ISSN: 2707-1146
e-ISSN: 2709-4189

https://doi.org/10.36719/2707-1146/52/21-25

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Adsorption Study of Fe (III) Ions By Cellulose/Fe_3O_4/Sio_2/4-Aminoantipyrine

Abstract

A magnetic sorbent was synthesized by modifying the cellulose/Fe_3O_4/SiO_2 nanocomposite with 4-aminoantipyrine. The sorption of iron (III) ions with the synthesized sorbent was studied under static conditions. It was found that the extraction of Fe(III) ions was maximal at pH = 4.0. The study of the sorption of iron (III) ions over time showed that complete sorption occurs within 2 hours under static conditions. The ionic strength of the solution up to 1.2 M does not affect the sorption of iron (III) ions. The results showed that a significant decrease in sorption occurs in solutions with ionic strength higher than 1.2 M, and as the concentration of iron (III) in the solution increases, the amount of sorbed metal increases, with the maximum observed at a concentration of $7.0 \cdot 10^{-3}$ mol/L. The sorption capacity of the sorbent is 384 mg/g. In the final stage, desorption of mineral acids (HCl, H_2SO_4, $HClO_4$, HNO_3) with different concentrations was performed. It was established that iron (III) ions are maximally extracted from the sorbent when using 1.0 M $HClO_4$, with a desorption degree of 96 %.

Keywords: *iron (III) ion, magnetic sorbent, sorption, ionic strength, desorption*

Introduction

Magnetic sorbents have garnered significant interest in recent years for their versatile applications in environmental remediation, catalysis, and biomedical fields. These materials, particularly magnetic nanocomposites, offer unique advantages such as high sorption capacities, easy recovery from solutions using external magnetic fields, and tunable surface functionalities for selective ion capture (Liang et al., 2019; Ge et al., 2012). Among these, cellulose-based magnetic nanocomposites stand out due to their biocompatibility, renewability, and environmentally friendly nature (Mishra et al., 2021; Wu et al., 2022).

Magnetic nanoparticles are most commonly composed of metals such as nickel, iron, cobalt, and their oxides (Foroutan et al., 2002; You et al., 2021; Azeez & Al-Zuhairi, 2022). Magnetic iron oxide nanomaterials offer significant advantages for wastewater treatment, providing higher efficiency and more effective removal of harmful contaminants (Raha & Ahmaruzzaman, 2022; Pinto et al., 2020).

Research

Metal nanoparticles without special coatings possess high chemical activity and easily oxidize in air, leading to the loss of their dispersive and magnetic properties. Therefore, it is important to design and develop approaches for protecting magnetic nanoparticles for chemical stabilization without using special coatings. These surface modification approaches for magnetic nanoparticles include methods such as grafting or coating with an inorganic layer, such as carbon or silicon, or coating with organic compounds, including polymers and surfactants (Lu, Salabas, & Schüth, 2007; Laurent, 2008).

A variety of methods for synthesizing iron oxide nanomaterials and their versatile composites have been developed. Recent studies highlight that the surface properties of nanoparticles play a crucial role in determining their colloidal stability, magnetic behavior, and physicochemical characteristics (Alizadeh et al., 2020; Gupta, 2005).

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This work is devoted to the concentration of Fe(III) ions using a magnetic sorbent obtained by modifying the cellulose/Fe_3O_4/SiO_2 nanocomposite with 4-aminoantipyrine.

Experimental Section

Cellulose/Fe_3O_4 Nanocomposite: Synthesized via chemical co-precipitation. $FeCl_2 \cdot 4H_2O$ and cellulose solutions were ultrasonicated for 30 minutes and purged with nitrogen gas for 30 minutes. The Fe(II) solution was added dropwise to the cellulose dispersion with stirring (800 rpm). At 90°C, ammonia solution (28 %) was added to adjust the pH to 11–12. The black precipitate was magnetically separated, washed, and dried at 60°C for 12 hours.

Cellulose/Fe_3O_4/SiO_2 Nanocomposite: Coated using the Stöber method. Cellulose/Fe_3O_4 was dispersed in ethanol, ultrasonicated for 50 minutes, and mixed with ammonia (28%). Tetraethyl orthosilicate (350 µL) was added dropwise, and the mixture was stirred for 4 hours at room temperature. The product was magnetically separated, washed, and dried at 60°C for 12 hours.

Cellulose/Fe_3O_4/SiO_2/4-Aminoantipyrine nanocomposite: Prepared by impregnation. Cellulose/Fe_3O_4/SiO_2 and 4-aminoantipyrine (9:1 weight ratio) were stirred in acetone at room temperature for 8 hours. The resulting material was separated, washed, and dried at 40°C for 1 hour.

Apparatus

The pH of the solutions was measured using a PHS-25 ion meter with a glass electrode. The optical density of the solutions was measured using a KF-2 photocolorimeter in cuvettes with an absorption path length of l=1.0 cm. For mixing the solutions, an ORBITAL SHAKER TS-1 thermomixer was used. The sorbent was dried in a Zymark Turbo Vap LV drying oven.

Reagents and Solutions

A standard $1.0 \cdot 10^{-1}$ M iron(III) solution was prepared by dissolving a calculated amount of metallic iron following the method described in. Working solutions of $1.0 \cdot 10^{-2}$ M and $1.0 \cdot 10^{-3}$ M were obtained by diluting the stock solution with distilled water prior to use. Solutions of $2.0 \cdot 10^{-3}$ M 3-((2-hydroxyphenyl) diazenyl) pentadione-2,4 (R) and 1,10-phenanthroline (Phen) were prepared by dissolving the respective amounts of reagents in ethanol. To adjust the required acidity, acetate-ammonia buffer solutions (pH 3–11) and Fixanal HCl (pH 0–2) were used. All reagents used had a qualification of at least analytical grade.

Experimental Methodology

Sorption was studied under static conditions. To maintain a constant ionic strength, potassium chloride solutions were used. The concentration of iron(III) was determined in the form of a mixed-ligand complex with 3-((2-hydroxyphenyl) diazenyl) pentadione-2,4 and 1,10-phenanthroline, based on a previously constructed calibration curve (Nagiyev et al., 2020).

Results and Discussion

Effect of pH on Sorption: To determine the effect of pH on the concentration of iron (III) using a chelating sorbent, 30 mg of the sorbent was added to 2.0 mL of a $1.0 \cdot 10^{-2}$ M iron (III) solution and left in a buffer solution at pH = 4.0. The resulting mixture was filtered, and the concentration of iron (III) ions was determined using a photometric method with 3-((2-hydroxyphenyl) diazenyl) pentadione-2,4 and 1,10-phenanthroline. The number of adsorbed ions was calculated. The obtained results are presented in Table 1.

Table 1

Sorption capacity at different pH values

pH	1	2	3	4	5	6	7
SC, mg/g	187	272	349	384	318	126	23

It was found that the extraction of iron ion is maximized at pH = 4.0. All subsequent studies were conducted at pH = 4.0.

Contact Time

To establish the relationship between sorption and time and to achieve sorption equilibrium, 30 mg of the sorbent was placed into a flask, followed by the addition of 2.0 mL of $1.0 \cdot 10^{-2}$ M iron

ISSN: 2707-1146
e-ISSN: 2709-4189

(III) solution and acetate-ammonia buffer solution at pH = 4.0. Under static conditions, full sorption of iron occurred within 2 hours.

Effect of Ionic Strength

To study the effect of ionic strength on the sorption of iron (III) ions, an equal volume (20 mL) of solution was introduced into chemical glassware of the same volume at pH = 4.0. Conditions for different ionic strengths (0.1-1.2) were created by adding different amounts of KCl with a concentration of 2 mol/L. The solution was left for 2 hours, and after filtration, the amount of absorbed metal was determined using the calibration curve. It was found that increasing the ionic strength up to 1.2 had no effect on sorption, but further increases resulted in a significant decrease in sorption. This is due to the fact that as the ionic environment of the functional groups increases, the probability of forming a sorbent with magnetic properties of iron (III) decreases.

Effect of Concentration

To study the effect of initial concentration of iron (III) ions on the sorption process, 30 mg of sorbent was placed into the sorption flask, followed by the addition of a specific amount of $1.0 \cdot 10^{-2}$ M iron (III) solution and buffer solution at pH = 4.0. The analysis results showed that the maximum sorption capacity of the sorbent for iron (III) ions was observed at a concentration of $7.0 \cdot 10^{-3}$ M.

To investigate the optimal sorption conditions for iron (III), a sorption isotherm was constructed. For this purpose, after 2 hours, the mixture was filtered, and the content of unadsorbed iron (III) was determined using a previously constructed calibration curve. It was found that the sorption capacity of the sorbent at pH 4.0 was 384 mg/g (Figure 1)

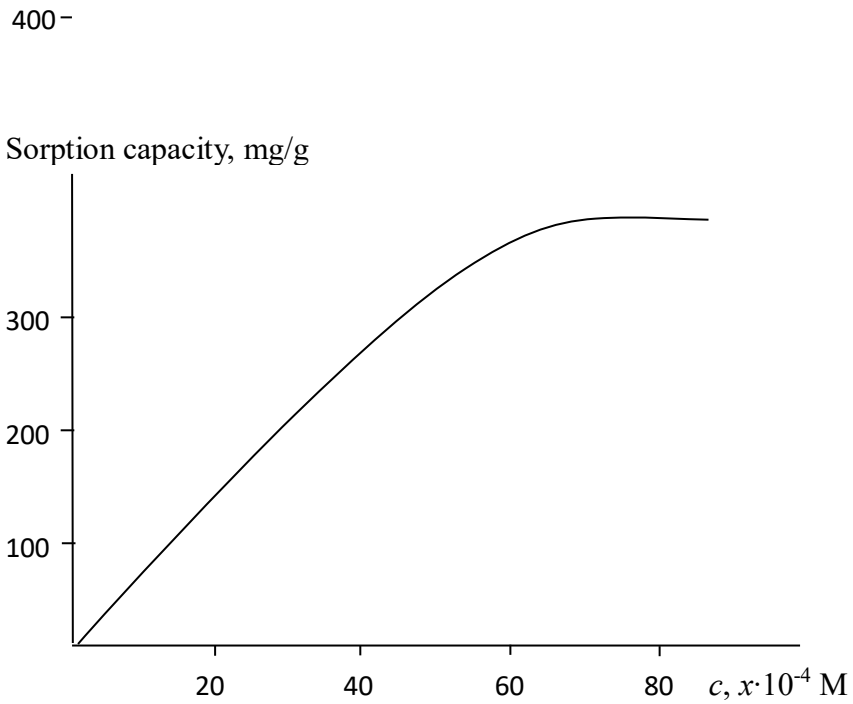

Fig. 1 Isotherm of iron (III) sorption by magnetic sorbent
m_{sorb} = 50 mg, V=20 ml, pH 4.0

Effect of Acid Solution Concentration on Desorption of Iron (III) Ions: The effect of various acids (HCl, H_2SO_4, $HClO_4$, HNO_3) on the desorption of iron (III) ions was studied (Table 2). For this purpose, equal masses of sorbent samples containing the same amount of Fe (III) ions were added to chemical beakers of the same volume. Then, solutions of the specified acids with different concentrations (0.5-2.0 mol/L) and varying volumes (5-20 mL) were added to the sorbents, and the concentration of iron (III) ions that transitioned into the solution was determined photometrically.

ISSN: 2707-1146
e-ISSN: 2709-4189

The results showed that the desorption degree (%) was higher when using a solution volume of 5 mL of acids with different concentrations, which was consistent across all experiments. It was found that the desorption degree was maximal when using 1.0 M $HClO_4$ (96 %).

Table 2

Effect of different acids on the desorption degree of iron (III) (%) (n=5)

Acid	Concentration, mol/l,	Desorption Degree, %
HCl	0,5	69
	1,0	71
	1,5	75
	2,0	73
H_2SO_4	0,5	82
	1,0	84
	1,5	91
	2,0	92
$HClO_4$	0,5	92
	1,0	96
	1,5	93
	2,0	88
HNO_3	0,5	75
	1,0	82
	1,5	84
	2,0	87

Conclusion

As a result of the study, a new sorbent with magnetic properties was synthesized by modifying the cellulose/Fe_3O_4/SiO_2 nanocomposite with 4-aminoantipyrine. The sorption properties of iron (III) ions with the synthesized sorbent were studied under static conditions. It was found that the sorbent quantitatively extracts iron (III) at pH = 4.0, with the sorption capacity of the sorbent being 384 mg/g. Additionally, according to the analysis, Fe (III) ions are maximally extracted from the sorbent when using 1.0 M $HClO_4$, with the desorption degree being 96 %.

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Received: 14.10.2024
Revised: 19.11.2024
Accepted: 11.12.2024
Published: 25.01.2025