SORPTION PROPERTIES OF TiO$_2$ AND TiO$_2$/KAOLINITE COMPOSITE

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Abstract

Many researchers described sorption properties nanoparticles of titanium dioxide. Different ions, for example ion of Cr, Cu, Fe, Mn, Ni, and Zn, can be removed from waste water by mentioned nanoparticles. Nanoparticles handing is connected with health risk because there are little information about nanoparticle toxicity. It is suitable immobilized they on balk material. In this work a comparison of sorption properties of titanium dioxide nanoparticles with TiO$_2$/kaolinite composite were done. TiO$_2$/kaolinite composite could have better sorption capacity than kaolinite as well. Nanoparticles of TiO$_2$ and composite of TiO$_2$/kaolinite were prepared by thermal hydrolysis using the titanyl sulphate as a titanium precursor. Prepared materials were characterized by chemical and phase analysis. The sorption of Cd, Cu and Zn in model water solution was studied at constant temperature (at 25 °C). Experiments were carried out batch techniques. The concentration of adsorbate in solution after sorption was determined by AAS-FA. Surface of the materials after treatment was studied by electron microscopy. The measured results were described by adsorption isotherms. Calculated adsorption capacities were compared.

Keywords: sorption, kaolinite, cadmium, zinc

1. INTRODUCTION

The multifold increase in the use of heavy metals in recent years has led to an increase in the concentration of these metals in the environment. Toxicological effects of heavy metals are well understood and have been a global concern for environmentalists. Due to persistent in nature and their accumulation through food chain, it is necessary to remove toxic heavy metals from wastewater. Metals are non-biodegradable and have great environmental, public health and economic impacts.

Such metals are for example cadmium and zinc. Cadmium, which is very toxic, can cause serious damage to the kidneys and bones. The major sources of cadmium are industrial waters such as metal plating, cadmium-nickel batteries, phosphate fertiliser, mining, pigments, stabilisers and alloys. Zinc is widely used in many important industrial applications such as dry battery, electroplating industry, insecticides, foundry, metallurgy, pigments and explosive manufacturing. Zinc is often found in high concentrations in wastewater from many sources, including mine drainage, galvanizing plants, pharmaceuticals production, and pigments manufacturing.

Many worldwide research groups have been trying to find various methods to solve the environmental pollution. The aim is to prevent the pollution or to remove the industrial pollutants from the environment. One important technique for removing dispersed pollutants is adsorption. There are many materials that could be used as sorbent of toxic ions or compounds. The nanoparticles of metal oxide have good properties to use them as new sorbents.

Many different studies are engaged in the use of various sorbent for removal cadmium and zinc ions. Within the framework of these studies, different factors such as sample pH, sample flow rate, type, concentration and volume of sample were optimized.
For example batch and fixed-bed system studies are used for adsorption of cadmium and zinc ions on boron enrichment process waste in aqueous solutions. The results show that the Freundlich isotherm describes the adsorption cadmium and zinc ions. Batch and column tests demonstrate that boron enrichment process waste is a highly effective adsorbent for metal ion removal [1].

Nanoparticles of titanium dioxide are considered as very suitable and effective adsorbent for removal of toxic ions from aqueous solutions due to their high stability, low cost and safety toward both humans and the environment. However due to the potential toxicity of nanoparticles, it is preferable to use them in the form of a composite in which the nanoparticles are anchored to the inert material. Study of adsorption of toxic substances onto specially modified composite nanomaterials is a first necessary step before their industrial use.

The batch techniques were also used for the desorption of lead (II), copper (II) and zinc (II) from commercially prepared TiO$_2$ nanoparticles (anatase). The evaluation of isothermal, kinetic and thermodynamic properties was investigated in this study [2].

Magnetic nanoparticles are exceptional adsorbent materials due to their unique magnetic properties and good adsorption capacity.

The magnetic hydroxyapatite nanoparticles are used for the removal cadmium and zinc ions from aqueous solutions. In study was proposed synthesis magnetic hydroxyapatite nanoparticles and prepared nanoparticles was characterized by scanning electron microscopy (SEM), energy dispersive analysis system of X-ray (EDAX), X-ray powder diffraction (XRD) analysis, zeta potential, BET surface area measurements and magnetization curves [3].

Also new absorbent magnetic nanoadsorbent prepared from an agricultural waste-orange peel powder by co-precipitating it with Fe$_3$O$_4$ nanoparticles was successfully used for removal cadmium ion from aqueous solutions [17].

A new method combining magnetic separation and nanoparticle adsorption was investigated for the removal of cadmium ions from the drilling fluid and its efficiency was studied in this study. Magnetic iron oxide nanoparticles were successfully synthesized, characterized and evaluated by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Infrared spectroscopy (IR) [19].

Sorption on natural sorbents has important environmental implications for pollutant transport and bioavailability. For removal of cadmium and zinc can be used various natural or synthetized mineral sorbents.

Synthetic zeolite A was investigated for use to adsorptive removal of zinc and cadmium ions from aqueous solutions. The results indicated that synthetic zeolite A can be used as an efficient ion exchange material for the removal of zinc and cadmium ions from industrial and radioactive wastewaters [4]. Also other type of zeolite, for example zeolite 4A, zeolite 13X, clinoptilolite and bentonite were used for sorption of cadmium and zinc from aqueous solutions with positive results [5, 9, 12, 14, 21]. Also alkaline Ca-bentonite was used for removal zinc from aqueous solution using batch technique and compared with the adsorption onto raw bentonite [11].

Different natural zeolites and bentonite minerals, i.e. chabazite, clinoptilolite 1, clinoptilolite 2, phillipsite, analcime, bentonite, were used for adsorption and desorption of zinc. The capability for zinc adsorption using natural zeolite and bentonite was increased in the following order: chabazite > analcime > clinoptilolite 1 > bentonite > clinoptilolite 2 > phillipsite. The results indicate that natural zeolites, particularly chabazite and bentonite minerals, have a high potential for Zn sorption with a high capacity for slow release fertilizers [13].

Clay mineral, vermiculite, was applied as adsorbent for removal of cadmium, zinc, manganese, and chromium from aqueous solutions. Article describes investigation various parameters such as time of reaction, effect of pH and cation concentration with positive results [6].
The study [18] was conducted to study the influence of pH, temperature and aging on Cd desorption from other mineral sorbent, goethite.

In other study, which investigates an ability of removal cadmium ions from montmorillonite, is described in article [20]. In this study was synthesized Fe-montmorillonite by using Ca-montmorillonite directly under ultrasonic treatment with the aim to enhance the ability of removal of heavy metal ions from wastewater.

The current expensive methods for removing heavy metals from wastewater can be replaced by low-cost activated carbon derived from bagasse, an agricultural waste material. The studies of adsorption were carried out both in single- and multi-component systems [7].

The surfactant-modified carbon adsorbents were used for sorption of cadmium from aqueous solutions [22]. This study describes the sorption of Cd(II) from aqueous solution using indigenously prepared and surfactant-modified carbon adsorbents from husk and pods of M. oleifera. Adsorption was found to be strongly dependent on pH, adsorbate, adsorbent dosage and contact time.

Other experiment utilizes a low-grade phosphate as an absorbent for zinc and cadmium cations in a range of initial metal ions concentrations (10 - 50 ppm), agitation time (5 - 210 min), adsorbent concentration (1 - 7 g/l) and pH (2 - 6). The adsorption equilibrium of zinc ions are decreased with the increase in the initial cadmium ions concentration and that of cadmium ions are decreased as the initial zinc ions concentration increases [8].

The chemical adsorbent activated alumina and other adsorbents can be also used for the removal zinc (II) from aqueous solution. The adsorption of Zn(II) increased with increased concentration of the adsorbents and reached maximum uptake at 10 g/L and pH between 5 and 7 [10].

The study [15] presents that also bamboo charcoal is appropriate for the removal of Cd (II) ions in water treatment.

The adsorption of cadmium on phosphogypsum, a waste material from the manufacture of phosphoric acid by wet process, was investigated with the effect of initial pH. Also this material provides the positive results in the pH range of 9.5 and 11.5 [16].

2. MATERIALS AND METHODS

2.1. Materials

Kaolinite theoretical formula is Si₂Al₂O₅(OH)₄ and other formulas are Al₂O₃.2SiO₂.2H₂O and Al₂O₃.2SiO₂.2H₂O. Kaolinite sample SAK47 (LB MINERALS s.r.o.) dried for 3 hours at 105 °C was used for sorption experiments and for the photoactive composite preparation.

2.1.1. Kaolinite/TiO₂ composite

Thermal hydrolysis of dried kaolinite and TiOSO₄ suspension were used to prepare photoactive composite containing TiO₂. Prepared composite was dried at 105 °C (KATI16). The chemical composition of kaolinite and prepared composite is shown in Table 1. Preparation and characterization of the composite are described in details in [23].
Table 1 Chemical composition dried kaolinite (K) and composite kaolinite/TiO2 with 60 wt. % of TiO2 (KT).

<table>
<thead>
<tr>
<th></th>
<th>K (wt. %)</th>
<th>KT (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>35.8 ±0.1</td>
<td>11.9 ± 0.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>47.7 ± 1.0</td>
<td>18.5 ± 0.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.16 ± 0.1</td>
<td>0.38 ± 0.1</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.001 ± 0.1</td>
<td>0.941 ± 0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.12 ± 0.1</td>
<td>0.08 ± 0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.06 ± 0.1</td>
<td>0.07 ± 0.1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.097 ±0.1</td>
<td>0.46 ± 0.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.84 ± 0.1</td>
<td>51.0 ± 1.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.57± 0.1</td>
<td>0.214 ± 0.1</td>
</tr>
<tr>
<td>LOI</td>
<td>11.6 ± 0.1</td>
<td>16.0 ± 0.3</td>
</tr>
</tbody>
</table>

2.1.1. TiO₂ nanoparticles

TiO₂ nanoparticles were prepared by thermal hydrolysis of titanyl sulphate (TiOSO₄). The first step was heating the solution up to 100 °C. The second step included 90 minutes long thermal hydrolysis of solution at 100 °C performed by addition of the appropriate volume of warm water. After the thermal hydrolysis, the solution was cooled down. The prepared TiO₂ was washed several times with distilled water. The obtained sample was dried at 105 °C. The prepared particle size was smaller than 100 µm.

2.1.2. Adsorption of Cd and Zn on sorbents

The experiments were carried out with the 0.2 g of each sorbent that were suspended in 50 ml solution of different Cd and Zn concentrations (1 – 1000 mg/l). The suspensions were mixed for 1 hour at the laboratory temperature. Then the adsorbents were separated by filtration through a 0.45 µm membrane filter (Whatman EO47). The concentration of Cd and Zn in filtrate was determined by AAS-FA (UNICAM 969) after stabilization of solution by HNO₃ in both experiments. The experimental data were processed by using Langmuir and Freundlich sorption isotherm.

3. RESULTS AND DISCUSSION

Adsorption of Cd and Zn onto kaolinite/TiO₂ composite and TiO₂ are shown in Fig. 1 as the quantities of Cd and Zn which are adsorbed at steady state on 1 g of adsorbent.

![Fig. 1 Adsorption isotherm of Cd (left) and Zn (right)]
Fig. 1 represents dependence of adsorption amount $a$ (mg/g) on concentration $c_r$ (mg/l) of metal ions in solution after treatment.

The Freundlich isotherm has better agreement with the experimental data than the Langmuir isotherm. Correlation coefficients are shown in Table 2.

Table 2 Correlation coefficients of linear form of the Langmuir and the Freundlich isotherm of Cd and Zn

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zn</th>
<th></th>
<th>Cd</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freundlich</td>
<td>Langmuir</td>
<td>Freundlich</td>
<td>Langmuir</td>
</tr>
<tr>
<td>KT</td>
<td>0.8760</td>
<td>0.8260</td>
<td>0.7857</td>
<td>0.8740</td>
</tr>
<tr>
<td>K</td>
<td>0.9795</td>
<td>0.8440</td>
<td>0.9450</td>
<td>0.7347</td>
</tr>
<tr>
<td>T</td>
<td>0.8110</td>
<td>0.8960</td>
<td>0.8360</td>
<td>0.8796</td>
</tr>
</tbody>
</table>

Results showed in table 2 that the Freundlich isotherm fitted adsorption of Cd and Zn on kaolinite. The adsorption Zn and Cd on kaolinite/TiO$_2$ composite and TiO$_2$ probably should be described by other isotherms.

4. CONCLUSION

The adsorption of Cd and Zn onto kaolinite, kaolinite/TiO$_2$ composite and TiO$_2$ nanoparticles were studied by batch procedure for 1 hour. The concentrations of adsorbate were determined by AAS-FA. The experimental data were described by Langmuir and Freundlich adsorption isotherms. The results show that the Freundlich isotherm describes Cd and Zn adsorption better. The results show the possibility of removing Cd and Zn from water solution by kaolinite.

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LITERATURA


