Modeling Cobalt Ion Adsorption with Synthesized Magnetite Bentonite (SMB) Nano-Absorbent: by CCD

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ABSTRACT: *Magnetic nanoparticles are very effective in removing heavy metals from wastewater that can be produced by adding to mineral adsorbents, a modified adsorbent with high adsorption properties. The addition of magnetite nanoparticles to bentonite increases the cationic adsorption power of bentonite. In this paper, the adsorption of cobalt ions on metal ions is investigated using synthesized magnetite bentonite nano-absorbent (SMB) (30-40 nm). First, The nano-absorbents were produced by co-precipitation and analyzed by Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), and Fourier Transform InfraRed (FT-IR) spectroscopy, then used as adsorbent. The experiments were designed and evaluated by design expert software. Optimal conditions were obtained by CCD model for metal ion adsorption (removal). The optimum amount of adsorption of* Co^{2+} *ion from the solution was 95%.*

KEYWORDS: *Magnetite; Bentonite; Wastewater; Design expert; Cobalt.*

INTRODUCTION

Environmental pollution is one of the problems of human societies. One of the most important pollutants is industrial and mineral wastewater that emits various pollutants including heavy metals into the environment [1]. Removal of heavy metals from wastewater is important because of their harmful effects on human health and the environment [2, 3]. The most common heavy metals in wastewater are lead, copper, zinc, cadmium, cobalt, nickel, chromium. Due to their toxicity and carcinogenicity at low concentrations and no biodegradation, they cause problems not only for plants and animals but also for humans that accumulate in living tissues and ultimately in the food chain [4, 5]. Heavy metals are mainly produced from mines, industry, electrical machines, metal plating, etc [6, 7]. Different methods such as chemical precipitation, ion exchange, adsorption, and reverse osmosis have been used to remove heavy metals from wastewater[8-10]. The use of nanoparticles has always been of interest due to their good reactivity and efficacy in wastewater treatment. Combining nanoparticles with adsorbent minerals can double the ability of adsorbents to remove pollutants [1]. Bentonite is one of the clay minerals with high adsorption properties due to the presence of ionic species on their surface [11].

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The physical and synthetic properties, such as small particle size, high porosity, surface area, and ion exchange capacity make it applicable to a wide range of sciences [1, 12]. The mechanism of adsorption of Cd^{2+} ions a heavy metal by bentonite is the result of electrostatic interaction and the result of ion exchange between cations in bentonite adsorbent [13]. Using the ion exchange properties of bentonite and investigating the effective parameters, Ding et al. showed that the adsorption of Zn^{2+} ion was performed well under optimal conditions [14].

According to properties of low cost, simplicity of use, easy availability, and environmental friendliness, Magnetite (Fe_3O_4)-based nanomaterials are used [15]. Many studies have been conducted on their use in heavy metal treatment [16 -21]. *Baghani et al.* made synthesized amino Fe_3O_4 nanoparticles by using a simple one-pot method. They studied the adsorption of Cr (VI) and Ni (II) ions with it [18]. The addition of magnetite nanoparticles to other adsorbents increases the ability to remove heavy metals from the effluent. Copper ion removal using chitosan-coated with magnetic fluid at different pH, showed kinetics of adsorption corresponding to the first-order rate and the adsorption of Cu (II) equal was 78.13 mg/g [19]. *Adeli et al.* were applied from sodium dodecyl sulfate-coated Fe_3O_4 nanoparticles (SDS–Fe_3O_4 NPs) to remove Cu^{2+}, $Ni^{2+,}$ and Zn^{2+} ions. In addition to the optimum adsorption of the ions in question, they showed that the presence of salts had a negative effect on the adsorption efficiency and changed the adsorption mechanism [20]. The adsorption isotherms of metal ions from aqueous solution onto the bentonite also showed that the presence of iron oxide produced an increase in the adsorption capacity of the bentonite [21].

The importance of removing heavy metals due to their environmental detrimental effects has led to new methods for their elimination. Due to the easy availability of bentonite and magnetic nanoparticles, the combination of these two materials can form a unique adsorbent. In this study, the nano-absorbent was synthesized by the co-precipitation method, which is obtained by maintaining the inherent properties of bentonite and the magnetic properties of magnetite. Experiments are then designed using design expert software and the Central Composite Design (CCD) model. Finally, optimum conditions for cobalt ion removal are investigated and determined.

EXPERIMENTAL SECTION

To prepare magnetite nanoparticles (SMB) of appropriate size, the bottom-up chemical co-precipitation method was used. Chemical materials such as iron (II) chloride, iron (III) chloride as the precursor, and ammonia as the precipitating agent were used to perform this process [22, 23]. The iron chloride (II) and iron chloride (III) were added to the bentonite-distilled water mixture (10 g of bentonite (75 mμ) in 500 mL of water) at a 2: 1 molar ratio. Dissolved iron chloride solution was heated at ambient temperature in the three-Span Balloons. To minimize the amount of dissolved oxygen, the solution was subjected to a constant flow of nitrogen gas. Then the ammonium solution (20 mL) was gradually added to the balloon for 45 minutes. From another span, the solution was stirred with a high-speed vertical agitator (glass head).

Experiments designed by design expert software, pH parameters (X1), nano-magnetic absorber dose (X2), contact time (X3), metal ion concentration (X4) were selected as independent variables, and their separate and combined effects on the percentage of Co^{+2} removal are studied.

RESULTS AND DISCUSSION

In each experiment, the magnetic nano-absorbent (SMB) was added to 50 mL of the solution containing Co ions. This mixture was stirred with a mechanical stirrer (glass head) at a constant speed and at ambient temperature. The percentage of metal ion removal was calculated according to equation (1):

$$\% R = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where C_o and C_t are the primary and secondary concentrations of Co^{2+} ions (mg/L) [24].

Design of Experiment and CCD Model

The experiment design method of RSM is high performance and accuracy. This design method consists of both Box-Behnken Designs and Central Composite Designs (CCD) methods. The CCD method is a powerful method that is used most often when there is little information available on the factors under study and the range of their effects. It is a repeat-based method for minimizing errors and is often recommended for continuous trials because this method is about interpolating information the factorial experiments designed [24, 25]. In the design of the experiments, each parameter was evaluated, resulting in the design of 30 experiments. For each variable, three levels are defined as low

Table 1. Variables and their different levels.

Factor name	Unit	First level (-1)	Second level (0)	Third level (+1)
pH	------	4	7	10
The amount of adsorbent	mg	20	60	100
Contact time	min	15	37	60
Metal ion concentration	ppm	30	90	150

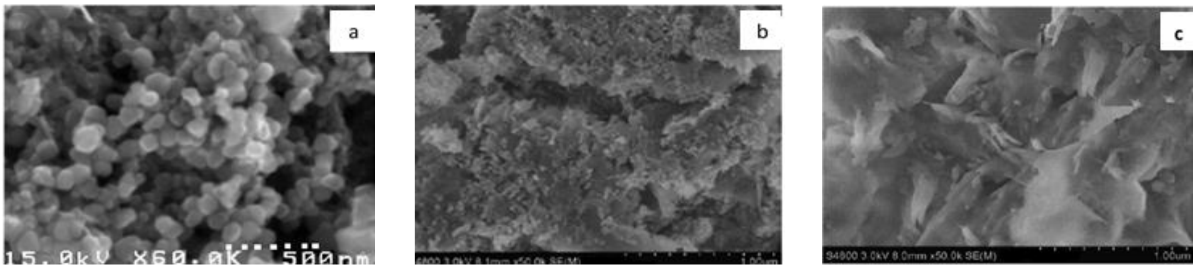

Fig. 1: SEM image, a: Fe_3O_4 nanoparticles, b: bentonite - Fe_3O_4 nanoparticles, and c: bentonite.

(-1), medium (0) and high (+1). Table 1 mentioned the parameters examined and the different levels.

Absorbent characterization

Fig. 1 shows the SEM image of a 500 nm bentonite and magnetized bentonite (SMB). This type of structure and dimensions increase the specific surface area of the particles and increase their efficiency. In Fig. 1, a. the nanoparticles within the bentonite still have a spherical and quasi-spherical shape. The problem of nanoparticles aggregation within bentonite is not observed and bentonite does not cause particle aggregation [26].

In the XRD analysis of Fig. 2, b six peaks of the magnetite nanoparticles are seen. These peaks confirm the presence of Fe_3O_4 magnetic nanoparticles in the bentonite structure. Peaks also show that magnetic nanoparticles are embedded in it without altering the bentonite phase.

Also in FT-IR spectrum, as Fig. 3, a., one peak at 569 cm^{-1} is seen for the magnetic nanoparticle, and this peak appears again in Fig. 3, b in the bentonite matrix. These results prove that magnetite nanoparticles are located between the bentonite layers.

Software Testing and Results

According to the 30 tests designed by the software, the experiments were performed under the proposed conditions. Table 2 shows the experiments designed and the percentage of cobalt ion absorption from the solution.

Looking at the table, it can be seen that in alkaline pH metal ions are better absorbed and are removed from the solution. But in acidic environments, the percentage of adsorption decreased sharply. The compliance degree of the experimental results with the predicted values of recovery is plotted in Fig. 4. The diagram shows the appropriate match between the experimental and predicted recovery results.

By performing 30 experiments determined by software with four factors; pH, adsorbent amount, metal ion concentration, and contact time, the results were analyzed, as shown in Table 3. Software analysis using CCD model and considering the effect of the above four factors led to Equation (2,) that it shows the effect of pH, metals ion, and adsorbent concentration on CO^{+2} ion removal from solution but contact time was ineffective.

The R^2 = 0.925 values for Co^{2+} ion removal models showed the well fitness of regression models for predicting the removal results which has performed better than reports of *Goleij et al.* [25]. Regarding the effective P-values and coefficients obtained for each factor, the regression equation for cobalt ion adsorption recovery is:

$$\%Y = 32.45+39.55X_1+1.36X_2-7.17X_4+ 6.04X_1^2+0.01X_1X_4 \quad (2)$$

Where *X1, X2, X3* and *X4* are the pH, the amount of adsorbent, the contact time and the cobalt ion concentration, respectively.

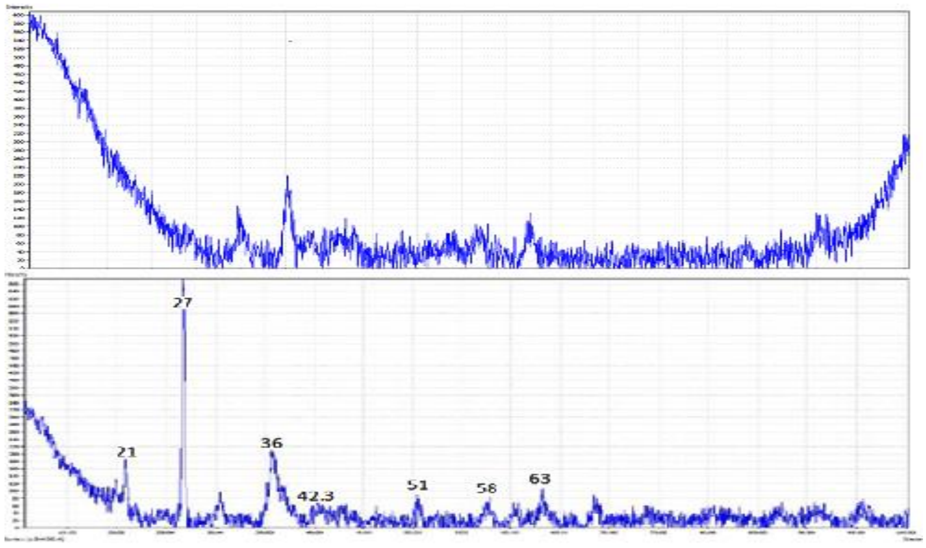

Fig. 2: XRD spectrum, a: bentonite and b: bentonite-Fe_3O_4.

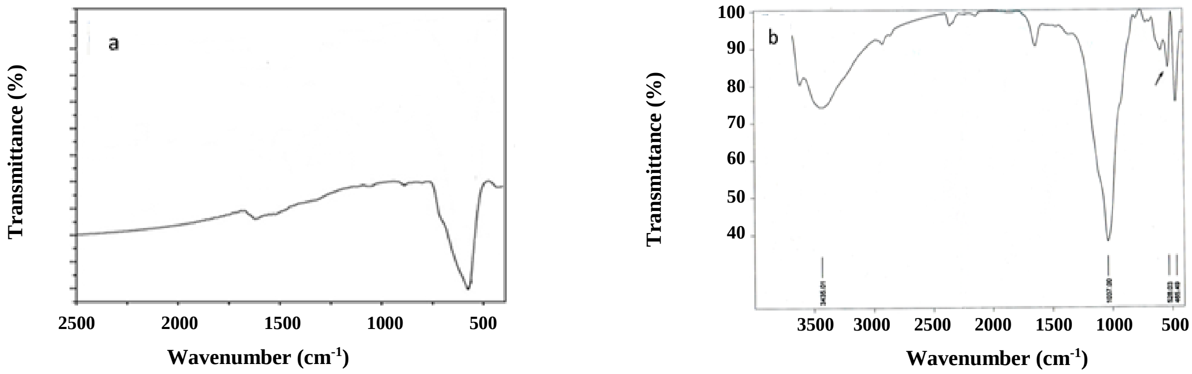

Fig. 3: FT-IR Images, a: Bentonite, b: bentonite-Fe_3O_4.

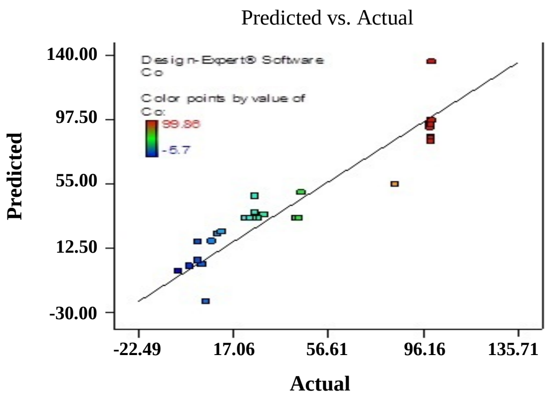

Fig. 4. Scatter diagram of predicted recovery values relative to experimental results.

The results of regression analysis show that the pH parameter appears with a positive effect on the regression equation and has the smallest P-value. The most effective factor is due to the larger coefficient in the regression equation and the smaller P-value. Investigations showed that the optimum pH is 10, where both the magnetite adsorbent and the cobalt metal ion are fully active in the environment. According to Table 3, it can be seen that as the pH of the environment increases and its playing time, the amount of metal ion adsorbent is increased, with the highest at pH=10 followed by a decrease at 7 and 4, respectively. Obviously, as the amount of adsorbent increases, the efficiency and efficiency of the process (adsorption of pollutants on the substrate) also increases.

Table 2: Designed experiments by software and Co^{+2} ion recovery value.

R	pH	Adsorbant(mg)	Time(min)	Metal(ppm)	Rec (%)co
1	10	20	60	30	98. 85
2	4	100	60	150	0.97
3	7	60	37	90	43.11
4	7	60	37	90	27.44
5	4	100	60	30	12.50
6	4	20	15	30	2.57
7	7	60	37	90	44.43
8	7	140	37	90	45.59
9	1	60	37	90	5. 89
10	4	100	15	30	10. 65
11	7	10	37	90	26.41
12	7	60	37	90	25.28
13	4	20	60	30	8. 30
14	10	20	60	150	99. 41
15	13	60	37	90	99.86
16	7	60	37	10	84.51
17	10	100	15	30	99.75
18	7	60	37	90	22/43
19	10	90	15	30	99.13
20	4	20	15	150	4.32
21	7	60	37	90	24.13
22	10	20	15	150	99.44
23	10	100	60	30	99.78
24	4	100	15	150	2/36
25	10	100	15	150	99.47
26	7	60	37	210	26.21
27	7	60	82	90	29.97
28	10	100	60	150	99.46
29	4	20	60	150	5.70
30	7	60	5	90	29.19

Table 3. Estimation of the regression coefficient. Response Surface Regression: Rec. Co% versus pH; Adso; Time; ppm

Source	Squares	Square	Prob > F
pH	37541.62	37541.62	<0.0001
Adso	76.71	76.71	<0.0001
Time	8.35	8.35	0.1700
ppm	709.63	709.63	<0.0051
pH*pH	10.9659	10.9659	<0.0001
Adso*Adso	1038.9	1038.9	0.1163
Time*Time	215.6883	215.6883	0.4594
ppm*ppm	934.0024	934.0024	0.1349
pH*Adso	1.87827	1.87827	0.9444
pH*Time	0.620681	0.620681	0.9680
pH*ppm	26.84449	26.84449	0.0494
Adso*Time	11.23479	11.23479	0.8647
Adso*ppm	73.41919	73.41919	0.6641
Time*ppm	7.545093	7.545093	0.8890

R^2 =92.48

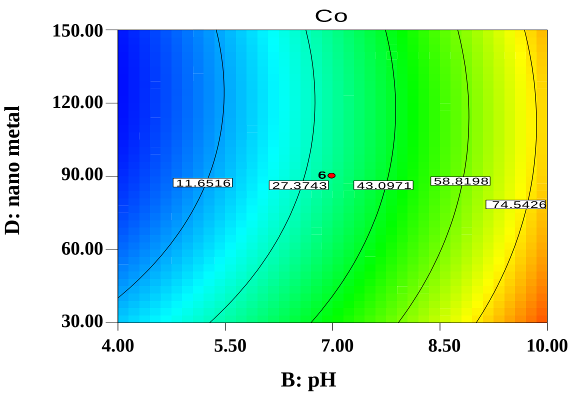

Fig. 5: Contour plot of simultaneous effect of pH and metal ion concentration on Co^{2+} ion recovery in 60 mg adsorbent and 37.5 min contact time.

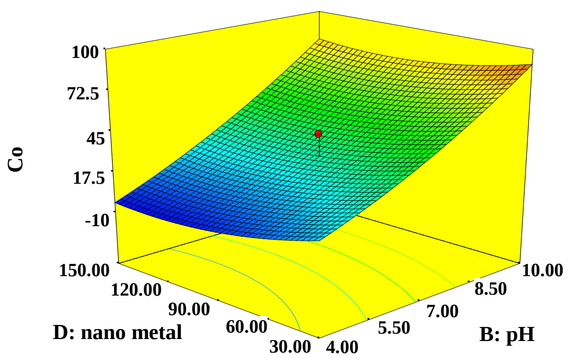

Fig. 6: Plane plot of the interaction of pH and metal ion concentration on Co^{2+} ion recovery rate.

Regression results also show that the adsorbent parameter with a positive sign and a small P-value appears, which is the second factor affecting the recovery of the adsorbent amount. Cobalt ion concentration (P-value = 0.005) also had a significant effect after pH and the amount of bentonite nano magnetite adsorbent (SMB), which could have a serious effect on the adsorbent content. The coefficient value for this effect is negative because increasing the concentration of Co^{2+} ions decreases the adsorption rate for a constant amount of adsorbent.

Investigation of interactions affecting cobalt adsorption

We deduced from Table 3, the only interaction that has an effect on Co^{2+} ion recovery is the simultaneous effect of pH and metal ion concentration. To investigate the interaction of the two factors, the other factors were considered constant at the second level. Fig. 5 shows the simultaneous effect of pH and concentration of metal ions on the second level constant of the adsorbent and the contact time of 37.5 min as a contour plot.

Table 4: Optimal conditions for maximum adsorption of Co^{2+} ions by magnetized adsorbent (SMB).

Factor type / Metal ion	pH	Absorbent amount		Time (Minutes)	Metal ion concentration (ppm)	Predicted removal(%)
		mg/L	mg			
Co^{2+}	10	90.87	1.97	29	30	95.38
	10	89.40	1.79	20	30	95.13

Table 5: The best conditions are selected to achieve maximum absorption.

Factor type / Metal ion	pH	Absorbent amount		Time (Minutes)	Metal ion concentration (ppm)	Predicted removal(%)
		mg/L	mg			
Co^{2+}	10	90.87	1.97	20	30	95

Table 6: Parameters of adsorption isotherms of cobalt ion with magnetite nanoparticles (SMB).

Isotherm type	Isotherm constants		R
Langmuir	K_L = 0.0691 (l/mg)	q_m =12.92356 (mg/g)	0.961
Freundlich	K_F = 1.75432($mg^{1-n}L^n$/gr)	n=1.73201	0.978
Temkin	K_T = 5.21013	b=419203.6258 (j/mol)	0.966
Dubinin–Radushkevich	K_F =0.1011	q_m =358.1786	0.9691

Also, the plane plot of the interaction of pH and the metal ion concentration in Fig. 6 shows that increasing the pH increases the rate of Co^{2+} ion adsorption. The effect of this factor is an important factor because of its large coefficient in the regression equation. So that even the increase of the metal ion, which has an adverse effect on the adsorption rate, could not have an effect on the adsorbent at high pH.

Optimal conditions were determined using software and CCD model. In Table 4, the best case of each factor is proposed to reach the maximum metal ion adsorption using the desired adsorbents. As shown in the table, the time is the same in all cases, and the optimum concentration of metal ions is 30 ppm.

Therefore, the two best choices for metal ions with respect to pH, adsorbent, and remove values are shown in Table 5.

Also, in the case of adsorption of cobalt ion by nanomagnetic bentonite adsorbent (SMB), the obtained R^2 values are close together, in Table 6. In general, the Freundlich isotherm with the coefficient R^2 of 0.978 is selected as the optimal adsorption isotherm. The highest monolayer adsorption capacity calculated with Langmuir isotherm for the cobalt adsorption process was 12.92356 mg/g. The value of K_L coefficient in the Langmuir isotherm was calculated to be 0.0691.

Accordingly, the R_L coefficient using Eq. (3) equals 0.198, indicating that it is desirable to describe the adsorption process.

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

In this equation, K_L Langmuir constant is the maximum concentration C_0 (mg/L) used in the experiment. The equilibrium data were well fitted by the isotherm adsorption which was consistent with previous studies, but in this study, the percentage or coefficient of cobalt recovery was obtained higher [25, 21].

CONCLUSIONS

In this study, Synthesized Magnetite Bentonite (SMB) nano-absorbent was prepared and used to remove Co^{2+} ions from an aqueous solution. The bottom-up co-precipitation method in alkaline media has been used for the synthesis of nanoparticles. The results of the device analysis confirmed the proper synthesis of magnetite nanoparticles in the bentonite structure and the lack of particles accumulation within the bentonite structure was one of the advantages of this method. Experiments were designed using design expert software and CCD model and the main parameters were analyzed and statistically analyzed at three levels. Analyzes for four factors show that metal ion removal can be described in a polynomial model with a relatively high coefficient of R^2 = 92.48. The optimum pH and absorption percentages were obtained 10 and 95%, respectively. The adsorption theory for cobalt ions was desirable and the Freundlich isotherm was chosen as the optimal isotherm.

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