Adsorption properties of nanostructured form of aluminium hydroxide $\gamma$-modification

E G Filatova, V I Dudarev, L A Begunova

Department of chemistry and food technology, Irkutsk National Research Technical University, Lermontova st., 83, Irkutsk 664074, Russia

E-mail: efila@list.ru

Abstract. Adsorption properties of aluminium hydroxide $\gamma$-modification towards toxic copper(II) and zinc(II) ions were studied. In a neutral medium at $\text{pH}=7.6$, the ion adsorption capacity was 264 mg/g for copper(II) and 338 mg/g for zinc(II). The study of the temperature effect on the absorbability of toxic ions established that the adsorption capacity is characterized by an increase followed by a decrease as the equilibrium value is reached. The absorbability increase in the initial moment is caused by an increase in the formation rate of hydroxo aqua complexes of copper(II) and zinc(II) ions. The differential heat of adsorption was determined. It demonstrated a decrease from 27 to 20 kJ/mol during the process, which is caused by the fact that, as the most active centres of nanostructured form of aluminium hydroxide $\gamma$-modification are saturated, heavy metal ions are adsorbed by decreasingly active regions of its surface.

1. Introduction

It is known that active alumina and hydroxide $\text{Al(OH)}_3$, in addition to coagulating ability, also have adsorption properties [1-4]. In the case of the practical use of reagent adsorbents-coagulants, for example, aluminum sulfate [5-9], in addition to coagulating cations, the concentration of anions in aqueous solutions increases significantly, leading to secondary pollution of water [10-13]. The practical use of electrically generated coagulant adsorbents, i.e. aluminum hydroxide obtained by the electrochemical method significantly increases the efficiency of removing contaminants [14], and also avoids secondary pollution of water.

The aim of this work is to study the adsorption of copper(II) and zinc(II) ions from aqueous solutions by nanostructured form of aluminum hydroxide $\gamma$-modification.

2. Formatting the title, authors and affiliations

Nanostructured form of aluminium hydroxide $\gamma$-modification was synthesized by the electrochemical method, the electrolysis of aqueous solutions performed using aluminium electrodes under the appropriate conditions [15]. The studied hydroxide was synthesized within the first five minutes of electrolysis.

The phase composition of aluminium hydroxide was studied by X-ray analysis using a D8-ADVANCE automated diffractometer. The mean quadratic error of the X-ray analysis methods is about 2–5 %; if the conditions are favourable it decreases to $\pm 0.5$ %.

Using a scanning electron microscope (electron microscopy) the sizes of nanostructured form of aluminium hydroxide were determined. A JIB-4500 scanning electron microscope (multibeam system)
is equipped with a LaB6 electron gun and an ion gun; it performs the functions of a scanning electron microscope and a focused ion beam. For the determination of the particle size of coagulated contaminants, the turbidimetric analysis method was also used.

The adsorption properties of aluminum hydroxide towards copper(II) and zinc(II) ions were studied using model solutions prepared using chemically pure reagents of CuSO₄·5H₂O and ZnSO₄·7H₂O and distilled water. The choice of the initial concentration of model solutions was justified by the actual composition of industrial wastewater. The metal ion contents in solutions were determined using the standard techniques [16,17].

The adsorption ability was studied by the static method. In this work, the method of constant weights (0.05 g) and variable concentrations (1 to 200 mg/dm³) was used. The studied solutions were prepared in the volume of 100 cm³. The weight ratio of the liquid to solid phase was 1:100. The adsorption capacity (A, mg/g) was calculated using the following formula:

\[ A = \frac{(C_0 - C_{eq})V}{m} \]  

where \( C_0 \) and \( C_{eq} \) the initial and equilibrium metal concentrations in a solution, mg/dm³; \( V \) the solution volume, dm³ and \( m \), the sorbent weight, g. Please follow these instructions as carefully as possible so all articles within a conference have the same style to the title page. This paragraph follows a section title so it should not be indented.

3. Formatting the title, authors and affiliations

Electrically produced aluminium hydroxide in a neutral medium at pH = 7.60 was studied using X-ray analysis. It was established that the resulting spectrum is identical to that of aluminium hydroxide \( \gamma \)-modification. It is known that aluminium hydroxide \( \gamma \)-modification is characterized by the amorphous state and a mesh structure and, consequently, by a good adsorption ability [18]. The electrochemical process performed at pH = 7.60 provides aluminium hydroxide flakes saturated with hydrogen, which are floated well.

An important factor that affects the absorbability of heavy metal ions is the wastewater temperature. In Figures 1 and 2, the adsorption isotherms of copper(II) and zinc(II) ions for nanostructured form of aluminum hydroxide \( \gamma \)-modification at different temperatures (298, 318, and 338 K) are presented.

As can be seen from the data in Figure 1, under the temperature increase, at first, the absorbability of copper(II) ions increases and then, as the equilibrium value is reached, it decreases. At 298 K, the adsorption capacity is 264 mg/g.
The absorbability of zinc(II) ions, under the temperature increase, also increases in the initial moment of time and, as the equilibrium value is reached, decreases. The increase in the absorbability of heavy metal ions in the initial moment in caused by the increase in the formation rate of hydroxoaqua complexes of toxic ions $[\text{Cu(OH}_2)_2(\text{OH})_2]$ and $[\text{Zn(OH}_2)_2(\text{OH})_2]$. The adsorption capacity at the standard temperature is 338 mg/g.

The derivatives of the isotherms are the adsorption isosteres $\ln C_{eq} = f \left( \frac{1}{T} \right)$. The isosteres reflect the relation of the equilibrium concentrations and temperatures at the constant adsorption capacity (Figures 3 and 4).

The presented experimental data (Figures 3 and 4) were used for the calculation of the differential heats of adsorption using the Clausius–Clapeyron relation [19]:

$$\left( \frac{\partial \ln C_{eq}}{\partial \left( \frac{1}{T} \right)} \right)_A = \text{const} = -\frac{Q}{R} \quad (2)$$

where $Q$ is the isosteric heat of adsorption, kJ/mol and $R$ is the universal constant, J/mol·K. Based on the isostere slopes, the differential heats of adsorption were calculated for copper(II) and zinc(II).

The dependence of the differential heat of adsorption on the amount of adsorbed substance can be represented by the dependences shown in Figure 5.

The higher the adsorption capacity of the studied ions becomes, the lower the differential heat of adsorption is. The differential heat of adsorption decreases during the process because, as the most
active centres of nanostructured form of aluminium hydroxide γ-modification are saturated, heavy metal ions are adsorbed by less and less active regions of its surface. For the purpose of successful floating of a mass of coagulated contaminants formed as a result of purification, the particle sizes of aluminium hydroxide γ-modification with adsorbed hydroxo aqua complexes of heavy metals were determined. For model solutions containing Cu(II) and Zn(II) ions, according to the turbidimetric analysis data, the particle sizes of coagulated contaminants were 123 – 144 nm. According to the electron microscopy data, the largest particles of the precipitate are characterized by the size of about 15-20 µm. Based on the turbidimetric analysis and electron microscopy results, the fractional separation of particles was performed. It was proved that, for the successful extraction of a mass of coagulated contaminants from the water surface using the hydrogen bubbles formed on a cathode, wastewater from the electroplating industry with the low iron content should be used or the initial iron content in wastewater should be decreased to 1.0 g/m3 before treatment [20].

4. Conclusion

The adsorption properties of nanostructured form of aluminium hydroxide γ-modification were studied. It was established that, at pH = 7.6 and T = 298 K, the adsorption capacity is 264 mg/g for copper(II) ions and 338 mg/g for zinc(II) ions.

The study of the temperature effect on the absorbability of copper(II) and zinc(II) ions established that, in the initial moment, the adsorption capacity increases and then, as the equilibrium value is reached, decreases. The increase in the absorbability of heavy metal ions in the initial moment in caused by the increase in the formation rate of hydroxo aqua complexes of toxic ions [Cu(OH2)2(OH)2] and [Zn(OH2)2(OH)2].

The differential heat of adsorption was determined. It demonstrated a decrease from 27 to 20 kJ/mol during the process, which is caused by the fact that, as the most active centres of nanostructured form of aluminium hydroxide γ-modification are saturated, copper(II) and zinc(II) ions are adsorbed by decreasingly active regions of its surface.

References

[1] Gupta A G A, Manohar C S and Kumar B S 2019 Optimization of cation-doped nano-hydroxyapatite in combination with amorphous aluminium hydroxide for defluoridation J. Water science and technology-water supply 19(6) 1686–1694
[2] Das D and Nandi B K 2019 Defluoridization of drinking water by electrocoagulation (EC): process optimization and kinetic study J. of dispersion science and technology 40(8) 1136–1146
[3] Zelentsov V I, Datsko T Ya, Politova E D et al. 2019 Preparation and properties of an aluminum hydroxide-modified diatomite sorbent for removal of fluorides from waters J. Surface engineering and applied electrochemistry 55(4) 455–462
[4] Wan B, Huang R, Diaz J M et al 2019 Polyphosphate adsorption and hydrolysis on aluminum oxides J. Environmental science and technology 53(16) 9542–9552
[5] Pinotti A, Zaritzky N 2001 Effect of aluminum sulfate and cationic polyelectrolytes on the destabilization of emulsified wastes J. Waste management 21(6) 535–542
[6] Zhao Y X., Gao B Y, Shon H K 2010 Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts Journal of hazardous materials 185(2-3) 1536–1542
[7] Guocheng Z, Huaili Z, Wenyuan C 2012 Preparation of a composite coagulant: Polymeric aluminum ferric sulfate (PAFS) for wastewater treatment J. Desalination 285 315–323
[8] Hussain S, Leeuwen J, Chow C et al 2013 Removal of organic contaminants from river and reservoir waters by three different aluminum-based metal salts: Coagulation adsorption and kinetics studies J. Chemical engineering 225(6) 394–405
[9] Tong S, Chun-hua S, Guo-li Z et al. 2011 Preparation and coagulation performance of polyferric-aluminum-silicate-sulfate from fly ash. *J. Desalination* **268**(1-3) 270–275

[10] Zhonglian Y, Baoyu G, Qinyan Y. 2010 Coagulation performance and residual aluminum speciation of Al$_2$(SO$_4$)$_3$ and polyaluminum chloride (PAC) in Yellow River water treatment. *J. Chemical engineering* **165**(1) 122–132

[11] Shahin G, Hamidi A, Bashir Mohammed J K. 2010 The use of poly-aluminum chloride and alum for the treatment of partially stabilized leachate: A comparative study. *J. Desalination* **257**(1-3) 110–116

[12] Tociu C, Diaucu E. 2015 Quality assessment of the aluminium sulphate coagulant recovered from metallurgical slag based on a correlation of the removed phosphorous from municipal wastewaters. *University politehnica of bucharest scientific bulletin series b-chemistry and materials science* **77**(2) 29–40

[13] Guocheng Z, Huaili Z, Zhi Z et al. 2011 Characterization and coagulation-flocculation behavior of polymeric aluminum ferric sulfate (PAFS). *J. Chemical engineering* **178** 50–59

[14] Mouedhen G, Feki M, Wery M D P et al. 2008 Behavior of aluminum electrodes in electrocoagulation process. *J. of hazardous materials* **150**(1) 124–135

[15] Filatova E G. 2016 Optimization of electrocoagulation technology of purifying wastewaters of ions of heavy metals. *J. of water chemistry and technology* **38**(3) 167–172

[16] Marczenko Z. 1976 *Spectrophotometric Determination of the Elements, Ellis Horwood Series in Analytical Chemistry* (New York: John Wiley and Sons) p 502

[17] Lur’e Yu Yu, Rybnikova A I. 1974 *Chemical Analysis of Industrial Waste Waters* (Moscow: Khimiya) p 336

[18] Gypser S, Hirsch F, Schleicher A M et al. 2018 Impact of crystalline and amorphous iron- and aluminum hydroxides on mechanisms of phosphate adsorption and desorption. *J. of environmental sciences* **70** 175–189

[19] Tsivadze A Yu, Rusanov A I, Fomkin A A et al. 2011 *Physical Chemistry of Adsorption Phenomena* (Moscow: Granitsa) p 456

[20] Filatova E G, Soboleva A A, Dudarev V I and Anziferov E A. 2014 Patent RU2519412 C1, MPK C02F1/463, C02F 101/20 No 2012158159/05