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Review

Solvent effect on the electrophoretic mobility and adsorption of Cu on iron oxide

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ABSTRACT

The adsorption of Cu^{2+} from the aqueous and aqueous–organic mixed solution on the iron oxide was studied as a function of temperature, pH and concentration of metal ions. The sorption of Cu^{2+} in the presence of different solvents followed the trend: aqueous–ethanol > aqueous–methanol > aqueous media, which is parallel to the increasing order of their dielectric constants. The electrophoretic mobility of the solid was studied to probe the adsorption mechanism. We observed that the electrophoretic mobility of the iron oxide in the presence of Cu^{2+} increases with the increase in pH of the suspension. However, a decrease in the electrophoretic mobility with the increase in concentration of metal cation showed the onset of the precipitation of the corresponding hydroxide on the surface of Fe_2O_3 particle. The solvent effect on the electrophoretic mobility of iron oxide followed the trend: aqueous > aqueous–methanolic > aqueous–ethanolic. We applied different models to explain the mechanism of the adsorption process.

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1. Introduction

Metal oxides/hydrous oxides are naturally occurring discrete minerals and exist in various amorphous and crystalline forms [1–4]. Oxides/hydrous oxides of metals in aqueous suspension develop surface electrical charges by surface hydration followed by dissociation of surface hydroxyl groups [5–10]. The surface charge at the metal oxide–aqueous solutions interface depends upon the pH, temperature, nature and concentration of the ions, and co-organic solvent. Numerous research workers [11–17] have reported the adsorption properties of metal oxides/hydroxides in aqueous solution.

Compared with purely aqueous systems, less attention has been paid to the adsorption of metal ions by metal oxides/hydroxides

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in mixed solvent systems. The presence of the organic co-solvent in the system may lead to its adsorption by solid, which may result in changing the surface properties of the oxides/hydroxides. Among the organic co-solvents employed for the purpose, particular attention has been given to alcohol, as they are inexpensive, easily available and are known to adsorb positively by a number of oxides/hydroxides [18].

Misak and Ghoneimy [19] studied the sorption behavior of hydrous zirconia in mixed solvents. They reported that the adsorption capacity of Na and Li increases in the presence of methanol than in pure water due to dehydration of Na and Li and their stronger interaction with the exchange site. Jansuz et al. [20] observed similar results for the adsorption of Na from a mixed ethanol–water solution of NaCl at the hematite–electrolyte interface. Bessonov and Krylova [21] outlined that the Sr removal by Al_2O_3 was considerably greater in a 90% methanol–10% water mixture than in pure aqueous system. Kosmulski [18] noticed that the presence of alcohol in water solution decreases the adsorption of alkali metal cations on silica.

Adsorption of metal ions on the solid surface is considered to be an important phenomenon in environmental and catalytic chemistry [1,22–24]. Iron oxide has industrial, medicinal and environmental importance and can effectively be used for the purification of alcohols. With regard to previous studies on the behavior of oxides/hydrous oxides in mixed solvents, the work reported until now in the literature is rather scanty and inconclusive.

This present study describes the sorption of Cu on the iron oxide (α-Fe_2O_3) from aqueous and aqueous–organic mixed solutions under different experimental conditions of concentration, temperature and pH of the system. Various adsorption models, like those of Forbes et al. and Kurbatov were tested to the experimental data to probe the mechanism of the adsorption process. We also conducted the electrophoretic mobility (EPM) studies of the iron oxide in aqueous and aqueous–organic mixed solution in the presence of Cu by varying the concentration and pH of the system.

2. Materials and methods

2.1. Reagents

Analytical grade reagents were used in this study. All the solutions were prepared in pyrex glass vessels. Chlorides of hydrogen, potassium, and copper were supplied by Merck while iron oxide was supplied by BDH.

2.2. Characterization of iron oxide

Air-dried samples of iron oxide were subjected to the X-ray analysis. The X-ray patterns of the powder samples were determined using a JEOL X-ray diffractometer, model JDX-7E with Mn-filtered Cu KD radiation. FTIR spectrum of iron oxide was taken by FTIR spectrometer, model Perkin Elmer 1 6PC FTIR. The sample of iron oxide was mixed with KBr and was ground to fine powder, using an agate mortar. The fine powder shaped into a disc form. The infrared spectrum of the sample was recorded by subjecting the disc to the IR radiation of FTIR spectrometer, and the recorded spectrum was then analyzed from the resulting peaks with known wave numbers. Surface area of Fe_2O_3 was determined by the nitrogen adsorption method using BET equation after 24 h degassing at 378 K.

2.3. Sorption studies

In this method 30 ml of the suspension containing constant amount of 10^{-3} M KCl solution as a background electrolyte and various amounts (5–40 mg/L) of Cu^{2+} were added separately to conical flasks. Then 0.1 g Fe_2O_3 was dispersed to each flask. The pH of each solution was adjusted to 5 ± 0.20 with 0.1 M HCl or 0.1 M KOH solutions. The samples were shaken in an air-dry thermostat at 293, 303 and 313 ± 1 K for 6 h. Equilibrium pH of the solution was measured using pH/ISE meter model 710 A Orion with a combination of pH electrodes of research grade. The samples were centrifuged and the supernatants were decanted for the determination of the metal remaining in solution. The concentration of Cu^{2+} in the solution was determined with Perkin Elmer model 3100 atomic absorption spectrophotometer. The metal adsorbed was calculated from the difference between the initial and equilibrium metal ion concentration.

The experimental procedure for the effect of organic solvent on the adsorption of the Cu^{2+} was the same as described above, however, 10% of alcohols (methanol, ethanol) were added in case of aqueous–organic solvents. The refractive indices of these prepared mixtures were also noted before and after the adsorption process with the help of Abb's refractive meter type RL.NO: 3062 (Poland).

2.4. Electrophoretic mobility studies of iron oxide

The electrophoretic mobility of the Fe_2O_3 was determined with Zeta potential analyzer model No. EP-MH. Aqueous solutions containing 10^{-3} M KCl as a background electrolyte in the presence of Cu^{2+} in the concentration range 5–150 mg/L were taken in reaction vessels with a final volume of 250 ml. The sample Fe_2O_3 (0.1 g) was added to each vessel and the initial pH of each sample was adjusted to 5, 7 and 9 ± 0.20 with either 0.1 M HCl or KOH solutions. The samples were kept overnight for shaking at desired temperature. The equilibrium pH of the suspension was determined before the electrophoretic mobility measurements. To study the effect of organic solvent on electrophoretic mobility, different aqueous–organic mixed solvents in the range 10, 20 and 30% alcohols were used. Each sample was run five times on Zeta Potential analyzer model No. EP-MH. The time (t) of the particle to cross the distance ($d = 0.00\,1$ cm) was measured during each run. The average value (t') was used to calculate the electrophoretic mobility (particle velocity potential gradient) for a cell length ($L = 2.6$ cm) at an applied potential ($U = 300$ V), to the following relationship [25].

$$\text{EPM} = \frac{Ld}{t'U} \tag{1}$$

The point of zero charge (PZC) of the sample was determined by either obtaining zero electrophoretic mobility or interpolating the data to zero electrophoretic mobility. Measurements of particle velocity at the stationary level were made within an hour of filling the cell, as soon as thermal equilibrium was established. All experiments were carried out at 293 K.

3. Results and discussion

3.1. Characterization of iron oxide

X-ray diffractogram of iron oxide showed some major interplanar spacing at 2.680, 2.560, 2.510, 2.257, 1.714 and 1.685 Å, which represents that solid sample under investigation consists mainly the synthetic hematite (Fe_2O_3). The result obtained here is similar to that reported elsewhere [26]. The FTIR spectrum of Fe_2O_3 showed five major bands at 604, 790, 900, 1640 and 3826 cm^{-1}. The band observed at 3826 cm^{-1} is assigned to OH stretching vibration and the one at 1640 cm^{-1} to the OH bending vibration of surface –OH groups. Similarly, the band at 604 cm^{-1} can be assigned to the Fe–O vibration whereas the bands at 790 and 900 cm^{-1} may be assigned to the Fe–OH vibrations as reported elsewhere [27]. Sur-