Annual of the University of Mining and Geology "St. Ivan Rilski"
vol. 44-45, part II, Mining and Mineral Processing, Sofia, 2002, pp. 93-97

INVESTIGATION THE ADSORPTION PROPERTIES OF THE NATURAL ADSORBENTS ZEOLITE AND BENTONITE TOWARDS COPPER IONS

Valeria Kovatcheva-Ninova
University of Mining and Geology
“St. Ivan Rilski”
Sofia 1700

Nina Nikolova
University of Mining and Geology
“St. Ivan Rilski”
Sofia 1700

Marin Marinov
University of Mining and
Geology “St. Ivan Rilski”
Sofia 1700

ABSTRACT
The possibilities for using Bulgarian natural adsorbents bentonite and zeolite is have been investigated for purification of model solution of Cu^{2+} at correlation of liquid to solid phase, v:m=100:1. It has been found out, that the specific surface of the both minerals takes leading part at the adsorption of Cu^{2+} from model solutions with concentration higher than 70 mg/dm^3. The cation adsorption capacity is highest at size of the particles of both adsorbents –0,071+0 mm. The thermodynamics of adsorption has been described with the most appropriate isotherms of uptake of Cu^{2+} from different particle sizes adsorbents. It has been reported, that the two natural adsorbents can be used to remove Cu^{2+} from model solutions with concentrations not higher than 10-20 mg/dm^3 with one stage of purification at adsorption time 5 min for reaching the Bulgarian standards for drinking waters. Under t these conditions the optimum values of pH for the zeolite are in a wider interval from 4,6 to 8 and for the bentonite 4,6.

Key words: zeolite, bentonite, adsorption of copper ions, adsorption isotherms

INTRODUCTION

In world-wide scale the volume of waste water reaches about 440 km^3/year. Due to that purification is one of the most wide spread technological processes. A perspective method for purification of waste water is adsorption. Using this method the adsorbents have to answer to number of requirements to be active, stable, accessible, cheap, easy to regenerate and most important is that the exchange ions should be harmless and should not provoke secondary water pollution. The natural minerals zeolite and bentonite respond to these requirements.

The big deposits of zeolite and bentonite near the town of Kurdjali, their low self value and their unique ion exchange and adsorption properties, make them attractive for purification of wastewater from ions of heavy metals.

Considerable amounts of mine and drain waters from the copper mines and mineral dressing enterprises “Asarel-Medet” and “Elazite-Med” contain mainly copper ions as well as iron, zinc, aluminium and other ions in lower quantities.

Due to that the aim of the research is: a) to compare the adsorption properties of both natural minerals depending on the size of their particles; b) to find the most appropriate equation describing the thermodynamics of the adsorption; c) to investigate the kinetics of adsorption under the same conditions for both minerals; d) to examine the influence of pH of the solutions on the adsorption of Cu ions from model solutions.

PHYSICOCHEMICAL CHARACTERISTICS OF ZEOLITE AND BENTONITE

Zeolite

The clinoptilolite zeolites are most wide-spread in NE Rodopi. The mian mineral is a clinoptilolite and its amount reaches up to 90% from the composition of the rock. The size of its grains vary from a thousand part of the millimeter up to 0.05-0.08 mm. The zeolites are built from (AlO_4) and (SiO_4) tetrahedrons, which alternate in grainy three-dimensional structure. The tetrahedrons can be connected in different ways, unified by common tops. Complex crystal structures with situated in determinate order micro-pores and canals with diameter in molecular order are formed in this way. The structural formula of cliniptilolite is $Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$ and the number of the tetrahedrons in the ring is 8 according to Andronikashvili, Kirov “et al.” (1985). The high selection of zeolite with respect to metal cations with large dimensions is due to the existence in the structure of eight numerical siliceousoxygen rings. The clinoptilolite possess the following more important physicochemical characteristics: good mechanical strength (3,3-4 by Moos), density 2,16 g/cm^3, ion exchange capacity $\approx$2.16 mgeq/g.

The adsorption ability of the zeolite is different in comparison with the ions of the heavy metals. According to Obal, Rozman “et al.” (1991) the adsorption order with respect to the counted metals is following: Pb>Cu>Zn>Ni>Fe>Cr. The selectivity order of the same ions for the clinoptilotite can be also observed in the work of Chelischev, Bernshtein “et al.” (1977): $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>>Na^{+}$. The exposed data show that the clinoptilolite zeolite reveal good selectivity with respect to the copper ions.

Bentonite

The bentonite deposits mainly are concentrated around Kardjali town. The bentonite is clay in which basic clay mineral is the montmorilonite. The crystal structure of montmorilonite is determinated by two layers of siliceous tetrahedrons with an inserted layer of aluminium octahedrons between them, i.e. the bentonite is also aluminium silicate but in contrast to zeolite possesses bedded structure. In the montmorilonite crystal different exchangeable cations take part - monovalence (Na^+, K^+, H^+) and divalence (Ca^{2+}и Mg^{2+}). The exchanging ability of the bentonite is determinated not only by the kind and the quantity of these ions, but also by the stirred crystal lattice of montmorilonite. The ideal chemical formula of montmorilonite is $[Si_8(Al_{3,34}Mg_{0,66})O_{20}(OH)_4]M_{0,66}.H_2O$, where M-ions of Na, Ca, H and Mg according to Pironcov, Stoev "et al."(1991). The behavior of bentonite depends very much on the predominate exchange ion, for example, if we put Na –bentonite in water it increases his volume up to 14 times, while Ca-bentonite practically does not swell. In comparison to Na-bentonite the Ca-bentonite has better adsorption and discolouring properties. The bentonite can be used for removing Pb, Cd, Cu and Zn ions from water solutions according to Bereket, Aroguz "et al." (1997).

EXPERIMENTAL STUDIES

Materials and methods

The natural clinoptilolite is from a big deposit "Beli Past" in NE Rodopi. The chemical composition by weight % is: SiO_2-66,16%, Al_2O_3-11,41%, Fe_2O_3-0,8%, TiO_2,-0,15%, MgO—0,06%, CaO-2,8%, Na_2O-0,22%, K_2O-2,9%. The content of clinoptilolite is≈70%, and the full exchange capacity is minimum100mgeq/100g. The correlation of Si:Al is 5, i.e. the zeolite is highly siliceous and is very stable to acid and basic solutions.

The natural bentonite is from deposit "Encher" near the town of Kardjali. The chemical composition of average probe by weight % is the folowing: SiO_2-52,7%, Al_2O_3-15,9%, Fe_2O_3-4,5%, MgO-3,5%, CaO-4,3%, Na_2O-0,9%, K_2O-1,1%. The content of CaO and MgO is respectively more than 1% and 2,5% and the correlation Na_2O:CaO is very little. This shows that the swelling property of bentonite in water will not be demonstrated. The density of bentonite is experimentally determined and it is 2,03 g/cm^3.

Three classes of natural minerals have been used for the accomplishment of the experiments: for zeolite -2,0+1,0; -1,0+0,071; –0,071+0 mm; and for the bentonite: +0,315; -0,315+0,071; –0,071+0 mm. The experiments have been carried out with model solutions of $CuSO_4.5H_2O$. The necessary concentrations of Cu ions are obtained by dilution with distillated water. The contact between the natural adsorbents and the solutions is realized in static conditions with the help of shaking machine CITRON, 150 min^{-1}, in correlation liquid:solid, v:m=100:1 for all experiments.

The cation adsorption capacity (CAC) for three classes adsorbents towards Cu ions was determinated during 24 hours, while in the first two hours a shaking machine is used.

The computer program "CURVE FIT 424" was used giving possibilities from 24 types equations to choose the best model describing the adsorption isotherms of Cu^{2+} for the three classes of adsorbents. The experiments were realized at the temperature of 17 °C. The pH values of the solutions were determinated with Metrohm E588 pH-mV meter and were modeled with solutions of H_2SO_4 and NaOH. The concentration of Cu ion in solutions was determinated by ICP-AES analysis.

CAC of the natural adsorbents towards Cu ions was calculated using the formula:

$$CAC = \left(\frac{c_1 - c_2}{m \cdot 1000}\right) \cdot V \quad or \; CAC = \frac{c}{m} \cdot \frac{V}{1000}$$

where, c_1 is the concentration of the element in initial solution, mg/dm^3; c_2 is the equilibrium concentration of the element in solution, mg/dm^3; c is the quantity adsorbed substance, mg/dm^3; V is the volume of investigated solution, dm^3; m is the weight of dry sorbent, g; CAC is cation exchange capacity, mgelm/g sorbent.

RESULTS AND DISCUSSION

Influence of the adsorbents particle size upon their CAC towards Cu

The value of CAC shows the influence of the bentonite and zeolite particle size upon the adsorption of Cu ions, reached during the time of contact 24 hours. It is considered, that during that time full equilibrium between the solid and the liquid phases is reached. For this purpose 1g from three different classes of zeolite and bentonite contact with 100 cm^3 model solution of $CuSO_4.5H_2O$ with different concentration of Cu^{2+}.

The influence of the bentonite particle sizes is showed in fig.1 and of the zeolite in fig.2 on CAC depending on the concentration of Cu ions in the initial solutions. Fig.1 and fig.2 show that at the lower contents of Cu ions in the initial solutions (up to 72,6 mg/dm^3) the size of adsorbent particles does not influence essentially on CAC. But, with raise of the content of Cu ions in the initial solutions, CAC of both minerals raises with decreasing their particle sizes, i.e. with increasing their specific surface.

Comparing the dates from the figures of both minerals one can observe higher CAC of the zeolite towards the bentonite for the three classes at concentrations of Cu ions higher than 72,6 mg/dm^3. At the initial concentrations of Cu^{2+} in the solutions up to 10-20 mg/dm^3, after adsorption are obtained remaining concentrations of the same ions <0,2 mg/dm^3. That shows, that both minerals can be used for purification of waters, containing this quantity Cu^{2+} with one stage of purification. Moreover, the standards of Cu content are achieved in waste waters (<0,2 mg/dm^3), at which they can be released into rivers and into open-air reservoirs.

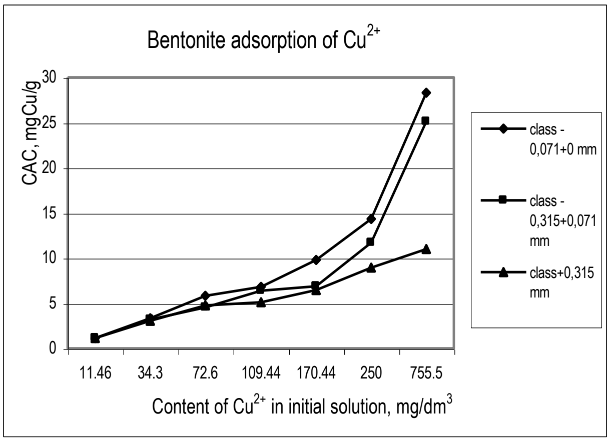

Figure 1. Influence of bentonite particles size on CAC towards Cu^{2+} from model solutions of $CuSO_4 5H_2O$

Thermodynamics of the copper adsorption from the natural adsorbents bentonite and zeolite

The adsorption such as desorption depends mainly on the thermodynamic parameters, temperature and concentration of adsorbtive and on the condition of the adsorbent surface. The quantity of strongly adsorbed adsorbate depends only on the concentration of adsorbtive, at certain temperature and established adsorption equilibrium. This dependence between the quantity adsorbed substance and the concentration of adsorptive is expressed by the adsorption isotherm. The adsorption isotherms of Cu^{2+} uptake from natural adsorbents were obtained with the help of computer program "CURVE FIT-424" at temperature 17 ^{0}C. From 24 types of equations the most suitable were chosen, describing the Cu^{2+} adsorption from different classes of bentonite and zeolite. The chosen equations give highest coefficient of correlation (r) of the dependence: $y=f(c_2)$,
where y is the quantity adsorbed substance (c) related to 1g bentonite or zeolite for contact time 24 hours, mgCu/g
$y=c/m$;
c_2 is equilibrium Cu^{2+} concentration, reached after 24 hours, mg/dm^3.

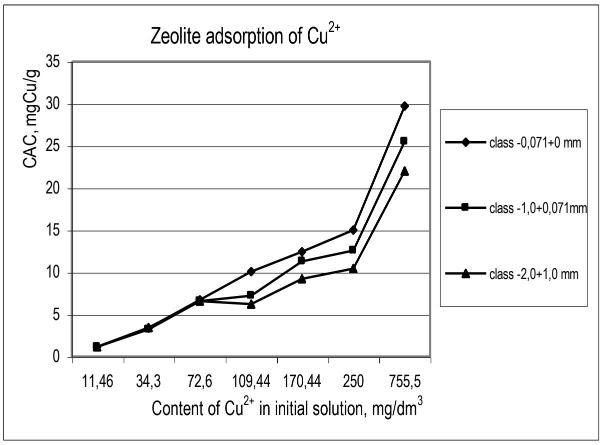

Figure 2. Influence of zeolite particles size on CAC towards Cu^{2+} from model solutions of $CuSO_4 5H_2O$.

Adsorption isotherms of Cu^{2+} uptake of bentonite:

for class –0,071+0 mm

$$y=\frac{c}{m}=2{,}5378+0{,}1204.c_2-1{,}3929.10^{-4}c_2^2\,;$$

$(r=0{,}9941)$

or

$$y=\frac{c}{m}=2{,}2839.1{,}0009^{c_2}.c_2^{0,3386};$$

$(r=0{,}9922)$

for class –0,315+0,071 mm

$$y=\frac{c}{m}=3{,}7899+4{,}2935.10^{-2}.c_2-\frac{0{,}1069}{c_2^2};$$

$(r=0{,}9902)$

or

$$y=\frac{c}{m}=1{,}9826.1{,}0016^{c_2}.c_2^{0,2775};$$

$(r=0{,}9896)$

for class +0,315 mm

$$y=\frac{c}{m}=1{,}9928.0{,}9999^{c_2}.c_2^{0,2671};$$

$(r=0{,}9826)$

or

$$y=\frac{c}{m}=1{,}9936.c_2^{0,2664};$$

$(r=0{,}9826)$

Adsorption isotherms of Cu^{2+} uptake of zeolite:
for class –0,071+0 mm

$$y=\frac{c}{m}=\exp\left[1{,}4841-\frac{0{,}1769}{c_2}+0{,}2958\ln\left(c_2\right)\right],$$

$(r=0{,}9845)$

or

$$y=3{,}0068.c_2^{0,3882};$$

$(r=0{,}9745)$

for class –1,0+0,071 mm

$$y=\frac{c}{m}=2{,}4115.c_2^{0,3706};$$

$(r=0{,}9827)$

or

$$y=\frac{c}{m}=2{,}4170.1{,}00007^{c_2}\,c_2^{0,3672};$$

$(r=0{,}9844)$

for class –2,0+1,0 mm

$$y=3{,}0191.1{,}00096^{c_2}.c_2^{0,2307};$$

$(r=0{,}9840)$

or

$$y=\frac{c}{m}=6{,}0039+2{,}9925.10^{-2}.c_2-\frac{0{,}1490}{c_2^2};$$

$(r=0{,}9907)$

Kinetics of Cu^{2+} adsorption by the natural adsorbents bentonite and zeolite

Class –0,071+0 mm for both adsorbents was chosen for studing the kinetics of Cu^{2+} adsorption. The concentration of Cu^{2+} in the initial model solutions is 11,46 mg/dm^3. The experiments were carried out at temperature 17 ^0C and pH of the solutions 4,62. The contact time between the solid and the liquid phases is accordingly: 5, 10, 25, 40 and 60 min at shaking with 150 min^{-1}. The selection of the content of Cu^{2+} in the initial solutions is based on the achieved remaining concentration <0,2 $mgCu/dm^3$ for all treated solutions with one stage of purification for both adsorbents. The achieved remaining concentration (<0,02 $mgCu/dm^3$) responds to the requirements of Bulgarian standards for potable waters (<0,05 $mgCu/dm^3$) and releasing of waste waters from mines and mineral dressing enterprises into rivers and into open-air reservoirs (<0,2 $mgCu/dm^3$).

The kinetics of Cu^{2+} adsorption is shown in fig.3, as relation between remaining concentration and contact time.

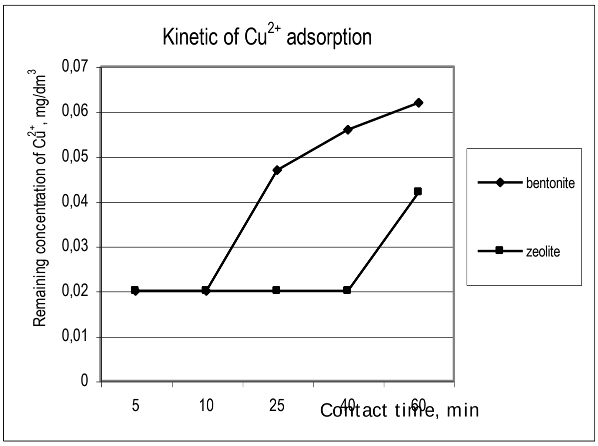

Figure 3. Kinetics of Cu^{2+} adsorption by bentonite and zeolite.

As we see in the figure, the kinetics of Cu^{2+} adsorption is very fast for both minerals and 5 min are sufficient for reaching the remaining concentration <0,02 mg/dm^3. An insignificant desorption of the copper ions from the bentonite were observed after the 10th min and form the zeolite after the 40th min. A conclusion can be made, that the Cu^{2+} adsorption is stable for both minerals under the indicated conditions.

Influence of pH of solution on the Cu^{2+} adsorption from bentonite and zeolite

The experiments were realized at the following conditions: temperature 17 ^0C; initial concentration of Cu^{2+} in the solutions 11,46 mg/dm^3; pH- 2, 4, 4,62, 6, 8, 10; contact time 5 min and size of the bentonite and zeolite particles –0,071+0 mm.

The low values of pH are reached by acidification with H_2SO_4 solution and the higher than 4,62 with a solution from NaOH. The influence of pH of the solutions upon the adsorption of Cu^{2+} is indicated in fig. 4. The change of the remaining concentrations of Cu^{2+} in function from pH of the solutions has been followed. It can be seen from the figure, that the remaining concentration begins to decrease, increasing the pH of the solutions after the process of adsorption. For the zeolite it is lowest at pH from 4,62 to 8 (c_2<0,02 mg/dm^3) and for the bentonite from 4,62 to 6 (c_2 from 0,02 to 0,13 mg/dm^3). It is due to the fact, that besides the process of adsorption there also runs precipitation of Cu^{2+} at pH>5 as a result of the removal of the reaction equilibrium to the right:

$$Cu^{2+}+2H_2O \leftrightarrow Cu(OH)_2+2H^+$$
$$\longrightarrow$$

An increase of the Cu^{2+} remaining concentration at pH >8 for both adsorbents was observed, which was probably due to their partial desorption from the adsorbents and the presence of unadsorbed $Cu(OH)_2\downarrow$ in solution.

The optimum pH value of the solutions at Cu^{2+} adsorption for zeolite is in wider range from 4,62 to 8 and for bentonite it is in more narrow range from 4,62 to 6. The results show that the zeolite has better adsorption qualities then bentonite.

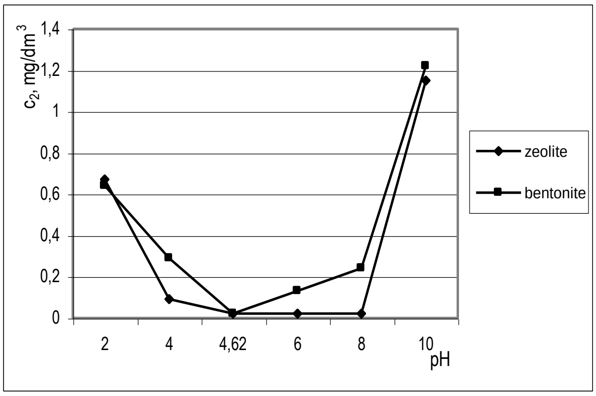

Figure 4. Influence of pH of the solutions on the Cu^{2+}adsorption.

CONCLUSION

1. The Bulgarian natural adsorbents zeolite and bentonite can be used for recovering Cu^{2+} with concentration between 10-20 mg/dm^3 in waste water, completing in one stage of purification by correlation liquid:solid=100:1. Both natural minerals have good adsorption properties towards Cu^{2+} with little superiority of zeolite.

2. The specific surface of the natural adsorbents does not play a significant role on the adsorption at concentrations of Cu^{2+} in the solutions up to 70 mg/dm^3. At higher concentrations the order of adsorption, according to the size of the particles of zeolite, is -0,071+0>+1,0-2,0>-1,0+2,0 mm and of bentonite is -0,071+0>+0,071-0,315>+0,315 mm.

3. The thermodynamics of the adsorption process at different sizes of the particles of both adsorbents was described by the most appropriate adsorption isotherms, obtained with the help of the computer program “CurveFit 424”.

4. The adsorption process at content of Cu^{2+} between 10-20 mg/dm^3 and pH of the solutions 4,6 is vary fast. The contact time is not more than 5 min for reaching the standard for potable waters, according to the content of Cu^{2+}, which is 0,05 mg/dm^3.

5. At adsorption with zeolite, the pH range of the waste waters containing Cu^{2+} between 10-20 mg/dm^3 is wide from 4,6

to 8, for reaching the standards of potable waters. The time of adsorption is 5 min for achieving remaining concentration of Cu^{2+} below 0,02 mg/dm^3. At adsorption with bentonite for the same contact time, the standards for potable waters are reached at pH 4,6. At pH value from 4,6 to 8 are reached the standards for releasing waste waters containing Cu^{2+} in rivers and open reservoirs.

REFERENCES

Andronikashvili, T.G., Kirov, G.N., Filizova, L.D. 1985. Prirodnie zeoliti, Himia, -p. 22.

Bereket, G., Aroguz, A., Ozel, M., Removal of Pb (II), Cd (II), Cu (II) and Zn (II) from aqueous solutions by adsorption on bentonite, J.colloid.Appl.Sci., 187, 338-343 (1997).

Obal, M., Rozman, S., Jader, R., Kolenc, M., Osojik, A., Kov.zvit.thehnol. 1991. -26, №1-2, p.234-239.

Pironkov, St.K., Stoev, St., Nacheva, L., Marinova, S. 1991. Nerudni izkopaemi. Tehnologichen I ikonomicheski pregled, Tehnika.

Chelischev, N.F., Bernshtein, B.G., Smola, V.I. 1977. Ispolzovanie prirodnih zeolitov dlia izvlechenia mislih gazov, redkih I zvetnih metallov iz promishlenih othodov, M., VEEMS, -p. 55.

Recommended for publication by Department of Mineral Processing, Faculty of Mining Technology