

Supporting information for the paper:

Co(II) Removal from Aqueous Solution by Birhodanine-Functionalized Magnetite Nanoparticles: Kinetic and Thermodynamic Studies

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1. Instruments

The FTIR (KBr) spectra were recorded on a PerkinElmer RXI spectrophotometer. NMR spectra were obtained on a Bruker Avance 250 MHz spectrometer using tetramethylsilane (TMS). TGA curves were obtained on a Linseis STA PT 1000 instrument with the scanning rate of 10°C/min. A Philips (X-Pro) X-ray diffractometer equipped with Ni-filtered Cu-K α radiation source was used for XRD measurements at room temperature with the scanning rate of 1°/min over a 2 θ range of 10–80°. SEM image of MNP@BIRD NPs was obtained on a LEO 1430VP instrument. The TEM image of the silylated NPs was obtained on a by using a Philips EM208. Dispersing of the NPs was done in an ultrasonic bath (Parsonic 7500S). A Vibrating sample magnetometer (VSM, Maghnatis Danesh-pajooh Kashan Co. Iran) with a maximum magnetic field of 10 kOe was used for magnetization measurements at room temperature. A spectrophotometer (Unico, 2100) was employed for analytical experiments.

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2. Materials

MNPs and methyl 2-(4-oxo-3-phenethyl-2-thioxothiazolidin-5-ylidene)acetate (**IV**) were prepared according to the literature reported methods (1, 2). (3-Aminopropyl)trimethoxysilane (APTMS) were obtained from Exir (Austria) and used as received. All solvents were of laboratory grade and dried according to the literature (3). The other chemicals were also of laboratory grade, purchased from Merck and used without further purification.

3. Adsorption study

The batch reactor was equipped with the ethylene glycol circulation arrangement to maintain the temperature at $20\pm^{\circ}\text{C}$. The vials were stirred for the desired time and then adsorbent was separated by magnetic decantation. The amount of adsorbed Co(II) cations was determined spectrophotometrically according to the method described earlier using nitroso-R (sodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate) as a chromogenic reagent (4). The effect of pH, adsorption time, amount of the sorbent and initial metal ion concentration on the removal of Co(II) cations were examined. For optimization of pH, suspensions of the sorbent (10 mg) in 25 ml of Co(II) solution (3.0 ppm) was stirred magnetically at pH 7.0, 8.0 and 9.0 for 30 min and the remaining Co(II) concentrations were determined after separation of the sorbent. For time optimization, the same experiments were done in optimal pH and the remaining metal ion concentrations were determined after 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, 7.0, 9.0, 10.0, 20.0, 30.0 and 45.0 min. For optimizing the adsorbent dosage, a series of experiments were done with 5, 7, 10, 15, 20, and 30 mg of the sorbent at optimal conditions of pH and time. Finally, the initial Co(II) concentration was optimized by doing a series of experiments in optimal conditions of pH, time and adsorbent mass with the initial Co(II) concentration of 0.5, 1.0, 3.0, 5.0, 7.0, 10.0 and 15.0 ppm. Adsorption capacity (Q_t) and the extracted percentage ($E\%$) were obtained using Equations 1 and 2:

$$Q_t \text{ (mg / g)} = \frac{(C_0 - C_t) \times V}{W} \quad (1)$$

$$E \text{ (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where, Q_t is the amount of metal ion adsorbed per unit mass (mg g^{-1}) of the sorbent at time t . C_0 and C_t are the Co(II) concentrations (ppm) at the beginning and at time t , respectively. V and W are the solution volume (L) and the sorbent mass (g), respectively.

4. Adsorption kinetic study

The adsorption kinetic experiments were carried out at the optimum conditions of pH and the sorbent mass with initial metal ion concentration of 3.0 ppm. For this purpose, suspensions of the sorbent were stirred in 25 ml of the aqueous Co(II) solutions at $20 \pm ^\circ\text{C}$. The remaining concentrations of Co(II) cations were then determined spectrophotometrically at different time intervals over 45 min and after separation of the sorbent.

5. Adsorption equilibrium isotherms

The adsorption isotherms were obtained at the optimum conditions of pH, time and the sorbent mass. These experiments were used to determine the maximum adsorption capacity of the Co(II) cations. For this purpose, suspensions of the sorbents, with initial metal ion concentrations of 0.5, 1.0, 3.0, 5.0, 7.0, 10.0 and 15.0 ppm, were stirred at the optimum conditions in 25 ml of the aqueous Co(II) solutions at 20°C . The remaining concentrations of Co(II) cations were then determined spectrometrically after separation of the sorbent.

6. Thermodynamic assessment of adsorption

The adsorption thermodynamic experiments were carried out at the optimal conditions of pH, time and the sorbent mass with initial metal ion concentration of 3.0 ppm. To this end, suspensions of the sorbent were stirred in 25 ml of the aqueous Co(II) solutions at 20, 25, 30, 40 and 50°C. The remaining concentrations of Co(II) cations were then determined spectrophotometrically after separation of the sorbent.

7. Desorption experiments

The recyclability of the sorbent was demonstrated by doing the desorption experiments. For this purpose, under optimal conditions, Co(II)-complexed MNP@BIRD NPs were irradiated in an ultrasonic bath for 30 min in a 25 ml aqueous solution of 0.2 M HCl and then additionally stirred for 30 min at room temperature. The NPs were separated from solution by magnetic decantation and re-dispersed in 25 ml of double distilled water. The pH of the solution was reach to 7.0 by addition of 2 M ammonia solution, irradiated in an ultrasonic bath for 30 min and then stirred at room temperature for additional 30 min. The adsorbent was separated from solution by magnetic decantation, washed with water and reused.

8. Optimization of adsorption conditions

8.1 Effect of pH

Figure S1a shows that pH of the medium can strongly affect the adsorption capacity (Q_t) and removal %. Summarized results in Table 1 reveal that the bare MNPs show small tendency for adsorption Co(II) ions at pH 7, but both Q_t and removal % values increase dramatically as the pH increases to pH 9 probably due to interaction of surface hydroxyl groups with the cobalt hydroxide formed at higher pHs. The adsorption capacity and removal % increase slowly as pH increase. We chose pH 8 for further experiments in order to prevent any probably cobalt hydroxide formation.

Table 1. Effect of pH on Co(II) adsorption. ^a

Sample	Adsorbtion Capacity (mg g⁻¹)		
	pH		
	7	8	9
Fe ₃ O ₄	0.17 (2.2) ^b	0.64 (8.5)	5.05 (67.3)
MNP@BIRD	4.34 (57.8)	5.36 (71.5)	6.07 (80.9)

^a Initial Co(II) concentration 3.0 ppm, Adsorption time 30 min, Sorbent mass 10 mg, Solution volume 25 ml.

^b The values in the parenthesis are *E* %.

8.2 Effect of contact time

The effect of adsorption time on the removal of Co(II) cations is shown in Figure S1b. The adsorption capacity reaches to a plateau ($Q_t = 5.4 \text{ mg g}^{-1}$, $R\% = 71.5$) over 30 min at optimal pH with 10 mg of the sorbent in 25 ml of aqueous solution. Therefore, contact time of 30 min was chosen as optimum condition for the adsorption of Co(II) ions.

8.3 Effect of adsorbent mass

The removal of Co(II) cations was studied at optimal conditions by varying the mass of MNP@BIRD NPs from 5 to 30 mg in 25 ml of aqueous solutions containing 3.0 ppm of Co(II), Figure S1c. As can be seen, the effective removal of Co(II) cations ($Q_t = 5.4 \text{ mg g}^{-1}$, $R\% = 71.5$) was achieved using 10 mg of MNP@BIRD NPs and then reaches to a plateau. Therefore, the adsorbent dosage of 10 mg was chosen as the optimal mass and used for subsequent experiments.

8.4 Effect of initial Co(II) concentration

The effect of initial concentration of Co(II) cations on the adsorption capacity was studied under optimal conditions. The initial metal ion concentration varied from 0.5-15.0 ppm. It was observed that, the adsorption capacity increases sharply until the concentration of Co(II) ions

increased up to 3.0 ppm, thereafter the adsorption capacity reaches a plateau, indicating saturation of the available binding sites on the adsorbent. Therefore, the initial concentration of 3.0 ppm was chosen as the optimal value for subsequent experiments.

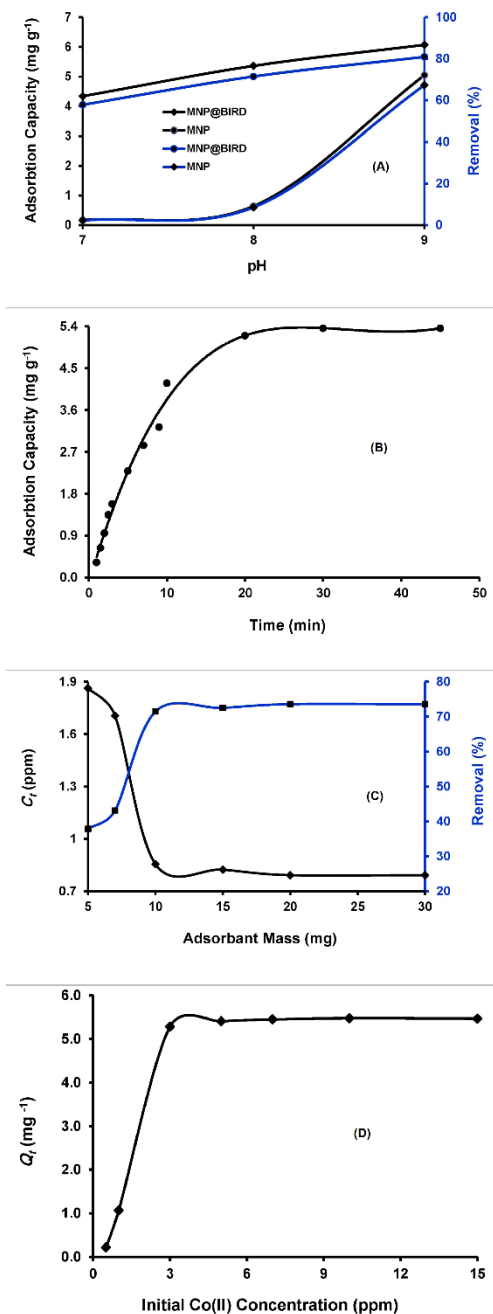


Figure S1. Optimization of adsorption conditions: Effect of (A) pH; (B) Contact time; (C) adsorbent dosage; and (D) Initial Co(II) concentration. At the beginning: Initial Co(II) concentration 3.0 ppm, Adsorption time 30 min, Sorbent mass 10 mg, Solution volume 25 ml.

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