

Cobalt-based Coordination Polymer (Co-ICP) Microparticles as Preferred Anionic Dye Adsorbent: Synthesis and Dye Adsorption

Maryam Mohammadikish^{a,b*} and Atefeh Ghaderi^a

^aFaculty of Chemistry, Kharazmi University, Tehran, Iran

^bResearch Institute of Green Chemistry, Kharazmi University, Tehran, Iran

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Development of highly efficient and fast-rate adsorbents has recently attracted intense attention of researchers for wastewater treatment. However, only few investigations have been done on the selective and fast-rate removal of Congo red and methyl orange by coordination polymers. In this work, a new cobalt-based coordination polymer was constructed via simple precipitation method by addition of diethyl ether to the methanolic solution of glutaric acid and cobalt acetate. Two anionic (Congo red and methyl orange) and two cationic (methylene blue and Rhodamine B) dyes were chosen as model targets to examine the adsorption efficiency of the prepared Co-ICP. The experimental data indicated that unlike the cationic dyes, the anionic dyes are excellent targets for adsorption by Co-ICP probably due to stronger electrostatic interactions. Furthermore, it was found that, only after 2 minutes the removal efficiency of Congo red by Co-ICP reaches to 88%. The analytical data confirmed the preservation of the primary structure of the Co-ICP even after 24 h Soxhlet washing. The efficiency of obtained Co-ICP for anionic dyes removal partly decreased after four cycles probably due to the occupation of some adsorption sites and reduction of adsorption capacity.

Keywords: Cobalt coordination polymer, Congo red, Dye adsorption, Methyl orange, Precipitation method

INTRODUCTION

Organic dyes in wastewater is one of the main environmental hazardous materials that provoked specific attention of researchers about the environment and ecosystem issues especially water contamination. Organic dyes show mutagenic, carcinogenic, toxic and allergenic effects [1,2]. One of the major concerns in wastewater purification is the existence of a tiny amount of organic dyes with stable aromatic structures which are resistant to atmospheric degradation. Hence, many researches have been focused on the organic pollutants removal from wastewater by degradation [3] or adsorption [4,5] techniques. Various photocatalytic procedures were proposed for degradation of organic dyes to produce less hazardous compounds under UV-Vis irradiation [6-9]. However,

adsorption of organic dyes from wastewater is the subject of numerous researches due to cost-effectiveness, simplicity, and high efficiency [10-12]. In this subject, several adsorbents have been inquired such as bio-sorbents [13,14], activated carbon [15], polymers [16], natural materials [17] and nanoporous structures [18].

Infinite coordination polymers (ICPs) as a new class of coordination polymers are prepared from metal nodes and organic linkers [19,20]. These compounds with well-defined shapes and sizes are constructed by crystal growth initiation at initial stages, so usually have amorphous nature [21-23]. ICPs are stable in many solvents and display significant applications as gas storage [24-28], drug delivery [29-31], catalysis [32-34], and separation [35,36]. Metal organic frameworks (MOFs) with good porosity recently introduced as extensive candidates for wastewater treatment [37-39]. However, because of their poor stabilities in hydrolytic conditions their utilization as adsorbents in aqueous media

*Corresponding author. E-mail: mohammadikish@khu.ac.ir

is limited [40]. Hence, more investigation to found stable ICPs in most of the solvents and conditions is required [41,42].

In order to obtain such an stable adsorbent based on ICP compound, herein, reaction of Co(II) as metal node with glutaric acid as carboxylate linker was conducted through the precipitation method to prepare Co-ICP. Then, for evaluating the dye removal efficiency, adsorption of some anionic and cationic dyes i.e. Congo red (CR), methyl orange (MO), methylene blue (MB) and rhodamine B (RB) by the obtained Co-ICP were studied.

EXPERIMENTAL

Materials and Apparatus

Glutaric acid (99%), Congo red, and Rhodamine B were purchased from ACROS Company. Co(OAc)₂.4H₂O (98%) was obtained from Alfa-Aesar. Methylene blue and methyl orange were purchased from Merck. All solvents were obtained from Merck and used as received.

The CHN elemental analyses were done on Perkin-Elmer 2400 SERIES II. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) were conducted on the SPECTRO ARCOS EOP ICP-OES analyzer. Fourier-transform infrared spectra of solid samples (as KBr pellets) were obtained on a Perkin-Elmer-RXI FT-IR spectrophotometer. Scanning electron microscopy (SEM) images were taken on a FEI-QUANTA 200 scanning electron microscope. Energy dispersive X-ray (EDX) analyses were obtained on EDAX-SDD. Thermogravimetric analysis (TGA) was conducted on a NETZSCH TG 209 F1 Iris thermogravimeter in the temperature range from room temperature to 700 °C at a heating rate of 10 °C min⁻¹ in static air. X-ray diffraction (XRD) patterns were recorded on a Rigaku D-max CIII X-ray diffractometer using Ni-filtered Cu K α radiation. The electronic spectra were taken on an Analytik Jena SPECORD 250 PLUS spectrophotometer. Zeta potential was carried out on Horiba Jobin Jyovin SZ-100z dynamic light scattering and zeta potential analyzer.

Synthesis of Cobalt-based Infinite Coordination Polymer (Co-ICP)

5 mL of degassed methanolic solution of

Co(OAc)₂.4H₂O (0.57 g; 2.29 mmol) was added slowly to 0.2 g (1.53 mmol) of glutaric acid in 15 mL of MeOH under N₂ atmosphere. After 1 h, 30 mL of degassed diethyl ether was added to the reaction mixture. Fine olive-colored powder of the product were formed immediately and the reaction mixture was stirred for another 30 min. Finally, the formed precipitate was centrifuged, washed three times with methanol, and dried under vacuum. Elemental Anal. Calcd. for C₅H₆O₄Co.0.7H₂O: C, 29.08; H, 3.70; Co, 29.23. Found: C, 29.37; H, 3.58; Co, 29.54.

Dye Removal and Recyclability of Co-ICP

Adsorption properties of Co-ICP in the presence of some anionic and cationic dyes such as Congo red (CR), methyl orange (MO), methylene blue (MB), and rhodamine B (RB) were investigated. 50 mg of the adsorbent (Co-ICP) was added to a 50 mL of 20 mg L⁻¹ dye solution. The obtained suspension was stirred vigorously at laboratory condition. Samples were taken from the reaction mixture at various times (2, 5, 10, 20, 30, 60 min and 24 h), centrifuged, and analyzed by UV-Vis spectrophotometry. To investigate the recycling properties of the Co-ICP, a separate test was designed after soxhlet washing of the used adsorbent with H₂O for 24 h.

Maximum absorbance wavelength of 500 and 486 nm was selected to measure dye concentrations of CR and MO via the corresponding calibration curves (R²-CR = 0.999 and R²-MO = 0.9991), respectively. In the presence of Co-ICP, the absorption intensities showed negligible change for the RhB and MB solutions, so the adsorption studies of these cationic dyes was not investigated. The adsorbed dye amount per gram of adsorbent (Q_t; mg g⁻¹) in time t and the removal efficiency (R; %) were calculated using the following equations:

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

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

where C₀, C_t, V, and M are the initial dye concentration (mg L⁻¹), concentration of dye at a given time t, solution volume (L), and the mass of used adsorbent (g), respectively.

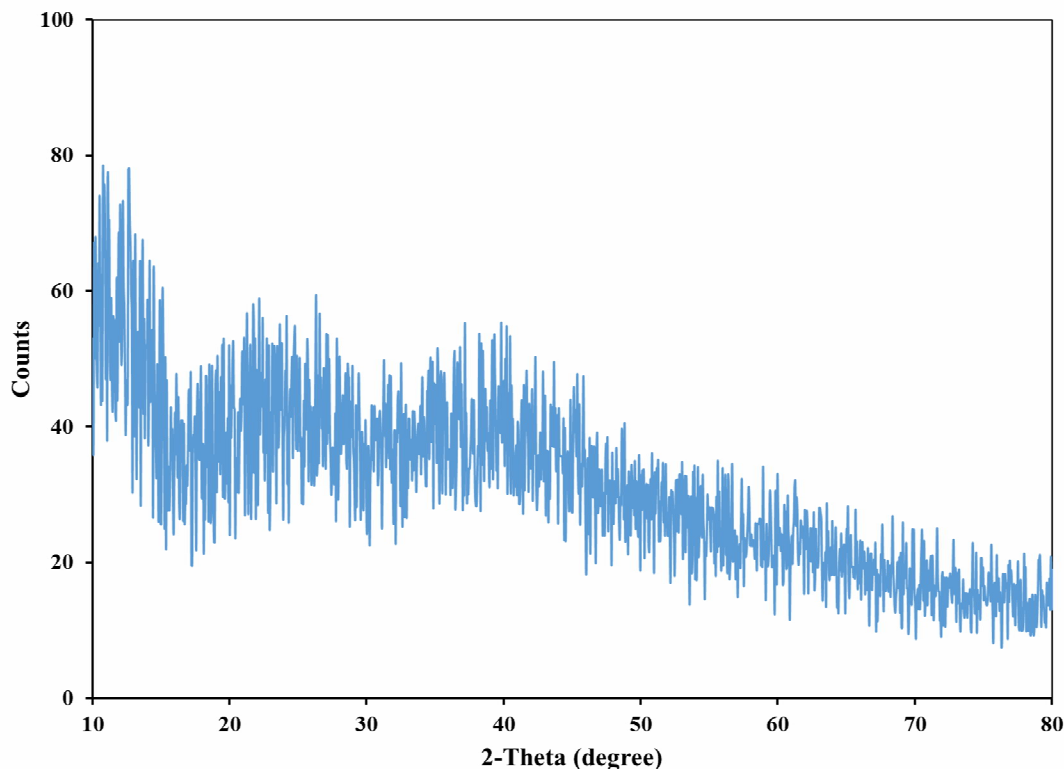


Fig. 1. XRD pattern of the Co-ICP.

RESULTS AND DISCUSSIONS

Characterization of the Prepared Co-ICP

Olive-colored powder of cobalt coordination polymer was isolated through precipitation reaction of Co^{2+} and glutaric acid in methanol/diethyl ether mixture.

XRD pattern of prepared Co-ICP is shown in Fig. 1. The diffraction pattern reveals the poor crystallinity of synthesized material. The main feature of the obtained pattern is the broadness and low signal to noise ratio of the peaks indicating the amorphous nature of prepared ICP due to the inhibition of crystal growth as predicted according to previous works [21,23]. Hence, X-ray crystallography cannot help to identify precise structure of the prepared compound.

Due to the amorphous nature of the prepared Co-ICP, elemental analysis, EDX, FT-IR and TGA analyses were used for appropriate characterization of the structure and

empirical formula of the product.

CHN and ICP-OES elemental analyses satisfactorily confirmed the chemical composition of Co-ICP with $\text{Co}(\text{C}_5\text{H}_6\text{O}_4)0.7\text{H}_2\text{O}$ empirical formula (see experimental section).

Energy dispersive X-ray (EDX) spectroscopy further support the proposed chemical composition of Co-ICP due to the presence of cobalt, carbon, and oxygen atoms in the sample (Fig. 2a). The morphology of prepared cobalt-based coordination polymer was studied via scanning electron microscopy (Fig. 2b) which revealed uniform microspheres with 200-300 nm diameter.

FT-IR spectroscopy is an appropriate technique to investigate the formation or appearance of functional groups in the sequence of reactions. The strong $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations of glutaric acid at 1695 and 1305 cm^{-1} were disappeared due to the coordination of carboxylic acid groups to the cobalt center (Fig. 3). Afterwards, a new band was appeared at 1557 cm^{-1} corresponding to resonance form

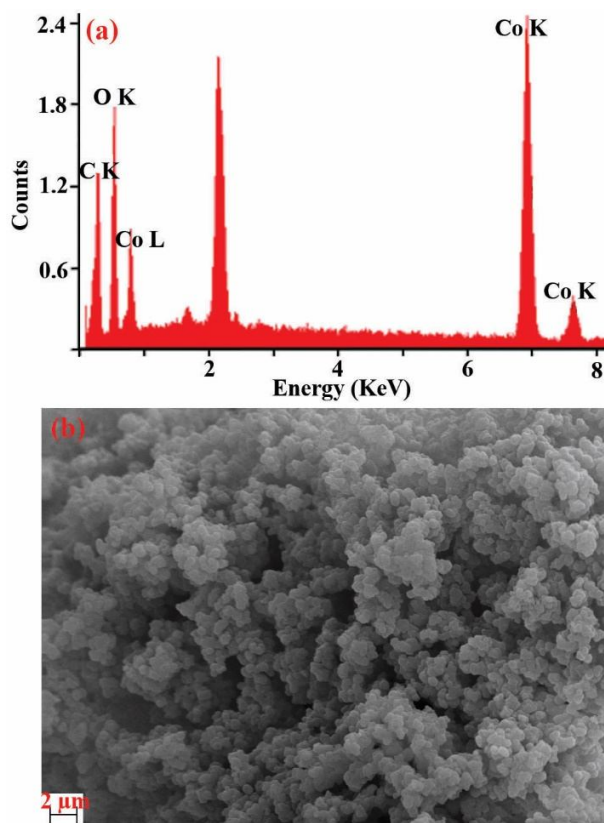


Fig. 2. EDX spectrum (a) and SEM image (b) of prepared Co-ICP.

of COO^- groups. This observation clearly confirmed coordination of the carboxylate groups to cation center [43,44].

TGA/DTG curves of Co-ICP were given in Fig. 4. From 50 to 150 °C, gradual weight loss was seen due to the loss of $0.66\text{H}_2\text{O}$ (found 6.26% and Calcd.: 5.89%), which corresponded to 0.7 water molecule per formula unit concluded *via* elemental analyses. Burning of the organic compounds led to the sharp weight loss from 250 to 350 °C. The 39.77% of remaining weight corresponded to the CoO as a final product of the burning (Calcd. 37.31%). Based on the above results, the Co-ICP can be deduced to be a composition of $\text{C}_5\text{H}_6\text{O}_4\text{Co}\cdot 0.7\text{H}_2\text{O}$.

Dye Adsorption Studies

The as-synthesized Co-ICP was studied to explore its utilization in dye removal for water treatment. Two anionic

(CR and MO) and two cationic (MB and RhB) dyes were selected as typical water pollutants. Figure 5 shows the absorption spectra of dyes aqueous solutions in the presence of Co-ICP at various times. As seen in Fig. 5, the CR absorption intensity steps down immediately after 2 min. In the case of MO, the absorption peak intensity diminishes instantly after 2 min and gradually until completely disappears after 60 min. However, the absorption peak intensities of the cationic dyes (MB and RhB) do not change even after 24 h.

In order to study the removal efficiency of Co-ICP towards CR and MO, removal efficiencies (R%) at various times were calculated. As seen in Fig. 6a, the removal efficiency of CR in the presence of Co-ICP is higher at all times compared to MO. After 24 h, the final removal efficiencies for the CR and MO dyes reach to 92.4% and 83.3%, respectively. As seen, removal efficiencies of 88%

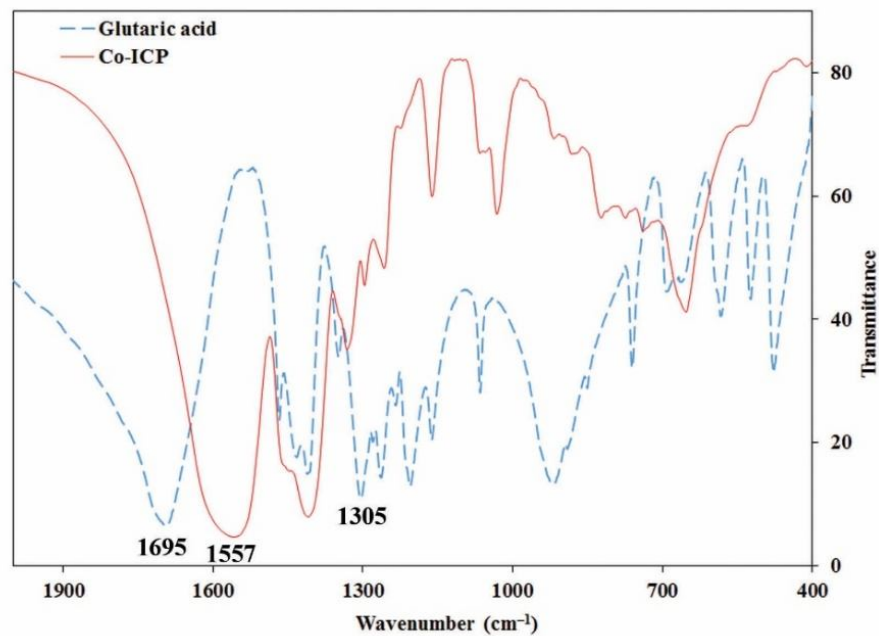


Fig. 3. FT-IR spectra of glutaric acid and prepared Co-ICP.

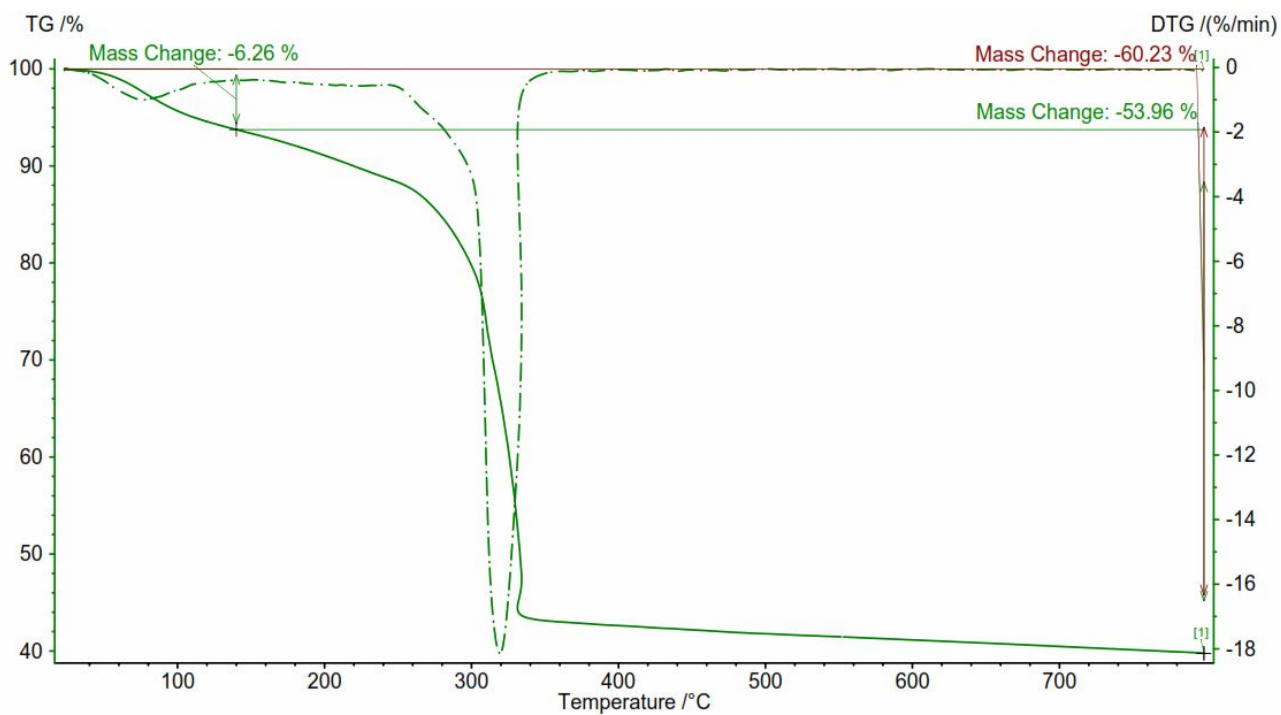


Fig. 4. TGA/DTG curves of as-prepared Co-ICP.

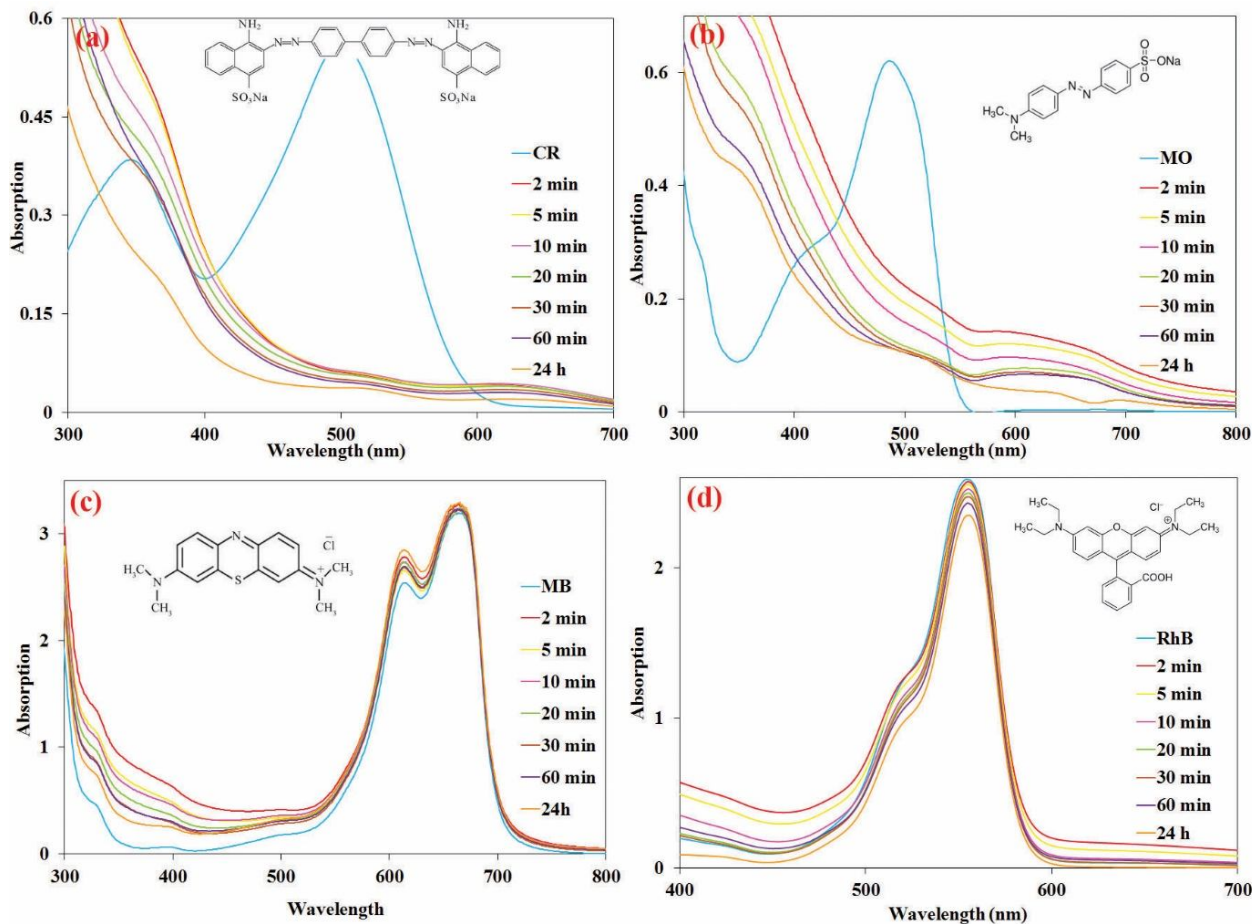


Fig. 5. The UV-Vis absorption spectra of (a) CR, (b) MO, (c) MB and (d) RhB solution (50 mL; 20 mg L⁻¹) in the presence of Co-ICP microspheres (50 mg) at different time intervals.

Table 1. Summary of Maximum dye Removal Efficiencies (R%) of Various Adsorbents

Adsorbent	Dye	Removal efficiency (R%)	Ref.
Co-ICP	Congo red	92.4	This work
	Methyl orange	83.3	
Co coordination polymer	Methyl orange	92.5	[45]
	Orange II	86.5	
Viologen-based β -cyclodextrin polymer	Congo red	80	[46]
	Methyl orange	77	
ZIF-8@SiO ₂ @MnFe ₂ O ₄	Methyl orange	5.9	[47]
	Malachite green	92.5	
Fe ₃ O ₄ @Tb/AMP	Alizarin Red	94	[48]

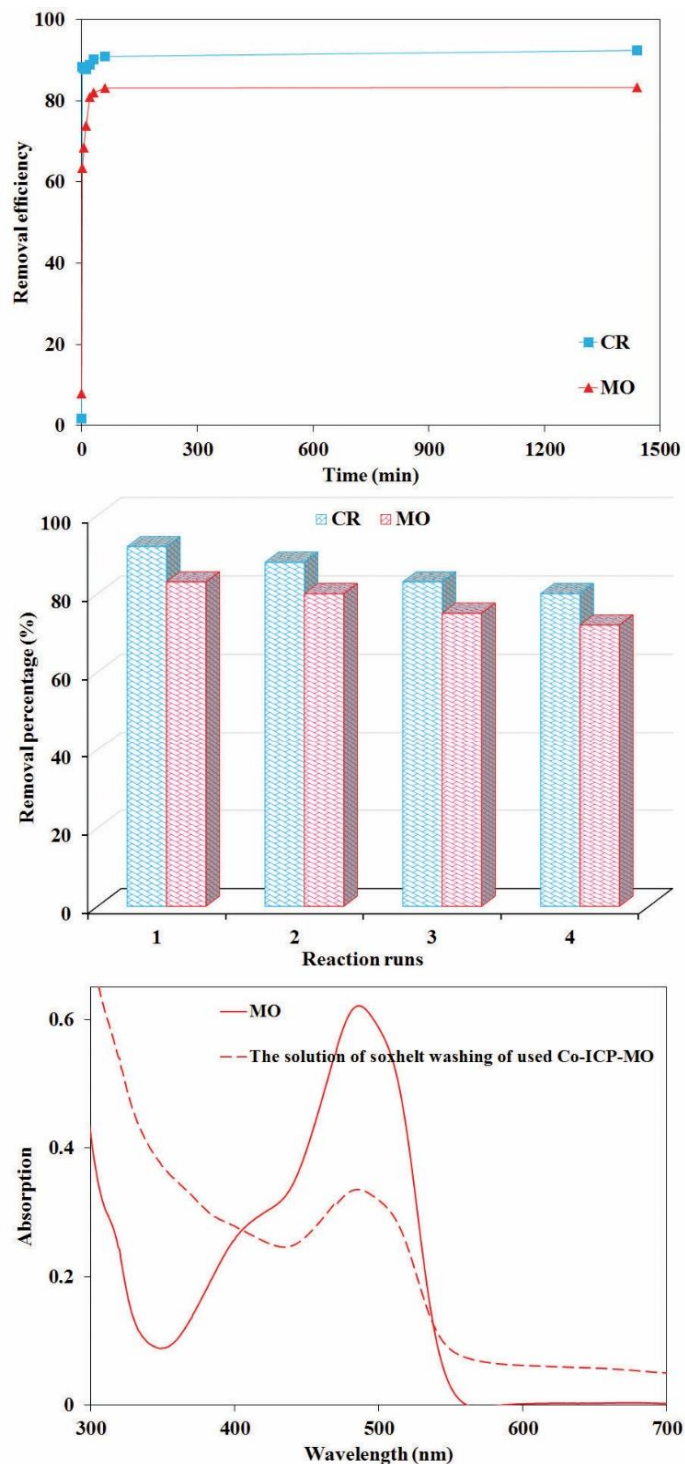


Fig. 6. (a) Removal efficiency of 20 ppm dyes (CR or MO) solutions by Co-ICP adsorbent, (b) reusability of Co-ICP adsorbent for removal of 20 ppm solution of CR or MO after 24 h, and (c) the UV-Vis spectra of fresh MO and the solution obtained after soxhlet washing of used Co-ICP adsorbent.

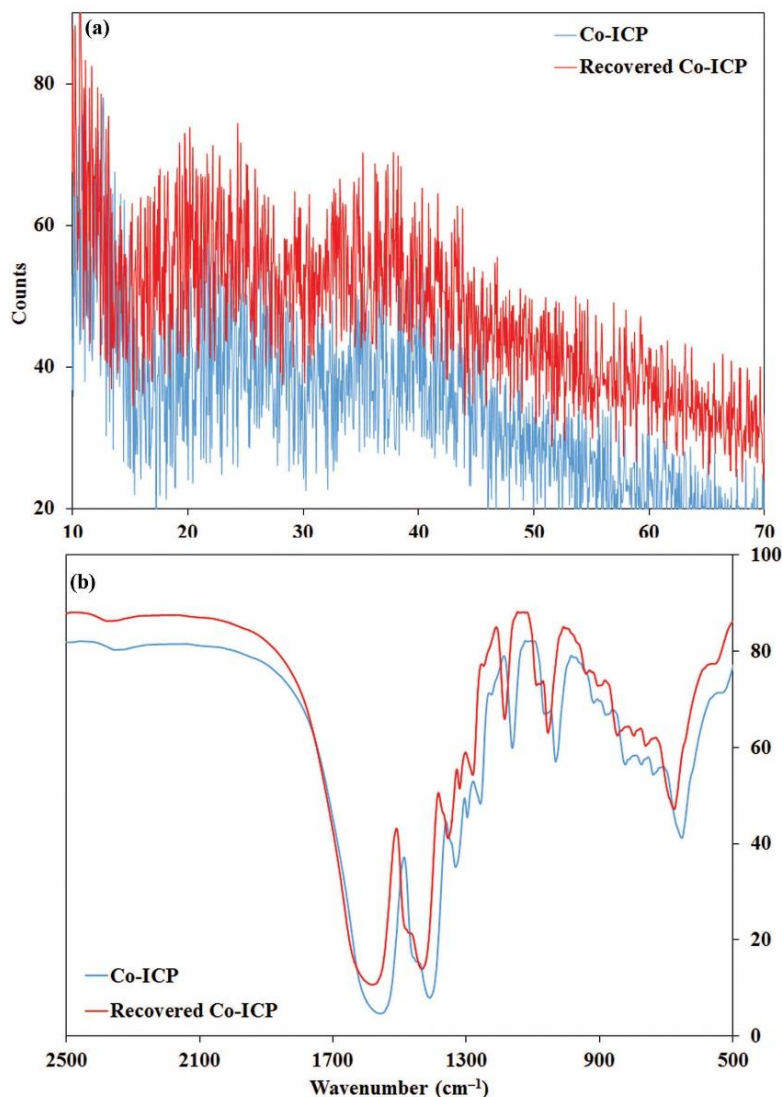


Fig. 7. XRD pattern (a) and FT-IR spectra (b) of the Co-ICP and recovered Co-ICP after soxhlet washing.

and 63% after 2 min for CR and MO, respectively, confirm the high performance of Co-ICP for adsorption of anionic dyes. The zeta potential analysis indicated zeta potential value of +26.9 eV for the synthesized Co-ICP. So, higher negative charge of the CR (-2) compared to MO (-1) can be accounted for higher adsorption of CR which reveals the effect of dye charge on the adsorption process.

Table 1 compares the results of current work with some previously reported adsorbents to display the Co-ICP efficiency in dye adsorption. As seen, the removal

efficiency of Co-ICP is comparable and somewhere notably more than listed adsorbents in Table 1.

Recovery and reusability of the adsorbent is one of the major factors essential for industrial-based adsorption systems. So, the used Co-ICP was recovered *via* soxhlet washing with H₂O for 24 h, characterized by XRD and FT-IR analyses (Fig. 7), and reused for CR and MO adsorption in the same conditions. The results presented in Fig. 6b indicate that Co-ICP can be reused at least four times without major loss of its efficiency.

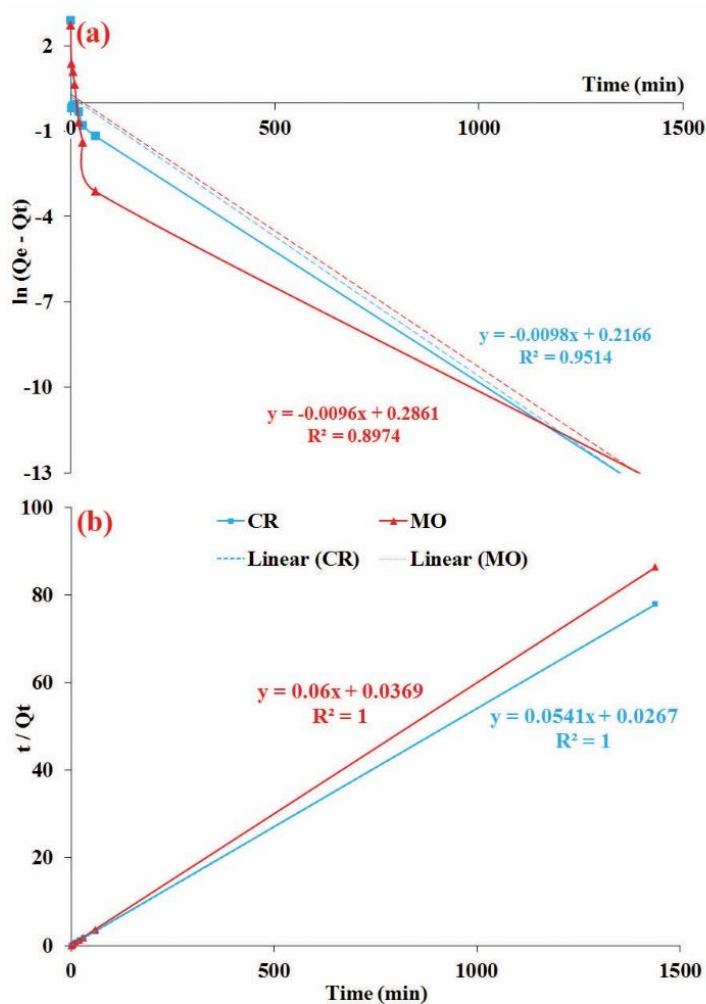


Fig. 8. Model fits of the experimental data with (a) pseudo-first-order and (b) pseudo-second-order kinetics models for CR and MO adsorption onto Co-ICP.

Table 2. Kinetics Parameters for CR and MO Adsorption by Co-ICP

Dye	$Q_{e,exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (min^{-1})	$Q_{e,cal}$ (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$Q_{e,cal}$ (mg g^{-1})	R^2
CR	18.48	0.0098	1.24	0.9514	0.11	18.48	1
MO	16.66	0.0096	1.33	0.8974	0.097	16.67	1

For examining the dye adsorption or degradation role of the Co-ICP, the Soxhlet washing solution of used Co-ICP in MO adsorption was concentrated and analyzed by UV-Vis spectroscopy. The UV-Vis spectrum represents the similar absorption peaks for Soxhlet washing and fresh MO solutions which approves the adsorption role of Co-ICP in this experiment (Fig. 6c).

Two common kinetics models *i.e.* pseudo-first-order and pseudo-second-order models [49], were used to evaluate the dye adsorption kinetics, as described by the following Eqs. (3) and (4):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

where t is the adsorption time (min), Q_t and Q_e (mg g^{-1}) are the dye concentrations at time t and at equilibrium, respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively. For pseudo-first-order kinetics model, by plotting $\ln(Q_e - Q_t)$ vs. time, the k_1 and Q_e are calculated from slope and intercept, respectively. Also, in pseudo-second-order kinetics model, k_2 and Q_e can be determined from the intercept and slope of t/Q_t against time. The fitting curves in Fig. 8 show that the pseudo-second-order kinetics model, with regression coefficient equal to 1, very well demonstrated the kinetics of the CR and MO adsorption onto Co-ICP, whereas the pseudo-first-order model with low regression coefficient cannot describe properly the adsorption kinetics [11,50-52]. The experimental and calculated value of the kinetics parameters based on these two models at Table 2 demonstrated that the obtained Q_e values from the pseudo-second-order fitted better with the experimental data compared to pseudo-first order.

CONCLUSIONS

Cobalt-based coordination polymer (Co-ICP) was synthesized by precipitation method using glutaric acid and cobalt acetate as organic linker and metal node, respectively. The obtained Co-ICP adsorbed just anionic

dyes due to its positive surface charge. The results of dye removal experiments showed that the Co-ICP exhibited more efficiency in the CR removal probably due to the higher negative charge of the CR relative to MO. Dye removal process followed pseudo-second order kinetics model with higher k_2 for CR. The prepared Co-ICP showed high reusability and stability over four cycles.

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