Sorption of chromium (VI) ions by anionites based on epoxidized derivatives of aniline and benzylamine

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Abstract. This work is devoted to studying the basic regularities of sorption of chromium ions (VI) by new anionites from standardized test solutions of potassium dichromate. They have been synthesized by polycondensation of epoxidized aniline derivatives and benzylamine with polyamines (polyethylene polyamine and polyethyleneimine). In order to determine optimal parameters for sorption of chromium (VI) ions, dependence of anionites exchange capacity on the pH value of $K_2Cr_2O_7$ solution, concentration of metal ions in the solution and the duration of ion exchanger contact with the solution has been studied. It has been found that in a more acidic medium at pH equal to 2.0 (sorption capacity is 499.2 mg Cr/g), anionites based on aniline absorb dichromate ions better than the anionites obtained from benzylamine, which exhibit their maximum sorption capacity at pH equal to 3.4 (468.0 mg Cr/g). Anionites feature high kinetic properties; the equilibrium state is reached after 1 to 5 hours.
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Introduction

Chromium is one of major heavy metal pollutants, usually present in aqueous environment due to effluents discharged from various industries like mining, metallurgy, electroplating, leather tanning, textile dyeing, paint and pigment production, preservation of wood, etc. Under common environmental conditions of pH and Eh, chromium appears in two stable oxidation states, Cr (III) and Cr (VI), which have different physicochemical characteristics and biological reactivity. Generally, Cr (VI) compounds are more soluble, mobile and biologically available in the environment compared with Cr (III) compounds. While Cr (III) at low concentrations is an essential nutrient for human, plant and animal metabolism, Cr (VI) is harmful in biological systems. Hexavalent chromium (Cr(VI)) is a strong oxidizing agent and can easily cross the cell membranes causing deleterious health problems such as dermatitis, ulcers, kidney and liver damage, respiratory problems, lung cancer, etc. [1,2]. Because of its highly toxicity and carcinogenic properties to living organisms, Cr (VI) has been considered to be an a-priory pollutant. The permissible limit for Cr (VI) in drinking water is 0.05 mg/L [3].

Therefore, removing large amounts of Cr (VI) from industrial effluents before their discharge into aquatic ecosystems is of considerable concern. The methods commonly used for chromium (VI) removal are reduction and precipitation as Cr (III) hydroxide, ion exchange, adsorption, membrane filtration and electrochemical treatment; choice of suitable method depends on the initial Cr (VI) concentration, environmental impact and operational cost of the process [4,5]. Therefore, it is important to create ion-exchange materials with high sorption and kinetic properties with respect to hexavalent chromium ions.

Out of aniline (A), benzylamine (AB) and epichlorohydrin (ECH) we have synthesized epoxyamines, by condensation of which with polyethyleneimine (PEI) and polyethylene polyamine (PEPA), we obtained new multifunctional anionites A-ECH-PEPA, A-ECH-PEI and AB-ECH-PEI [6].

The purpose of the work is studying sorption of chromium (VI) by anionites based on epichlorohydrin and various amines from standardized test solutions of potassium dichromate.

Main part

Experimental part

Sorption of $Cr_2O_7^{2-}$ ions—by A-ECG-PEPA, A-ECG-PEI and BA-ECG-PEI anionites in the OH form (grain size 0.5-1 mm) was studied in static conditions at sorbent to solution ratio equal to 1:400, room temperature 20±2 °C, by varying concentration of chromium in $K_2Cr_2O_7$ solution between 0.205 and 2.184 g/l and changing their acidity between pH 2.0 and 5.0 adding 0.1N of H_2SO_4 or NaOH solution. Duration of sorbent contact with the solutions was between 1 hour and 7 days. For preparation of standardized test solutions, chemically pure salt $K_2Cr_2O_7$ was used.

Sorption capacity (SC) was calculated from the difference between initial and equilibrium concentrations of the solutions, which were determined using the classical polarography method on the background of 0.1 n of KOH on $Cr_2O_7^{2-}$ (E1/2 = −1.17 V) reduction wave. Polarograms were taken using a universal polarograph PU-1 in a temperature-controlled cell at 25±0.50°C using a mercury dropping electrode. Oxygen was removed from the analyzed solutions by blowing with argon for 5 minutes. A saturated calomel electrode was used as a reference electrode.

Results and discussion

Fig. 1 shows the results of studying influence of concentration and pH of potassium dichromate solutions, as well as duration of their contact with the A-ECG-PEPA, A-ECG-PEI and BA-ECG-PEI anionites, on sorption properties of ion exchangers.

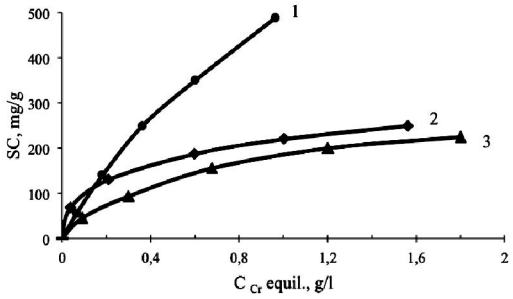

Fig. 1. Sorption isotherms of $Cr_2O_7^{2-}$ ions by anionites A-ECG-PEI (1), A-ECG-PEPA (2) and BA-ECG-PEI (3)

Duration of contact 7 days. Isotherms of sorption of $Cr_2O_7^{2-}$ ions by new anionites (Fig. 1) indicate that their selectivity for ions of chromium (VI) is reduced in the sequence:

BA-ECG-PEI > A-ECG-PEPA > A-ECG-PEI.

The highest SC values in extracting dichromate ions from $K_2Cr_2O_7$ solutions containing 2.2 g/l of chromium (pH 4.5), are equal to 488.8; 249.6 and 225.2 mg/g, respectively. However, at lower concentrations with chromium content equal to 0.2 g/l, the highest degree of $Cr_2O_7^{2-}$ ions extraction (82.6%) is observed for the A-ECH-PEPA anionite. For A-ECG-PEI and BA-ECG-PEI ion exchangers in the same conditions, it is 55.6 and 68.3% respectively. It should be noted that increasing concentration of chromium (VI) ions in $K_2Cr_2O_7$ solutions has the least impact on their extraction by the BA-ECG-PEI anionite. So, increasing chromium content from 0.2 to 2.2 g/l decreases the degree of $Cr_2O_7^{2-}$ ions extraction from 68.3 to 56.0 %. For other anionites in this case, a more significant decrease in the degree of chromium (VI) ions extraction occurs: for A-ECG-PEI—from 55.6 to 32.2%; for A-ECG-PEPA – from 82.6 to 28.6 %.

One of the determining factors that affect sorption of metal ions for a number of sorbents is the acid-base characteristic of the solution [7]. It is known that depending on the pH value, hexavalent chromium exists in the form of various ions. So, at pH<7, solution of chromium (VI) salts contain ions of $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}, at pH > 7 – ions of $HCrO_4^-$ and CrO_4^{2-}. In 0.5 – 2.0 n solutions of H_2SO_4, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ anions are formed. If sawdust was used for purifying water from chromium ions (VI) it was found [8] that at pH < 2, redox processes developed with Cr^{6+} transition to Cr^{3+}. In the range 3 ≤ pH <7, the process of chromium (VI) ions sorption occurs, and at pH ≥7, these ions are practically not adsorbed.

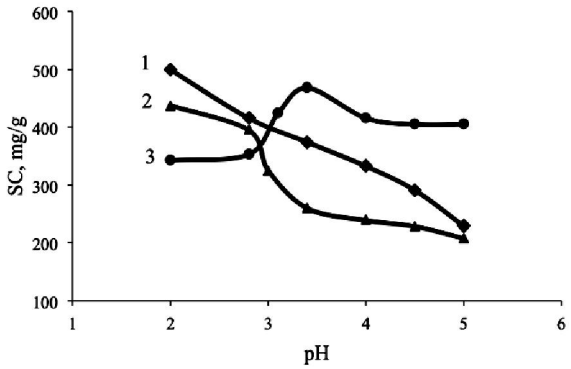

Fig. 2. Impact of acidity of $K_2Cr_2O_7$ (C_{Cr} = 2.1 g/l) solutions on sorption of chromium (VI) ions by anionites A-ECG-PEI (1), A-ECG-PEPA (2) and BA-ECG-PEI (3). Time of contact is 7 days

Fig. 2 shows dependence of dichromate ions sorption by anionites on the acidity of $K_2Cr_2O_7$ solutions; it can be seen that the optimum pH value for their extraction by A-ECG-PEPA and A-ECG-PEI ionites is 2.0, and by BA-ECG-PEI is 3.4. In these conditions, the SC of these anionites is equal to 499.2; 436.8 and 468.0 mg Cr/g, respectively.

Presumably, sorption of dichromate ions by synthesized anionites in the OH-form occurs similar to industrial anionite EDE-10P, depending on the pH value in schemes [9]:

$$2ROH + K_2Cr_2O_7 = R_2Cr_2O_7 + 2KOH$$
$$4ROH + K_2Cr_2O_7 + H_2O = R_2CrO_4 + 2KOH$$

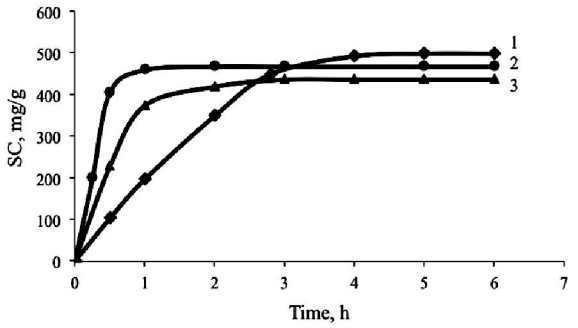

Fig. 3. Kinetic curves of sorption of $Cr_2O_7^{2-}$ ions by A-ECG-PEI (1), A-ECG-PEPA (2) and BA-ECG-PEI (3) anionites from $K_2Cr_2O_7$

From kinetic curves of dichromate ions sorption by anionites (Fig. 3), it follows that the equilibrium state between the $K_2Cr_2O_7$ (C_{Cr} = 2.1 g/l) solution and BA-ECG-PEI, A-ECG-PEI and A-ECG-PEPA anionites is reached within 1, 3 and 5 hours, respectively.

It is known [7] that the best results in chromium (VI) ions sorption in industrial macro-porous anionite AM-2b, which contains benzyldimethylamine and dibenzildimethylammonium functional groups, were obtained by acid treatment of the sorbent and pH of 4. With concentration of the initial solution of 4000 mg of CrO_3/dm3 its Static Exchange Capacity (SEC) is 350 mg CrO_3/g (182 mg Cr/g), and with concentration of initial solution of 2000 mg of CrO_3/dm3, it does not exceed 200 mg of CrO_3/g (104 mg Cr/g). The exchange capacity of AMP industrial gel anionite in case of sorption of Cr (VI) ions from a solution containing 2.56 g/dm3 of chromium (pH 0-2) and the anionite to solution rate of 1:100 is equal to 240 mg/g [10].

Conclusions

Efficiency of chromium (VI) ions extraction from standardized test solutions of potassium dichromate by new anionites based on epoxidized derivatives of aniline and benzylamine has been shown. It has been established that due to their sorption properties, they are 2-4 times superior to industrial anion exchangers of gel and macro-porous structure.

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References

1. Kotas J., Stasicka. Chromium occurrence in the environment and methods of its speciation. Environmental Pollution. 2000. - Vol. 107, № 3. - pp. 263 -283.
2. Mohan, D., C.U. Pittman Jr. and J. Hazard. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. Journal of Hazardous Material B137: 762-811, 2006.
3. World Health Organization, Guidelines for drinking water quality, 3rd edn, 2004. Geneva, Switzerland: WHO, pp: 124.
4. C. Balan, I. Volf, D. Bilba. Chromium (VI) removal from aqueous solutions by purolite base anion-exchange resins with gel structure. Chemical Industry & Chemical Engineering Quarterly 19 (4) 615−628 (2013), pp. 615-628.
5. Owlad, M., M.K. Aroua, W.A.W. Daud and S. Baroutian, Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review (2009). Water Air Soil Pollution, 200: 59-77.
6. Melnikov, Ye.A., T.K. Chalov, E.E. Ergozhin, K.Kh. Khakimbolatova and A.I. Nikitina, 2011. New polyfunctional anionites based on epoxyamines. In the Proceedings of the 2011 International Youth Research-to-Practice Conference: Alfred Nobel and Achievements of World Science and Civilization for the Last 110 Years, Kazan, pp: 68-69.
7. Voropanova, L.A. and E.Y. Getoeva, 2001. Regularities of chromium (VI) sorption from aqueous solutions based on AM-2b anionite. Applied Chemistry Journal, Vol. 74, 1: 25-28.
8. Zubareva, G.I., M.N. Filipieva and M.I. Degtev, 2005. Methods of wastewaters purification from chromium (VI) compounds. Ecology and Industry of Russia, 2: 30-33.
9. Alekseeva, S.L., S.N. Bolotin and T.G. Tsyupko, 2007. Studying of chromium (VI) ion sorption by exchange materials and sorbents. Applied Chemistry Journal, Vol. 80, 3: 378-380.
10. Voropanova, L.A., S.N. Alekseeva, E.A. Pavlyutina and E.E. Timanova, 2006. Patent of the RF #2288290: Sorption of chromium (VI) from aqueous solutions by the AMP anionite. Published on 27.11.2006.