for water purification, adsorption technologies have gained the most attention because of their low cost and easy operation (Rousseau, 1987; McKay, 1996). In recent years, an intensive research was conducted focusing on the selection and/or production of low-cost adsorbents with good metal-binding capacities, which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment-activated carbon. Natural materials of both organic and inorganic nature (such as chitosan, zeolites, clay and clay minerals, etc) and certain waste products from industrial operations (such as fly ash, coal and oxides) are classified as low-cost adsorbents because they are economical and locally available (Babel and Kurniawan, 2003; Wang et al., 2003).

The aim of this study was to investigate and compare the adsorption properties of raw, mineral adsorbents (Serbia), namely: zeolite, clay and diatomite.

Among natural zeolites, clinoptilolite exhibited high selectivity for certain heavy metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} (Babel and Kurniawan, 2003; Camilo et al., 2005; Sprynskyy et al., 2006).

Three basic types of clay minerals smectite (such as montmorillonite), kaolinite and micas (muscovite), have also been tested for heavy metal adsorption (Charnock et al., 1995; Kayaa and Oren, 2005; Adebowale et al., 2006; Bhattacharyya and Gupta, 2007).

Diatomite is fine-grained, low-density biogenic sediment, which consists essentially of amorphous silica ($SiO_2 \cdot nH_2O$) derived from opalescent frustules of diatoms. Due to the presence of silanol groups that spread over the matrix of silica, diatomite can react with many polar functional groups (Allen and Koumanova, 2005). It has been commonly used in water purification, filtration of commercial fluids, clarifications of liquors and juices and for separation of various oils and chemicals (Korunic, 1998). The adsorption properties of diatomite toward heavy metal ions were reported in the literature (Al-degs et al., 2001; Dantas et al., 2001; Al-Ghouti et al., 2004; Khraisheh et al., 2004). Furthermore, diatomite was found to be a promising agent for immobilization of cesium and cobalt radionuclides (Osmanlioglu, 2007), as well as uranium (Aytas et al., 1999).

As representative of heavy metal cations Cu^{2+} was chosen in this study. This element is one of the principal heavy metals responsible for causing degradation of the environment, and although essential for leaving in low concentrations, both acute and chronic exposure to excess copper is associated with various health effects (NRC, 2000). Release of Cu^{2+} into water occurs from weathering of soil, industrial discharge, sewage-treatment plants, and antifouling paints (IPCS, 1998). Such water has to be treated, and with respect to water quality standards, the concentration of the Cu^{2+}ions in wastewater should be reduced to 1.0–1.5 mg/L (Ekmekyapar et al., 2006).

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* Corresponding author. Tel.: +381 11 2453867; fax: +381 11 2455943.
E-mail address: marijasljivic@vin.bg.ac.yu (M. Šljivić).

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Nomenclature

A (L/mmol)	Tempkin equilibrium constant corresponding to the maximum binding energy
b (J/mol)	Tempkin isotherm parameter, variation of adsorption energy
β (mol^2/kJ^2)	DKR constant related to adsorption energy
C_e (mmol/L)	equilibrium Cu^{2+} concentration in the liquid phase
C_0 (mmol/L)	initial Cu^{2+} concentration
E (kJ/mol)	energy of adsorption
ε (kJ/mol)	Polanyi potential
ΔG (kJ/mol)	Gibbs free energy change
K_L (L/mmol)	Langmuir constant related to the energy of adsorption
K_t (L/mmol)	Toth isotherm constant
Q_e (mmol/g)	equilibrium Cu^{2+} concentration in the solid phase
q_m (mmol/g)	maximum adsorption capacity
R (J/mol K)	universal gas constant
R_L	separation factor
T (K)	absolute temperature
t	Toth isotherm constant

The natural adsorbents were characterized in respect to physico-chemical properties and Cu^{2+} adsorption at different pH and initial metal concentrations. The stability of the adsorbent–adsorbat products was studied through desorption experiments. The applicability of theoretical models for the equilibrium data fitting was tested. The results from the present study can be used for the evaluation and comparison of the selected adsorbent materials for Cu^{2+} removal from aqueous solutions, and for gaining insight into the phenomena that occur at mineral/Cu^{2+} interface in natural systems.

2. Materials and methods

2.1. Adsorbents

The adsorbents used for the Cu^{2+} uptake were local raw minerals: zeolite (Vranjska Banja), clay (Koceljeva) and diatomite (Kolubara). The adsorbents were washed with distilled water, in order to remove the surface dust, and dried at 105 °C.

The specific surface area was determined from the adsorption–desorption isotherms of N_2, at −196 °C, by Mc Bain gravimetric method. Before measurements, the samples were degassed at 120 °C in vacuum for 24 h. The specific surface areas were determined using BET equation, while the pore size distribution was estimated by applying the Barrett Joyner–Halenda (BJH) method (Barrett et al., 1951) to the desorption branch of the isotherm.

X-ray diffraction (XRD) analyses were carried out on a Philips PW 1050 instrument (CuKα Ni-filter).

The points of zero charge (pH_{PZC}) were obtained by batch equilibration technique (Smiciklas et al., 2000). Adequate masses of KNO_3 (p.a., Merck) were dissolved in distilled water to prepare the solutions of 10^{-1}, 10^{-2} and 10^{-3} mol/L. The solid/solution ratio (1:200), contact time (24 h), shaking velocity (120 rpm) and room temperature (20±1 °C) were fixed. The initial pH was varied between 2 and 12, by the addition of KOH or HNO_3, and the final pH values were measured. In addition, the upper described experiment was performed using zeolite and distilled water, instead of KNO_3 solution.

2.2. Adsorption experiments

The Cu^{2+} solutions were prepared from $Cu(NO_3)_2{\cdot}6H_2O$ salt (p.a., Merck) and distilled water. All initial pH values were adjusted using a small quantity of 0.01 mol/L of HNO_3 or KOH. The PVC flasks containing the fixed masses of adsorbents (0.1000 g) and 20 mL of Cu^{2+} solutions were placed on a horizontal shaker and shaken at constant speed (120 rpm) at room temperature. The preliminary kinetic experiments showed that 24 h of contact time was sufficient

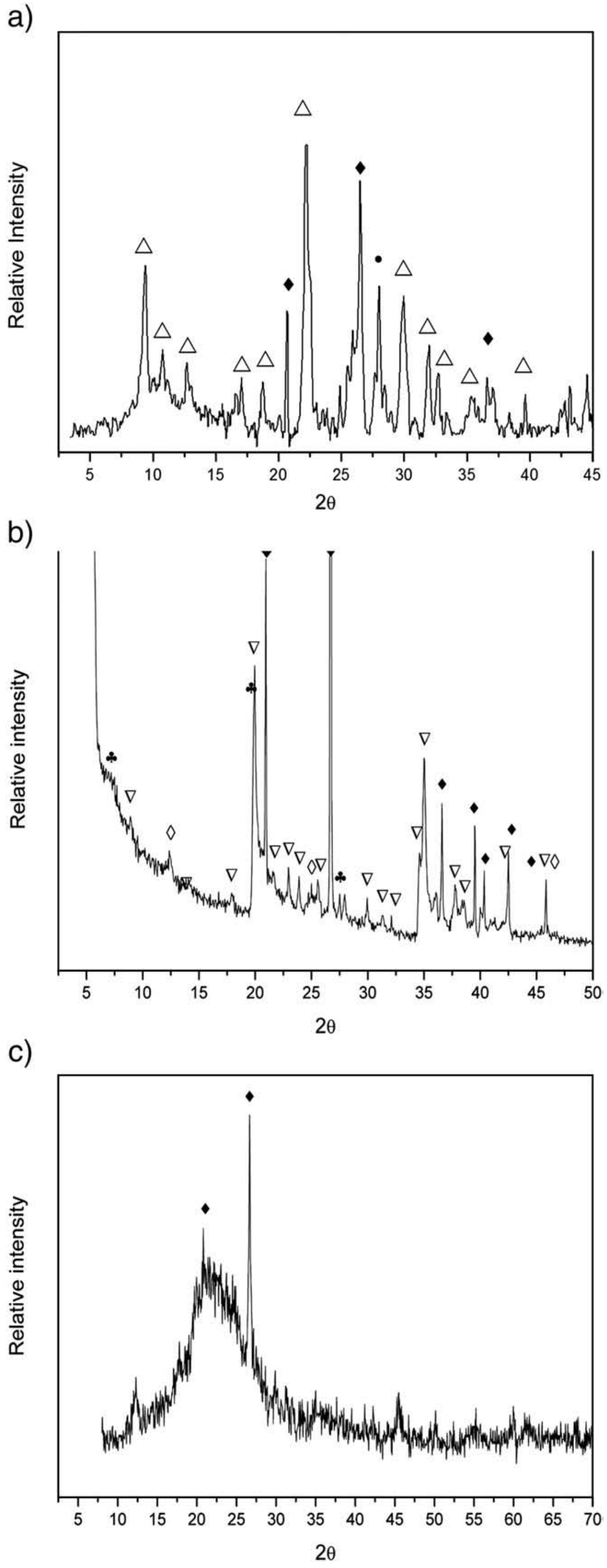

Fig. 1. XRD patterns: (a) zeolite, (b) clay and (c) diatomite. Symbols: clinoptilolite (△), quartz (♦), kaolinite (◊), albite (●), montmorillonite (♣), and illite (▽).