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Comparison of sorption properties of adsorbents with expandable and thermally expanded graphite and bentonite with respect to sodium and cadmium (II) ions

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The presented research work is devoted to the comparison of the ability of expandable graphite, graphite expanded at 300°C temperature and bentonite clay of Azerbaijani origin to adsorb Na^+ ions from NaCl solutions of a known concentration. From the conducted studies, it was found that expanded graphite at 300°C temperature can better adsorb Na^+ ions. In addition, the sorption properties of the same adsorbents with respect to Cd^{2+} ions were confirmed and it was established that bentonite and expandable graphite adsorb Cd^{2+} ions better.

Keywords: expandable graphite, bentonite, clay, sorption, cadmium ions.

Порівняння сорбційних властивостей адсорбентів з розширюваного і термічно розширеного графіту і бентоніту щодо іонів натрію і кадмію (II). *Солмаз Алієва*

Представлена робота присвячена порівнянню здатності графіту, що розширюється, графіту, розширеного при температурі 300°C, та бентонітової глини азербайджанського походження адсорбувати іони Na^+ з розчинів NaCl відомої концентрації. В результаті проведених досліджень встановлено, що графіт, розширений при температурі 300°C, краще адсорбує іони солей. Крім того, підтверджені сорбційні властивості цих сорбентів по відношенню до іонів Cd^{2+} і встановлено, що бентоніт і графіт, що розширюється, краще адсорбують іони Cd^{2+}.

1. Introduction

One of the most important human needs is fresh water. Conservation of freshwater resources is required to meet human water needs. In practice, physical, chemical, physico-chemical, and biological methods (membrane filtration, coagulation, flocculation, adsorption, ion-exchange, oxidation, ozonation, and biological decomposition) are used for the treatment of wastewater from pollutants. The choice of each method is determined by factors such as the type of pollutants, the composition of the wastewater, the operating costs, and the recovery of the waste. Since deep wastewater treatment is not possible using one method, several methods are usually implemented simultaneously. Adsorption treatment is the most acceptable group of methods for deep purification of wastewater from dissolved inorganic and organic impurities in pulp and paper, chemical, petrochemical, textile, and other industries.

The presented article aims to compare the adsorption of Na^+ and Cd^{2+} ions from aqueous solutions by expandable graphite (EG), expanded graphite at 300°C temperature (EG_{300}), and bentonite.

2. Experimental

The graphite used is of natural origin, while bentonite is obtained from the Dash Salahli region of Azerbaijan. H_2SO_4, HNO_3, NaCl, $CdCl2{\cdot}2.5H_2O$, Xylenol Orange (XO, $C_{31}H_{28}N_2Na_4O_{13}S$), KNO_3, urotropin were obtained from Sigma Aldrich and used without further purification.

The electrical conductivity of the solutions was measured by a BOYN 900 Multiparameter Water Quality Meter. The initial and equilibrium concentrations of the Cd^{2+} ions in Cd-XO complex compound solutions were determined in the UV-visible region on a spectrophotometer (Thermo Scientific(tm) GENESYS 30).

Synthesis of EG and EG_{300}

EG was synthesized according to a known methodology [1]. For the synthesis of expandable graphite, graphite was intercalated in a sulfuric acid/oxidizing agent (HNO_3) mixture. The synthesis of the EG_{300} compound was obtained by rapid heating of EG at 300°C.

Preparation of Na^+ and Cd^{2+}-containing solutions

In the presented research, the ability of EG, EG_{300}, and bentonite to adsorb Na^+ ions from NaCl aqueous solutions was investigated. For this, at the first stage, a "stock solution" of NaCl is prepared with a 58440 mg/l concentration in distilled water. Then, to obtain the calibration curve, samples are taken from the "stock solution" and diluted to a concentration of 50; 100; 200; 250; 300; 400; 450; 500; 600 mg/l to prepare "working solutions". By measuring the electrical conductivity of these solutions, a calibration curve for the dependence of electrical conductivity on concentration is constructed (Fig. 1).

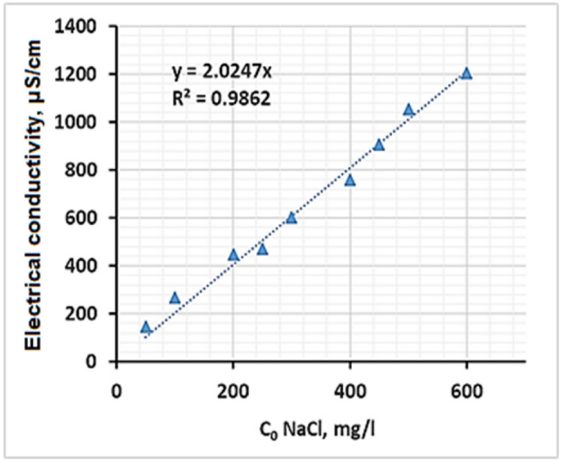

Fig. 1. Calibration curve for electrical conductivity versus concentration of NaCl solution.

As can be seen from the figure, the dependence of the lectrical conductivity (σ, µS/cm) on the concentration of the NaCl solution is linear and corresponds to the linear equation $\sigma = 2.0247C_0$?. This equation will be used to calculate the concentration of aCl solutions in the study of sorption processes.

After studying the Na^+ sorption, the sorption capacity of heavy metal ions by the same adsorbents was additionally investigated. A "stock solution" of $CdCl_2{\cdot}2.5H_2O$ in distilled water with a concentration of 1124.11 mg/l was prepared as a model of wastewater containing heavy metal ions. Based on this solution, "working solutions" were prepared by dilution with concentrations of 0.45 to 2.02 mg/l. Identification of Cd^{2+} ions in these solutions was carried

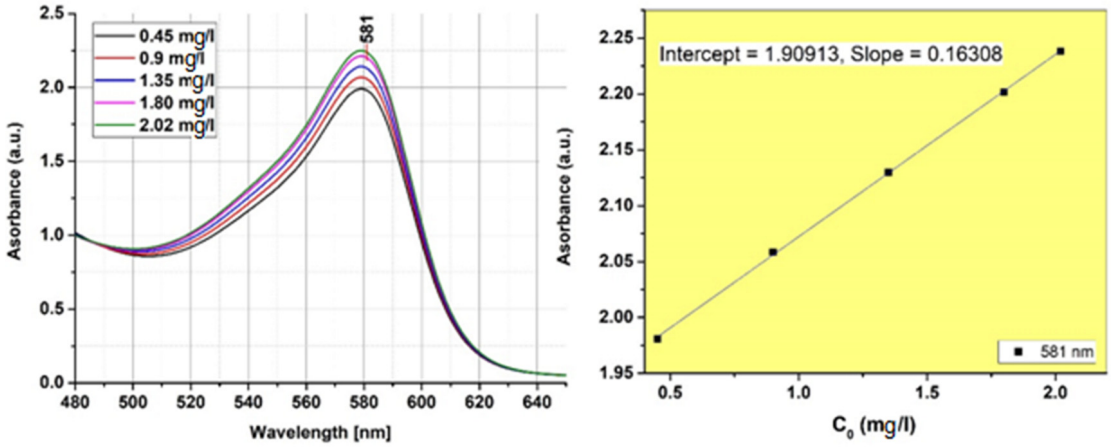

Fig. 2. Absorption spectra of solutions of Cd-XO complex with concentrations of 0.45 to 2.02 mg/l and a calibration curve at a wavelength of 581 nm.

Table 1. Sorption results for EG, EG_{300}, and bentonite clay

NaCl solution before sorption		NaCl solution after sorption	
Concentration, C_0, mg/l	Electrical conductivity, σ, μS/cm	Concentration, C_{eq}, mg/l	Electrical conductivity, σ, μS/cm
EG			
500	1055	454.4	920
EG_{300}			
500	1055	375.4	760
Bentonite clay			
500	1055	420.8	852

out according to the well-known method [2], based on the spectroscopic analysis of a red solution of a complex compound of XO, urotropine, and KNO_3. Then, a calibration curve is constructed based on the absorption coefficients of these solutions at 581 nm wavelength (Fig. 2).

Studying adsorption of Na^+ and Cd^{2+} ions from aqueous solutions

At the second stage, the adsorption property of 0.5 g of EG, EG_{300}, and bentonite with respect to Na^+ ion was studied. For this, 0.5 g of EG, EG_{300}, and bentonite clay were placed in chemical beakers, and a NaCl solution with a concentration of 500 mg/l was added to them. The chemical beakers with the adsorbent/NaCl mixture were kept under static conditions for 24 hours. After 24 hours, the electrical conductivity of these solutions was determined. Equilibrium concentration (C_{eq}) was calculated according to the calibration curve according to electrical conductivity for different samples.

At the next stage, the sorption capacity of EG, EG_{300}, and bentonite clay against Cd^{2+} ions was determined. For this, a $CdCl_2 \cdot 2.5H_2O$ solution was used at a concentration of 2.02 mg/l with continuous stirring with sorption substances for 30 minutes.

3. Results and discussion

The results of the studies conducted for the sorption of Na^+ ions by EG, EG_{300}, and bentonite clay are given in Table 1.

The electrical conductivity of distilled water used during this research was 2.60 μS/cm. According to the results given in Table 1, the electrical conductivity of the solution in which EG_{300} was used as an adsorbent significuntly decreased for 24 hours.

Fig. 3 shows the absorbance spectrum of the Cd-XO complex solution with a concentration of 2.02 mg/l before adsorption and after contact with EG, EG_{300}, and bentonite for 30 min.

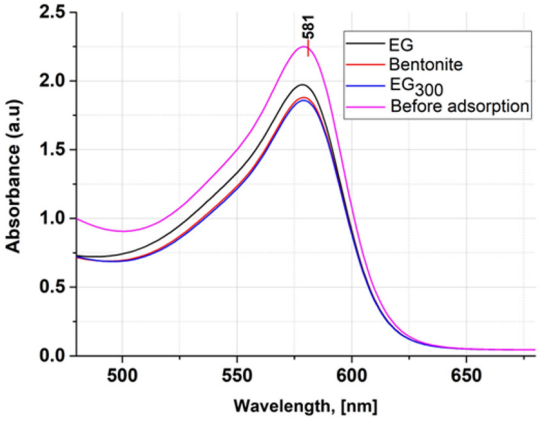

Fig. 3. The absorption spectrum of the Cd-XO complex solution with a concentration of 2.02 mg/l before adsorption and after contact with EG, EG_{300}, and bentonite for 30 min.

As can be seen from Fig. 3, the observed absorption coefficient at a wavelength of 581 nm decreased after interaction with all the adsorbents. These results show that all three adsorbents are capable of adsorbing Cd^{2+} ions. The following sequence of the absorption coefficient was established: before sorption (2.2383) > EG (1.9663) > Bentonite (1.8698) > EG_{300} (1.8485).

The results of both studies showed that EG_{300} exhibited higher adsorption properties for Na^+ and Cd^{2+} ions than other studied adsorbents. It is known from the literature that cation-π interaction forces can arise between aromatic rings and cations in the graphene sheets of graphite [3]. The reason why EG_{300} shows a better adsorption property than EG is the formation of more active centers involved in the formation of cation-π bond with the exfoliation of graphene layers during thermal expansion.

4. Conclusion

In the presented research, the adsorption properties of EG, EG_{300}, and bentonite with respect to Cd^{2+} and Na^{+} ions were compared. Based on the obtained results, it was determined that EG_{300} has a better adsorption property compared to other adsorbents. This is explained by the existence of cation-π interactions formed between graphene sheets and cations.

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