PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2015, № 1, p. 29–32

Chemistry

ON SORPTION OF POTASSIUM IONS BY MEANS OF SILICA–MANGANESE DIOXIDE SYSTEM

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Sorption properties of sorbents on silica–manganese(II) oxide binary systems base have been evaluated by means of conductometry method. The influence of different factors (particularly the influence of pH values during the precipitation of manganese oxide and silica gel) on sorption properties of such systems has been discussed. The role of thermal treatment on sorption properties has been studied as well. It has been revealed that definite most optimal values for thermal treatment temperature exist, which lead to the sorbents characterized by higher adsorption capacity.

Keywords**:** sorption of potassium ions, manganese dioxide, silica gel.

Introduction. Sorption of alkaline metal, alkaline-earth metal, actinoids and other metal ions has been applied firstly for analytical purposes and for purification of nuclear wastewater systems [1].

The main investigations dedicated to the sorption of the metal ions by means of manganese dioxide were published within the 70s of the previous century [2]. Later similar studies were carried out using δ-manganese dioxide as a sorbent [3, 4]. It had been shown that x $SiO_2 - y$ MnO_2 mixed oxide sorbents can efficiently adsorb above mentioned cations at pH 4.0 and they possess especially higher sorption capacity towards strontium ions. It was also shown that the sorption mechanism on manganese dioxide has ion-exchange character.

The use of manganese dioxide containing sorbents is urgent and studies are carried out to apply such systems for sorption of radionuclides. Particularly MnO_2–TiO_2 composites demonstrate higher affinity towards strontium and uranium from wastes at 7.0 value [5]. It is possible to obtain α-MnO_2 possessing selective sorption properties towards potassium ions by means of thermal treatment of manganese(II) carbonate and potassium formiate and/or manganese(II) carbonate and potassium butoxide mixtures. The obtained sorbents may be used as available sorbent for industrial separation of potassium ions [6]. Hydrated manganese dioxide may be usually obtained by means of interaction between potassium permanganate with hydrogen peroxide.

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The reaction is carried out in the presence of silica containing agents, for example sodium silicate (liquid glass). Hydrated manganese dioxide obtained in such procedure must be rinsed and then dried [3].

Experimental Part. The sorbents used in the present work have been obtained according to the scheme described in [3]. Nevertheless, the scheme has been appropriately modified by us.

The technique used by us was as follows. To the 200 *mL* volume of sodium liquid glass (390 *g*/*L* silica content) 1200 *mL* solution of containing 35 *g* sodium permanganate and then 350 *mL* of hydrogen peroxide (HP) was added. Then the system obtained was divided to six parts:

1) 160 *mL* of the initial system + 15 *mL* HP;

2) 160 *mL* of the initial system+4 *mL* phosphoric acid + 22 *mL* HP;

3) 160 *mL* of the initial system + 6 *mL* phosphoric acid + 22 *mL* HP;

4) 160 *mL* of the initial system + 9 *mL* phosphoric acid + 22 *mL* HP;

5) 160 *mL* of the initial system +12 *mL* phosphoric acid + 22 *mL* HP;

6) 160 *mL* of the initial system +15 *mL* phosphoric acid + 22 *mL* HP.

The ageing of the gel obtained was carried out at room temperature during 40 *h*. Gels have been separated and rinsed by distilled water (1 *L* for each sample) and baked at 600°*C* during half an hour. Then dry gels have been treated by acidic distilled water (5–6 mass. % hydrochloric acid), dried at 150°*C* and finally baked at 600°*C* temperature during half an hour.

The sorbents obtained by means of the described technique have been mulled and divided to fractions by sieves. The sorption processes were realized in dynamic regime in 500 *mm* × 10 *mm* columns. Potassium hydroxide solution (2.0 *g*/*L* of solute) has been prepared as an investigation object.

The sorption level has been evaluated by means of conductometry method using Hanna Instruments TDS1 TDS Tester (0 to 999 ppm working range).

Results and Discussion. The potassium ions sorption curves on the sorbents obtained at different pH values are presented below at the Fig 1. The numerals of curves correspond to the numerals 1–5 above.

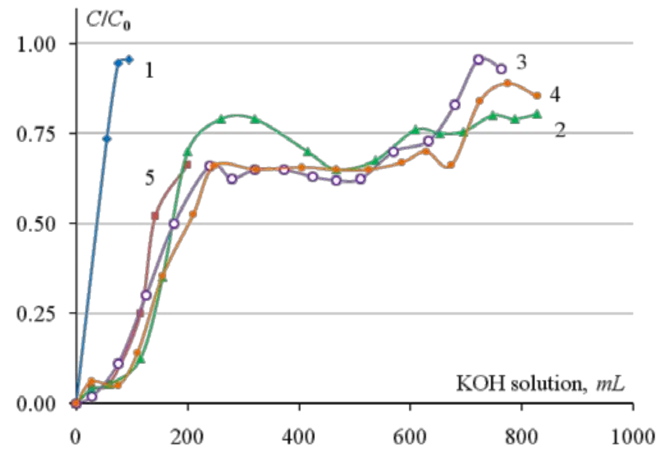

Fig. 1. The influence of the medium pH values on the sorption properties of SiO_2–MnO_2 sorbents. C/C_0 is the sorption level.

According to the well-known technique, gelation of system is not carried out. Only the precipitate is used obtained from liquid glass and manganese dioxide after adding hydrogen peroxide. However such procedure does not allow regulation of porous characteristics of obtained sorbents.

Besides, the sorption ability of such sorbents, as a rule, is essentially lower compared with sorbents obtained at lower pH values. Apparently, the structure formation and manganese oxide fixation on the silica surface may not occur at higher pH values. It is well-known that silica-water system at lower pH values is of silicate nature and the solubility is higher. So, it is very difficult to control porous structure formation in such labile state. And issuing from this consideration we carry out gelation by means of phosphoric acid. The gelation process secures fixation of manganese dioxide on the silica gel's structure. In addition, the use of silica containing agent (sodium liquid glass in this case) allows varying of the porous structure characteristics for the sorbents obtained.

Sample 1 shows worst sorption level (Fig. 1). This fact may be caused by its obtaining pre-history. No gelation was occurred in this case and this is the reason of incomplete manganese dioxide bonding on the silica carrier.

Samples 2–5 possess practically similar sorption ability towards potassium ions, and one can state that pH influence in alkaline medium is insignificant.

Presumably the most important factor during the sorption is manganese dioxide content in the sorbent. It follows from this observation that substantially wide range of pH values exists, within which one can carry the gelation in the liquid glass–potassium permanganate system.

Besides, it is also well-known that porous characteristic of silica systems obtained from the liquid glasses strongly depends on the solution acidity. And one can vary porous characteristics of the sorbents obtained in wide range controlling this factor.

Sample 6. Colorless gel is forming when decreasing pH of the phosphoric acid solution.

It means that instead of manganese dioxide other manganese compounds are forming, which are non-selective for potassium ions sorption.

The Influence of Temperature of Sorbent Thermal Treatment on its Sorption Properties. The ageing and subsequent treatment of gel systems is of great importance. According to the known technique powders were undergone only drying procedure at 80–120°*C* temperature.

Such low-temperature treatment cannot stabilize the structural parameters of the sorbents obtained, and the sorbents will possess different physical-chemical characteristics (porous structure and adsorption capacity, chromatographic separation ability).

Proper thermal treatment of porous silica systems is important procedure when obtaining sorbents with reliable and reproducible properties. Aiming to reveal the influence of thermal treatment conditions on the sorption properties of the obtained sorbents the samples have been divided to four groups and then undergone thermal treatment under 500, 600, 700 and 800°*C* temperatures during half an hour.

It follows from Fig. 2, that sharp decrease of sorption level is observed when increasing thermal treatment temperature. It is known that in the presence of less than 1 mass. % alkaline cations silica systems pass to crystalline modification. Apparently this may be the result of such crystallization of silica, pores sintering and, as a result, sharp decrease of specific porous surface.

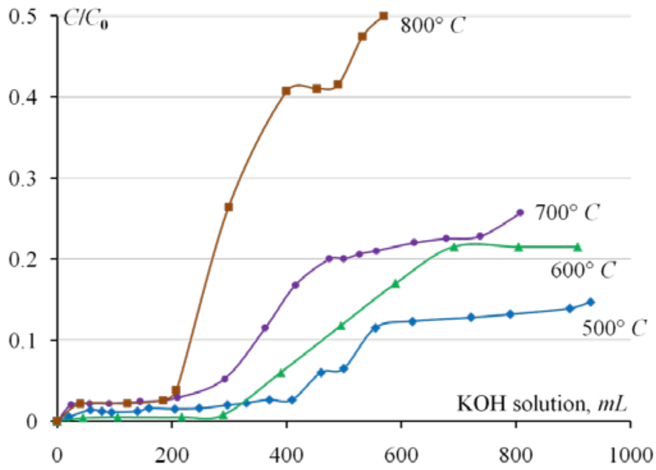

Fig. 2. The influence of the sorbent thermal treatment on their sorption properties. C/C_0 is the sorption level.

Conclusion.

1. The gelation in the silica–manganese dioxide system and control of pH values during precipitation of the manganese oxide on the silica surface become determining factor for potassium ions sorption.

2. The obtained sorbents thermal treatment temperature influences on their sorption properties (sorption level) as well.

This work was supported by State Committee of Science of MES RA in the frame of the research project № "13-1D267. New sorbents for removing radionuclides and heavy metals as well as extracting some valuable elements from waters".

Received 03.03.2015

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