Chemistry

SORPTION OF Co²⁺, Cu²⁺, Zn²⁺, Mn²⁺ METAL IONS FROM AQUEOUS SOLUTIONS ON ANIONIC SURFACTANT-MODIFIED BENTONITE

L. R. HARUTYUNYAN [1,2*], L. S. TANGAMYAN [1**], R. S. HARUTYUNYAN [1***]

[1] *Chair of Inorganic and Analytical Chemistry YSU, Armenia*
[2] *Armenian National Agrarian University, Armenia*

The sorption of Co²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ metal ions on anionic surfactant-modified bentonite was studied. The optimal conditions for the effective sorption of Co²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ metal ions from aqueous solution were obtained. It was established that sorption of studied metal ions on anionic surfactant-modified bentonite occurs both by ion-exchanging and adsorption mechanisms.

***Keywords*:** metal ions, sorption mechanism, surfactant-modified bentonite.

Introduction. Many metals are emitted to the environment as waste raising pollution of water and soil. This is a global problem, and, therefore, different approaches are suggested for decreasing environment pollution based on physico-chemical methods. The usage of aluminosilicate clays as sorbents is more prospective for removing different pollutants due to their low cost and availability, compared with active carbon, for example. Clays are also widely used due to their large specific surface, high chemical and mechanical stability and possibility of changing surface and structural properties. Sorption capacity of clays is a result of their chemical nature and porous structure. In the gas phase sorption occurs mainly due to the porous structure of clays, and the size of pores has a significant role, while in the liquid phase the chemical nature of surface groups of clays has a great effect on the sorption process [1–3].

For the purpose of improving sorption properties of clays, they are often modified by surfactants [4–8], after which they can be effectively used for removing different organic-pollutants and metal ions [4–7, 9, 10]. Based on this concept, anionic surfactant-modified bentonite (SMB) was used to determine the optimal conditions for the removal of Co²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ metal ions from aqueous solutions.

Experimental Part.

Adsorptives. Solutions of Co²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ ions were prepared by dissolving the appropriate amount of Co(NO₃)₂·6H₂O, Cu(NO₃)₂·6H₂O, Mn(NO₃)₂·4H₂O and ZnCl₂ in distilled water, respectively. pH of solutions was controled by 0.1 and 0.01 *M* of HCl.

---

* E-mail: lusinehar@ysu.am   ** E-mail: miss.tangamyan@mail.ru
*** E-mail: romik@ysu.am

Adsorbent. Bentonite from Sarigyugh deposite (Ijevan), which was modified by anionic surfactant sodium dodecylsulfate, was used as adsorbent. Modification degree is 42 % [11].

Adsorption Studies. Batch experiments were carried out at 298 ± 0.5 *K* in a thermostat-controlled orbital shaker at an agitation speed of 150 *rpm*. After shaking, the samples were filtered through 0.45 *μm* Whatman filter paper, and then were used for analysis. The sorption amount of metal-ions was calculated using the following formula [12]:

$$q_e = (C_0 - C_e)\frac{V}{M},\tag{1}$$

where q_e is the amount of metal ions sorbed on the adsorbent; C_0 is the initial concentration of metal ions; C_e is the equilibrium concentration of metal ions; V is the volume of solution used; M is the weight of sorbent used. The removal efficiency was also calculated from the batch experiments, using the below mentioned formula:

$$R = \left[(C_0 - C_e)/C_0\right]100\%.\tag{2}$$

Analytical Procedure. Concentration of metal-ions in solution was determined by using PG-990 atomic adsorption technique. pH of solutions was determined by using HANNA HI 4522 technique.

Results and Discussion. The sorption of Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} metal ions on SMB was studied at 298.15 *K* varying metal-ion concentration from 100 to 400 *mg/L* and keeping other parameters constant. The results are presented in Fig. 1. As it is seen from Fig. 1, the sorption of metal-ions reaches maximum at 200 *mg/L*.
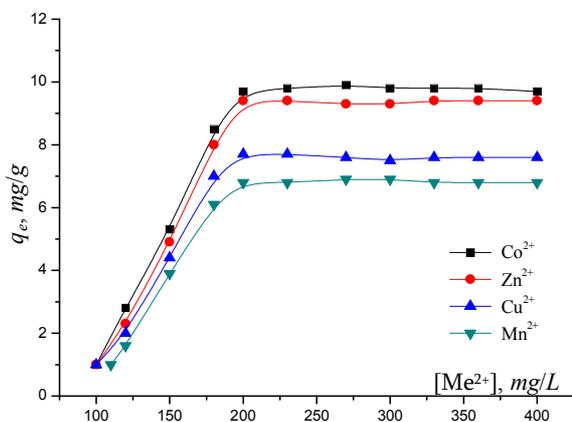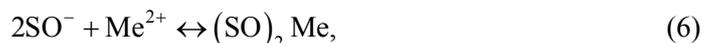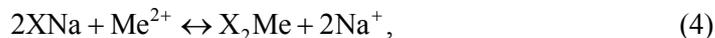

Fig. 1. Sorption amount of metal ions vs. metal ions concentration. $V_{sol.}$=100 *mL*, pH 5, contact time 3 *h*, sorbent amount 1 *g*, *T*=298 *K*.

The sorption of metal ions on SMB occurs by two mechanisms – ion-exchange and adsorption [2]. During ion-exchange process metal ions were introduced into inner layers of bentonite (and also of SMD) by pores and channels, and were exchanged by exchangeable cations (mainly by sodium and calcium). Diffusion of metal ions goes faster in pores and slows down when metal ions pass through small diameter having channels, and exactly during slow diffusion ion-exchange reactions occur in channels [2]. Ion-exchange reactions in aqueous solutions can be presented as follows:

$$XNa + H^+ \leftrightarrow XH + Na^+,\tag{3}$$

$$2XNa + Me^{2+} \leftrightarrow X_2Me + 2Na^+, \tag{4}$$

$$SOH_2^+ \leftrightarrow SO^- + 2H^+, \tag{5}$$

$$2SO^- + Me^{2+} \leftrightarrow (SO)_2 Me, \tag{6}$$

$$2RSO_4Na + Me^{2+} \leftrightarrow (RSO_4)_2 Me + 2Na^+, \tag{7}$$

$$RSO_4Na + H^+ \leftrightarrow RSO_4H + Na^+. \tag{8}$$

Non-modified bentonite has two acidic groups XNa (groups with exchangeable sodium ions) and SOH (surface-OH groups) [1], and in aqueous environment the surface of bentonite is charged negatively. But, despite this, the sorption of metal ions on non-modified bentonite is non-effective. After modification by anionic surfactant sodium dodecylsulfate the surface of bentonite was covered by negatively charged dodecylsulfate anions, which promote the increase of metal ions sorption by adsorption mechanism.
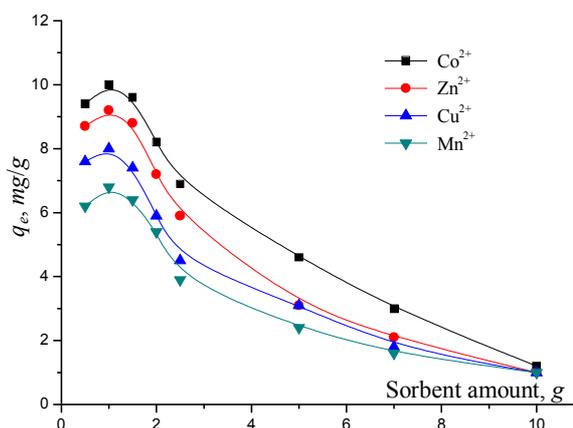

Fig. 2. Sorption amount of metal ions vs. sorbent amount. $V_{sol.}$=100 mL, pH 5, contact time 3 h, [Me^{2+}] = 200 mg/L, T=298 K.
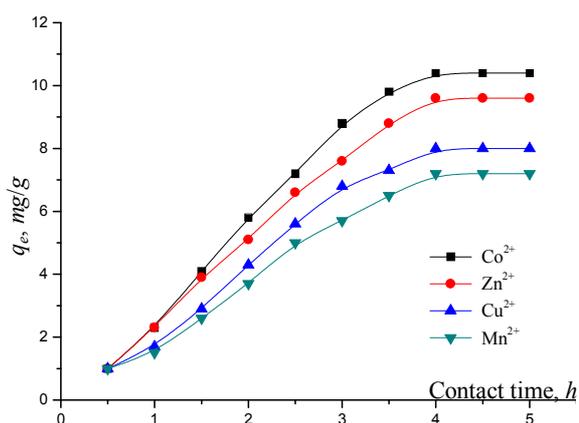

Fig. 3. Sorption amount of metal ions vs. contact time. $V_{sol.}$ =100 mL, pH 5, sorbent amount 1 g, [Me^{2+}]=200 mg/L, T=298 K.

In the next step the dependence of Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} metal ions sorption on the sorbent amount was studied. Based on the data of Fig. 1, 200 mg/L has been chosen as the optimal initial concentration of metal ions. As it follows from Fig. 2, the sorption amount of metal ions decreases with the increase of sorbent amount.

The influence of contact time on metal ions sorption was studied as well. The Fig. 3 shows that the maximum sorption was detected after 4 h.

Another important parameter for the effective sorption of metal ions is pH of the solution. From Eq. (3) and (8) it is seen that H^+ ions also participate in the sorption process. It means that at low values of pH (acidic environment) competitive sorption process occurs between metal ions and H^+. But in basic environment (pH > 7) there is another problem – metal ions form insoluble bases; it means that, though, the concentration of studied metal ions decreases in solution, it occurs not due to sorption. Based on the above-mentioned findings, it is suggested that pH 5 is more suitable for effective sorption of the metal ions under consideration.

Sorption amount of Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} metal ions on natural bentonite and anionic SMB. [Me^{2+}] =200 mg/L, sorbent amount 1 g, pH 5, $V_{sol.}$ =100 mL, contact time 4 h, T=298 K

	Co^{2+}		Zn^{2+}		Cu^{2+}		Mn^{2+}	
	q_e, mg/g	R, %	q_e, mg/g	R, %	q_e, mg/g	R, %	q_e, mg/g	R, %
Natural bentonite	6.6	33	6.0	30	5.4	27	5.2	26
Anionic SMB	10.4	52	9.6	48	8.0	40	7.2	36

The obtained data were compared with the metal ions sorption data on natural bentonite (see Table). From Table it follows that anionic SMB is a more effective sorbent for removing metal ions from aqueous solutions. It must be noted that modification of natural bentonite by surfactant is very ease apply and an in expensive process and, therefore, it does not increase the cost of the sorbent. On the other hand, it is known that after application of alumosilicate clays as sorbents for removing different pollutants, they are successfully used as additives in production of cement and bitumen (because sorption is irreversible) [7, 13]. Thus, as a result of modification, both the sorbent and the sorption processes are more effective, economically beneficial and environmentally friendly for removing harmful metals from aqueous solutions.

Conclusion. From presented studies it can be concluded that the sorption of Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} metal ions on anionic SMB occurs both by ion-exchange and adsorption mechanisms. The sorption degree of studied metal ions decreases in the order $Co^{2+} > Zn^{2+} > Cu^{2+} > Mn^{2+}$. The optimal conditions for the effective removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} metal ions are: [Me^{2+}]=200 *mg/L*, sorbent amount 1 *g*, pH 5, solution volume = 100 *mL*, contact time = 4 *h*, T=298 *K*.

REFERENCES

1. Barbier F., Duc G., Petit-Ramel M. Adsorption of Lead and Cadmium Ions From Aqueous Solutions to the Montmorillonite/Water Interface. *Colloids Surf. A: Physicochem. Eng. Asp.*, **166** (2000), 153–159.
2. Kumar P., Jasra R.V., Bhat T.S.G. Evolution of Porosity and Surface Acidity on Montmorillonite Clay On Acid Activation. *Ind. Eng. Chem. Res.*, **34** (1995), 1440–1448.

3. Teng B.K.G., Wells N. Assessing the Capacity of Some New Zealand Clays for Decolorizing Vegetable Oil and Butter. *Appl. Clay Sci.*, **9** (1995), 321–328.
4. Haggerty G.M., Bowman R.S. Sorption of Chromate and Other Inorganic Anions by Organo-Zeolite. *Environ. Sci. Technol.*, **28** (1994), 452–458.
5. Huh J.I., Song D.I., Jeon Y.W. Sorption of Phenol and Alkylphenols From Aqueous Solution onto Organically Modified Montmorillonite and Applications of Dual-Model Sorption Model. *Sep. Sci. Technol.*, **35** (2000), 243–259.
6. Juang R.S., Wu F.C., Tseng R.L. The Ability of Activated Clay for the Adsorption of Dyes from Aqueous Solutions. *Enviorn. Technol.*, **18** (1997), 525–531.
7. Krishna B.S., Murty D.S.R., Prakash B.S.J. Thermodynamics of Chromium(VI) Anionic Species Sorption onto Surfactant-Modified Montmorillonite Clay. *J. Colloid Interf. Sci.*, **229** (2000), 230–236.
8. Zhu L., Ren X., Yu S. Use of Cetyltrimethylammonium Bromide-Bentonite to Remove Organic Contaminants of Varying Polar Character from Water. *Environ. Sci. Technol.*, **32** (1998), 3374–3378.
9. Li Z. Chromate Extraction from Surfactant-Modified Zeolite Surfaces. 1: Clinoptlolite. *J. Environ. Qual.*, **27** (1998), 240–246.
10. Li Z., Bowman R.S. Counterion Effect on the Sorption of Cationic Surfactant and Chromate on Natural Clinoptilolite. *Environ. Sci. Technol.*, **31** (1997), 2401–2412.
11. Harutyunyan L.R., Tangamyan L.S., Harutyunyan R.S. Removal of Surfactants from Aqueous Solutions by Usage of Bentonite. *Proceedings of YSU. Chemical and Biological Sciences*, **52**:3 (2018), 161–166.
12. Tien C. *Adsorption Calculations and Modelling*. Boston, MA, Betterworth-Heinemann (1994), 244 p.
13. Leyva-Ramos R., Jacobo-Azuara A., Diaz-Flores P.E., Guerrero-Coronado R.M., Mendoza-Barron J., Berber-Mendoza M.S. Adsorption of Chromium(VI) from an Aqueous Solution on a Surfactant-Modified Zeolite. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **330** (2008), 35–41.