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DETERMINATION OF COBALT IN SEAWATER USING A MAGNETIC CELLULOSE/Fe_3O_4/SiO_2/ BIS(ACETYLACETONE)ETHYLENEDIIMINE ADSORBENT

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In this study, a novel magnetic adsorbent based on cellulose/Fe_3O_4/SiO_2, modified with bis(acetylacetone)ethylenediimine, was synthesized and utilized for the effective removal of Co(II) ions from aqueous solutions. Equilibrium concentrations of Co(II) ions in solution was set by using 2,2′,2″,2‴-{(1,1-dioxo-2,1λ^6-benzoxathiole-3,3(1H)-diyl)bis[(6-hydroxy-5-methyl-3,1-phenylene)methylenenitrilo]} tetraacetic acid (xylenol-orange) (R) as reagent. Various factors influencing the adsorption process were examined, including the effects of pH, contact time, ionic strength, and the initial concentration of metal ions. The sorption of cobalt (II) ions with the synthesized magnetic sorbent under static and dynamic conditions was studied. Optimal adsorption performance was achieved at a pH of 8. It was determined that 0.5 M HCl solution achieves the most effective desorption of Co(II) ions from the sorbent, with a desorption efficiency of 97%. The proposed method was employed for the detection of trace levels of cobalt (II) in water samples collected from the Caspian Sea.

Keywords: adsorption, cobalt, Caspian Sea, concentration, xylenol-orange

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INTRODUCTION

The contamination of aquatic ecosystems by heavy metals represents a critical environmental concern, primarily stemming from the uncontrolled discharge of industrial effluents and anthropogenic activities [1]. These metals are highly toxic even at low concentrations and have the tendency to accumulate in living organisms, potentially leading to various health disorders and diseases [2].

Cobalt contamination in natural water bodies has become a global environmental concern, as cobalt-contaminated water poses significant health risks to humans due to the element's high toxicity levels [3,4]. The primary anthropogenic sources of Co(II) in aquatic systems are industrial effluents, particularly those originating from nuclear power facilities, metallurgical operations, mining activities, the electronics sector, and the production of pigments and paints [5,6].

A range of conventional treatment technologies—including chemical precipitation, coagulation–flocculation, ion exchange, biological remediation, and chemical reduction—have been employed for the removal of Co(II) ions from wastewater. However, the practical application of these methods is often constrained by several limitations, such as high operational and maintenance costs, complex

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process requirements, and the generation of secondary pollutants that require additional treatment [7–10]. In contrast, adsorption has gained widespread attention as a highly efficient, cost-effective, and environmentally benign technique for the removal of heavy metal ions from aqueous solutions, owing to its operational simplicity, minimal sludge production, and potential for adsorbent regeneration and reuse.

Cellulose-based materials have garnered increasing attention as low-cost and sustainable adsorbents for the removal of heavy metal ions from aqueous systems, owing to their natural abundance and modifiability. The adsorption efficiency of these biopolymers can be significantly enhanced through targeted chemical modifications, which either amplify their inherent physicochemical properties or introduce novel functional capabilities [11,12].

Notably, chemically modified cellulose exhibits superior adsorption performance compared to its native form, largely due to the incorporation of functional groups that facilitate stronger interactions with metal ions. The high density of hydroxyl groups along the cellulose backbone serves as reactive sites, allowing for the attachment of various functional moieties that enhance its affinity for pollutants. While the native reactivity of cellulose is somewhat limited by extensive intra- and intermolecular hydrogen bonding, strategic modification disrupts this bonding network, thereby increasing the accessibility and reactivity of surface sites [13-15]. Such advancements underscore the promising role of modified cellulose derivatives in water purification and environmental remediation technologies.

This study aims to investigate the sorption behavior of cobalt(II) ions using a magnetic sorbent based on cellulose/Fe_3O_4/SiO_2 functionalized with bis(acetylacetone)- ethylenediimine. Furthermore, it focuses on developing a method for the extraction of cobalt(II) ions from seawater using this sorbent.

EXPERIMENTAL

Synthesis of Cellulose/Fe_3O_4/SiO_2 / bis(acetylacetone)ethylenediimine:

Magnetic cellulose-based nanocomposites were synthesized via chemical co-precipitation, where $FeCl_2 \cdot 4H_2O$ was added to a cellulose dispersion under ultrasonic treatment and nitrogen atmosphere. Precipitation was achieved by adjusting the pH to 11–12 with ammonia at 90°C. The product was magnetically separated, washed, and dried.

Silica coating was performed using a modified Stöber method by dispersing Cellulose/Fe_3O_4 in ethanol with ammonia, followed by dropwise addition of TEOS and stirring for 4 hours.

Finally, the composite was functionalized with bis(acetylacetone)ethylenediimine. (9:1 weight ratio) in acetone via an 8-hour impregnation at room temperature, then washed and dried.

Reagents and Solutions: All the chemicals used were of high purity.

A $2 \cdot 10^{-3}$ M cobalt solution was prepared by dissolving 0.05622 g of $CoSO_4 \cdot 7H_2O$ in 100 ml of distilled water.

To prepare the reagent solution, 0.067 g of xylenol-orange ($C_{31}H_{32}N_2O_{13}S$) is dissolved in 100 ml of distilled water.

To obtain the desired acidity, hydrochloric acid (pH 1-2) and ammonium acetate buffer solutions (pH 3-11) were used. The ionic strength of the solution was kept constant by adding potassium chloride (analytical grade).

Apparatus: The optical densities of the solutions were recorded using a KFK-3 spectrophotometer with 1 cm thick quartz cuvettes. The pH of the solutions was determined with a pH-meter, utilizing a pH-121 standard solution and a glass electrode. Distilled water was produced using a-10 device.

Sorption experiments: Sorption studies of Co(II) ions were conducted at ambient temperature. For each experimental setup, 2 mL of a metal ion solution with a known concentration of $2{\cdot}10^{-3}$ mol/L was added to 50 mL conical flasks. Each flask also received 30 mg of the sorbent and an appropriate pH buffer. The pH of the solutions was monitored using a pH-121 pH meter. The resulting mixtures were allowed to equilibrate for 24 hours, after which the liquid phase was separated from the solid phase by filtration through filter paper. The concentration of Ni(II) ions remaining in solution was determined using the reagent 2,2′,2″,2‴-{(1,1-dioxo-2,1λ^6-benzoxathiole-3,3(1H)-diyl)bis[(6-hydroxy-5-methyl-3,1-phenylene)methylenenitrilo]} tetraacetic acid (xylenol-orange) (R). The measurements were performed with a KFK-3 photoelectrocolorimeter at a wavelength of 540 nm.. The efficiency of metal ion removal was calculated using the following formulas:

$$\mathrm{R},\% = \frac{\mathrm{C_0} - \mathrm{C_e}}{\mathrm{C_e}}\mathrm{x}100 \qquad (1),$$

where R is a percentage of metal ion removal.

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2),$$

In this context, **C_0** represents the initial concentration of the metal ion (mol·L^{-1}), **C_e** denotes the equilibrium concentration of the metal ion (mol·L^{-1}), **V** is the volume of the solution (L), and **m** refers to the mass of the sorbent (mg).

RESULTS AND DISCUSSION

Effect of pH

It is widely recognized that the pH of a solution significantly influences the dissociation equilibrium of Co(II) in water, as well as the surface charge of adsorbent materials [16,17]. Research has identified four primary cobalt ion species that exist at varying pH levels: Co^{2+}, $Co(OH)^+$, $Co(OH)_2$, and $Co(OH)_3^-$ [18]. The dependence of the adsorption of Co(II) ions by a magnetic adsorbent on the acidity of the medium (pH 2.0-11.0) was studied.

For the experiment, 30 mg of the sorbent was accurately weighed and placed in separate containers. Then, 2 ml of a $2{\cdot}10^{-3}$ M metal ion solution and 18 ml of the solution with the appropriate pH were added, and the mixture was allowed to stand for 24 hours. After 24 hours, the solution was filtered through filter paper to separate the solid particles, and the absorbance was measured at a wavelength of λ = 540 nm using a KFK-3 spectrophotometer. The effect of the solution's pH on cobalt sorption is shown in the figure below (Figure 1).

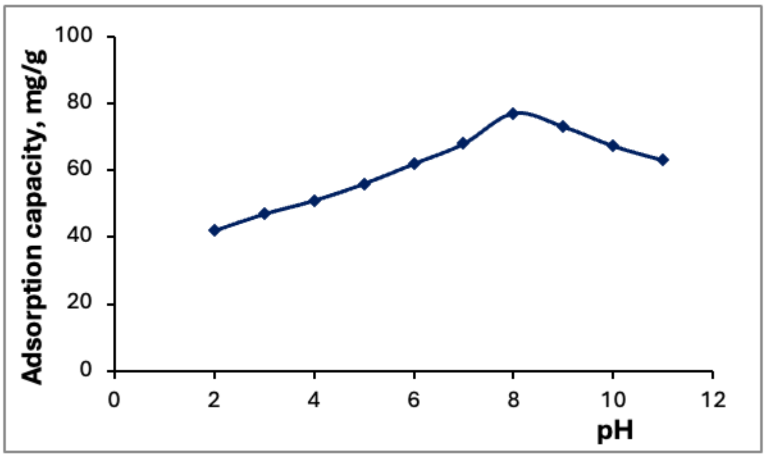

Figure 1. Effect of pH on the adsorption capacity Co(II)

It can be seen from Fig. 1 that the magnetic adsorbent demonstrates maximum cobalt(II) ion sorption in a buffer solution with pH 8.0. As a result, all subsequent studies were carried out in an acetate-ammonia medium with pH 8.0.

Effect of contact time

To determine the equilibrium time for Co(II) adsorption, experiments were carried out with contact times ranging from 10 to 270 minutes. To assess the time-dependent sorption and achieve equilibrium, 30 mg of sorbent was placed into a flask, followed by the addition of 2.0 ml of $2.0 \cdot 10^{-3}$ M cobalt (II) solution and an ammonium acetate buffer solution with a pH of 8.0.

The adsorption capacity increased sharply during the initial stages due to the abundance of available active sites on the surface of the adsorbent. The rate of sorption gradually slowed down as these sites became occupied.

Equilibrium was reached at approximately 120 minutes, after which no significant change in Co(II) removal was observed. This indicates that 120 minutes is sufficient for achieving maximum adsorption under the studied conditions. The relatively fast sorption kinetics suggests that the adsorbent possesses high affinity and effective functional groups for binding Co(II) ions.

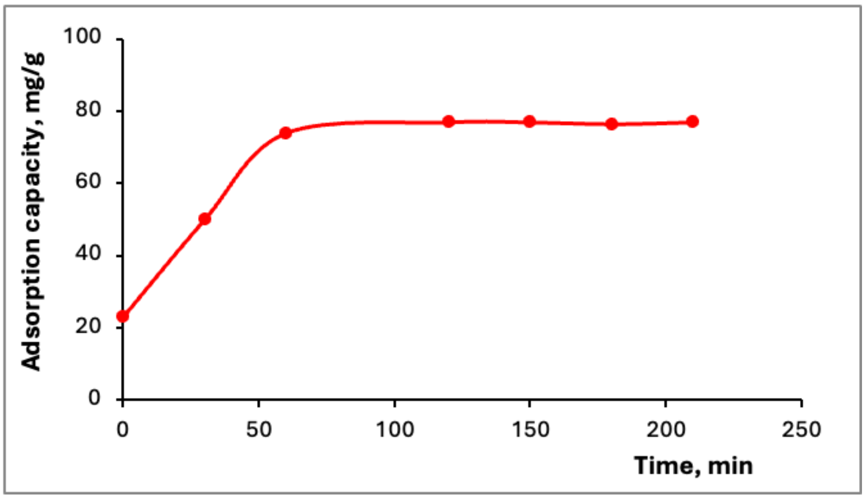

Figure 2. Effect of contact time on the adsorption capacity Co(II)

Effect of ionic strength

The effect of ionic strength on the sorption process was thoroughly investigated in order to evaluate the stability and efficiency of the sorbent under varying ionic environments. For this purpose, potassium chloride (KCl) solutions of different concentrations ranging from 0.2 to 1.4 mol/dm^3 ionic strength were prepared, and their impact on the sorption capacity of the magnetic cellulose/Fe_3O_4/SiO_2/bis(acetylacetone)ethylenediimine adsorbent toward cobalt (II) ions was assessed. The experimental results demonstrated that the sorption efficiency remained nearly constant and was not significantly influenced by the increase in ionic strength up to 1.2 mol/L. This indicates that the sorbent possesses a high selectivity for Co(II) ions and that the sorption mechanism is likely dominated by specific interactions, such as chelation or complexation, rather than simple electrostatic attractions. Such behavior is advantageous for practical applications, especially in real environmental or industrial wastewater systems, where high concentrations of competing ions are commonly present.

Effect of initial concentration

In this experiment, the influence of the initial concentration of metal ions on the adsorption efficiency of the synthesized sorbent was investigated. A concentration range of Co(II) ions from 2×10^{-4} mol/L to 8×10^{-3} mol/L was employed. For each test, 30 mg of sorbent was accurately weighed, followed by the addition of a specific volume of the metal ion solution adjusted to pH 8.0. After 120 minutes of contact time, the optical densities of the resulting homogeneous solutions were measured using a KFK-3 photoelectrocolorimeter at a wavelength of λ = 540 nm. The results of this study are presented in the figure below (Figure 3).

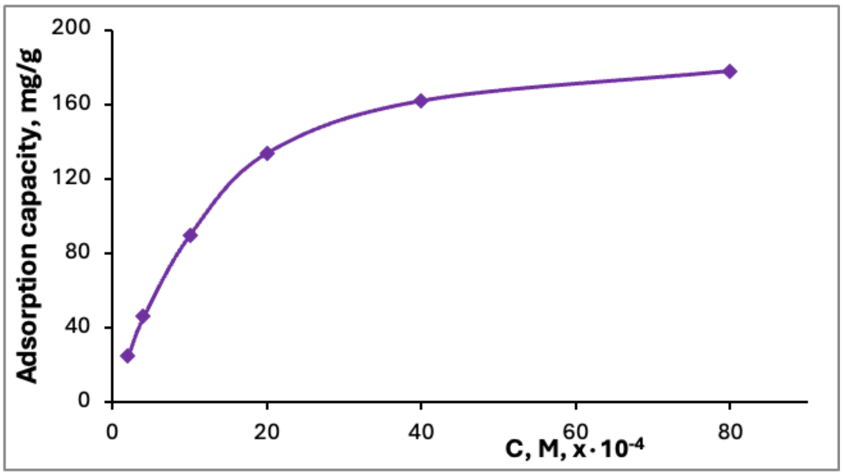

Figure.3. Effect of initial concentration on the adsorption capacity Co(II)

Desorption process

The preparation of adsorbents is typically a complex process that requires significant time and energy. Furthermore, the materials used for their synthesis are often costly and challenging to procure. As such, investigating the reusability of the adsorbent is crucial. Various methods are employed for the regeneration of adsorbents, including biological methods (using microorganisms), thermal methods (involving oxidation), and chemical methods, the latter being the most widely utilized. In the chemical method, the adsorbed substance is removed using an appropriate solvent [28]. This study focuses on examining the impact of different acids and their concentrations on the desorption process.

The desorption experiment was conducted using 0.5 mol·L^{-1} solutions of several inorganic acids, each prepared at the same concentration, including HNO_3, HCl, H_2SO_4, and CH_3COOH. To perform the experiment, 30 mg of the sorbent was placed into four separate flasks. Each flask received 2 mL of a $2 \cdot 10^{-3}$ M Co(II) solution and 18 mL of a solution adjusted to pH 8. The mixtures were then allowed to react for 24 hours. After this period, the solid phase was separated from the liquid phase by filtration. Subsequently, 20 mL of 0.5 M solutions of HNO_3, HCl, H_2SO_4, and CH_3COOH were added to the filtrate to facilitate the desorption process.

Of the eluents tested, the 0.5 mol·L^{-1} HCl solution exhibited the highest efficiency in desorbing Co(II) ions from the sorbent, highlighting its superior capacity for desorption.

Analysis Procedure:

To determine iron in water, 100 mL of the filtered sample is acidified with 5 mL of HNO_3 (1:1) and passed through a mini-column at a flow rate of 1.0 mL/min. The sorbed ions are eluted with 5.0 mL of 0.5 M HCl. The eluate is transferred to a 25 mL volumetric flask, followed by the addition of 2.0 mL of a 10^{-3} M solution of xylenol-orange, and then diluted to the mark with a pH 4.0 buffer solution. The optical density of the resulting solution is measured using a "Lambda-40" spectrophotometer at a wavelength of 540 nm in cuvettes with a 1 cm path length. The cobalt (II) content is determined using a calibration curve.

The obtained results are presented in Table 1 and compared with data from the atomic absorption spectroscopy (AAS) method. It can be seen that the results of the proposed method and AAS are in good agreement. Thus, the suggested procedure for determining cobalt(II) using 2,2′,2″,2‴-{(1,1-dioxo-2,1λ^6-benzoxathiole-3,3(1H)-diyl)bis[(6-hydroxy-5-methyl-3,1-phenylene)methylenenitrilo]} tetraacetic acid (xylenol-orange), after preliminary preconcentration on a magnetic sorbent, is simple, rapid, and provides reliable results.

Table.1. Results of cobalt(II) determination in seawater

Sample	Found Co, mg/l		S_r	
	The proposed methodology	AAS	The proposed methodology	AAS
Water of the Caspian Sea	0,1126±0,0075	0,1131±0,0084	0,033	0,036

CONCLUSIONS

A new magnetic nanocomposite based on cellulose/Fe_3O_4/SiO_2 functionalized with bis(acetylacetone)ethylenediimine has been successfully synthesized and applied for the sorption of Co(II) ions. The material exhibited high efficiency, reusability, and magnetic separability, offering a sustainable and cost-effective method for heavy metal removal from aqueous media.

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