

Sonochemical Removal of Highly Toxic Aqueous Cd²⁺ and Cr⁶⁺ Ions Using Dandelion-like Co₃O₄ Nanoflowers

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Abstract –In this work, cobalt(II/III) oxide (Co₃O₄) nano/microflowers were practically synthesized in laboratory conditions. Adsorbance properties of the nanoflowers were investigated for the removal of cadmium and chromium heavy metal ions. To assess the chemical and morphological characteristics of Co₃O₄ nanoflowers, Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry (XRD), field emission electron microscopy (FESEM), Energy dispersive spectroscopy (EDS), and was used. To determine the adsorbance mechanism in detail, eluent concentration, eluent type, solution pH, adsorbent amount, solution volume, and adsorption duration were studied. In these assessments, flame atomic absorption spectroscopy (FAAS) was used. For Cr⁶⁺, adsorption optimum parameters were determined as 3M HNO₃, pH 6.5, 150mg, 30mL, 60min. For Cd²⁺, optimum parameters were determined as 3M HNO₃, pH 6.0, 100mg, 10mL, 30min. Co₃O₄, nanoflowers are eco-friendly adsorbent materials for the adsorption of Cd⁶⁺ and Cd²⁺ heavy metal ions since the production method is affordable and practical.

Keywords: Co₃O₄ Nanoflowers; Solid phase extraction; FAAS; Cr⁶⁺; Cd²⁺

Yüksek Toksisiteye Sahip Cd²⁺ and Cr⁶⁺ İyonlarının Karahindiba Şeklindeki Co₃O₄ Nanoçiçek Yapılar Kullanılarak Sonokimyasal Yöntemle Sudan Ayrıştırılması

Öz - Bu çalışmada, hidrotermal yöntem ile kobalt(II/III) oksit (Co₃O₄) nano/mikroçiçek yapılar laboratuvar şartlarında pratik bir şekilde sentezlendi. Krom ve kadmiyum gibi ağır metal iyonlarının uzaklaştırılması için bu nanoflowerların adsorban olarak uygulanması araştırıldı. Co₃O₄ nanoçiçeklerinin, morfolojik analizi ve kimyasal bileşimini karakterize etmek için X ışını kırınım analizi (XRD), alan emisyonlu taramalı elektron mikroskopisi (FESEM), enerji dağılım X-ışınları spektroskopisi (EDS) ve FTIR teknikleri kullanılarak gerçekleştirildi. Adsorpsiyon sisteminin optimum koşullarını belirlemek amacı ile elüent derişimi ve türü, çözeltinin pH'ı, adsorban miktarı, çözelti hacmi ve adsorpsiyon süresi gibi parametrelerin etkisi incelendi. Elde edilen çözeltide metal iyonlarının alevli atomik adsorpsiyon spektrometrisi (FAAS) analiz sonuçları doğrultusunda optimumum parametreler belirlendi. Bu parametre sonuçları sırasıyla Co₃O₄ nanofloweri ile Cr⁶⁺ için 3 M HNO₃, pH 6.5, 150 mg, 30 mL, 60 dk; Cd²⁺ için 3 M HNO₃, pH 6.0, 100 mg, 10 mL, 30 dk olarak bulundu. Co₃O₄ nanoçiçekleri; adsorpsiyon kapasitelerinin yüksek olması, kolayca sentezlenebilir ve imalat maliyetlerinin nispeten düşük olmasından dolayı krom, kadmiyum ve diğer ağır metal iyonlarının sulu sistemlerden uzaklaştırılmasında verimli ve çevre dostu adsorbanlar olabileceklerini göstermektedirler.

Anahtar kelimeler: Co₃O₄ Nanoçiçekler; Katı faz ekstrasyonu; FAAS; Cr⁶⁺; Cd²⁺

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1. Introduction

Heavy metals were detected different water sources around the world, and they can be used in different industrial products including dyes, pharmaceuticals, personal hygiene products, etc [1, 2]. Contamination of fresh waters and aquatic systems by heavy metals is becoming an emerging problem for the world. Such contaminated waters could include different heavy metal ions such as Hg(II), Pb(II), Cr(VI), Cd(II), and Ni [2]. Such heavy metal ions were found to be toxic and can be dangerous to marine life and aquatic animals [3–5]. Different research illustrates that, several unit operations such as adsorption, membrane filtration, chemical precipitation, coagulation - flocculation and floatation, ion exchange, or liquid-liquid extraction can be utilized to separate heavy metals from the samples [5–8]. Among those, adsorption is a common method where a low cost, selective, reusable and simple application was promised [5–8].

Recently, various materials like activated carbon, activated alumina, clay, zeolite, etc. were used for the removal of heavy metal ions [5–8]. However, such materials have limited adsorption capacity and some of them are not reusable. On contrary, metal oxide nanostructures have outstanding adsorption capacity due to their high surface/volume ratio and well-defined surface morphology [9]. Therefore, they found to be promising materials as next generation adsorbent materials.

Nanostructures are becoming attractive materials for the people from different areas since they can be applied to semiconductors and different technological applications due to their interesting chemical and physical properties with outstanding morphology [10]. Recently, three dimensional (3D) nanostructures with well-defined morphologies increases their popularity [11, 12]. Among those, nanoflowers in fiber, tube and flake forms are becoming popular due to their unique structural characteristics [11]. Co₃O₄ nanoflowers are a special kind of nanoflowers with magnetic characteristics which can be used in magnetic applications, gas sensor applications, catalysis applications, etc. [13] Different groups around the world tries to produce Co₃O₄ nanostructures in 3D; some of them managed to produce nanospheres, nanocubes, nanorodes using physical and chemical methods [10]. For this purpose, different production methods like solvothermal synthesis, chemical spray pyrolysis, chemical vapor deposition, sol-gel hydrothermal synthesis, simple precipitation, etc. were reported [14–18]. Hydrothermal synthesis could be used in the production of inorganic or organic/inorganic (hybrid) nanomaterials and/or nanocomposites. While other methods are having different drawbacks like high calcination temperature, toxic reactants, long reaction durations, multiple reaction steps and low production efficiency, hydrothermal synthesis provide affordable and reliable experimental media. Hydrothermal method is a highly efficient production process with minimum production cost which enables researchers to control nanostructure morphology. The method also provide good nanostructure size and shape control [19].

In this work, heavy metal adsorption potential of Co₃O₄ nanoflowers, which were previously reported by our group [20], were investigated for the recovery of chromium and cadmium in sea water (SRM) sample. Co₃O₄ nanoflowers used in the investigation were produced using hydrothermal synthesis method. Structural characterization of the nanoparticles was performed using various characterization techniques such as FESEM, XRD, FTIR and EDS. Then, Cr⁶⁺ and Cd²⁺ heavy metal ion recovery potential of the nanoflowers were assessed. Adsorption processes were optimized where influence of different parameters like eluent type, eluent concentration, pH, adsorbent amount, solution volume adsorption duration, etc. on adsorption characteristics were studied. Analytical recovery activity was also assessed regarding the analysis result of metal ions obtained from flame atomic absorption spectroscopy (FAAS) (See Figure 1).

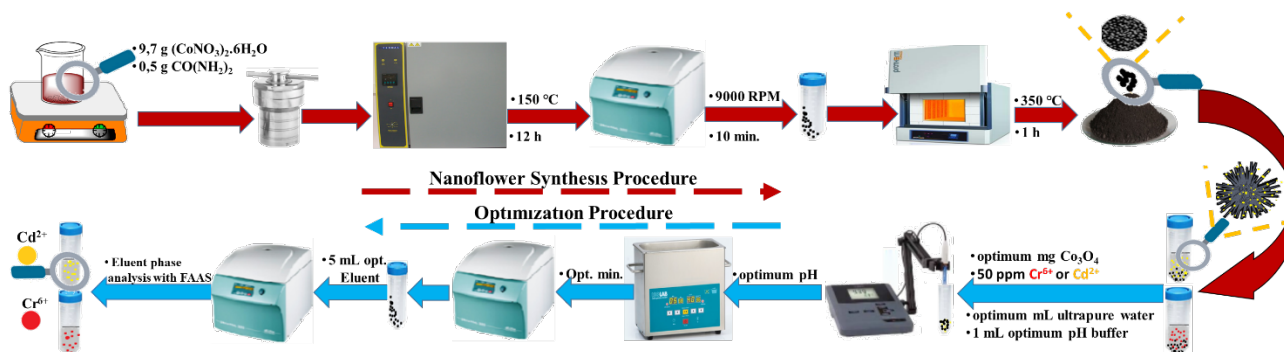


Figure 1. Schematics illustrate the production and investigation process followed in this work.

2. Materials & Methods

2.1. Spectroscopic and crystallographic investigation.

X-ray diffraction investigations were employed using RIKAGU diffractometer. Scanning was conducted between 10 and 90 degrees. Scanning electron microscope used in the structural investigation is FEI Quanta 400F supported with EDS (energy dispersive X-ray spectroscopy). Brunauer–Emmett–Teller (BET) investigation was performed using Quantachrome Nova 4000E. The infrared spectrum was recorded by a JASCO FTIR-6700 spectrometer between wavelengths of 400 and 4000 cm^{-1} . The FAAS investigation was performed using Agilent 240 AA Duo AAS. Cr^{6+} and Cd^{2+} heavy metal ions were assessed using Agilent hollow cathode lamps. Parameters used for the determination of metals are presented in Table 1.

Table 1. Parameters used in the FAAS analysis for the determination of metals

	Cr^{6+}	Cd^{2+}
Air Flow; mL/min	-	13.5
Slit Width (nm)	0.2	0.5
Lamp Current (mA)	7.0	4.0
Acetylene Flow	6.80	2.00
Used Flame	$\text{N}_2\text{O}/\text{Acetylene}$	Air/Acetylene
Wavelength (nm)	357.9	326.1
N_2O flow; mL/min	10.00	-

All chemicals utilized during the experimental process were analytical level (Merck quality). Ultra-pure water (ELGA, 18.2 $\text{M}\Omega\text{ cm}$) is used in the whole experimental process.

For standard metal solution, 1000 mg/L stock solutions (NIST standard) were used. 3; 2; 1; 0.5; 0.25; 0.1; and 0.05 mg/L solutions were prepared from standards of Cr^{6+} and Cd^{2+} which were prepared by dissolving 0.2 M HNO_3 . They were scanned by FAAS.

2.2. Production of Co_3O_4 nanoflowers

Co_3O_4 nanoflowers were synthesized using hydrothermal method in the lab regarding our previous recipe which was reported in our previous papers [20]. In the synthesis process 9.7 gr of cobalt nitride hexahydrate ($\text{Co}(\text{NO}_3)_2.6\text{H}_2\text{O}$) and 0.5 gr of urea $\text{CO}(\text{NH}_2)_2$ were stirred in 35 mL of deionized pure water for 1h. Solution was placed into the Teflon autoclave. The autoclave was placed in oven for 12 h at 150 °C. 12 h later autoclave was taken and left for cool. The solution was then centrifuged and several times to collect the precipitate in the solution. Precipitate was washed a couple of times using ethanol and deionized water. The precipitate was transferred to the oven set at 80°C and kept there for 24 hours. Precipitate was then transferred to the ash furnace at 150°C; the temperature of the furnace was increased step by step where 2°C/1 min step increase rate was employed. When the

temperature reach 300 °C, precipitate was kept there for 1 h whereas the calcinated Co₃O₄ nanoflower powder was obtained [20, 21].

2.3. Solid phase extraction methodology

50 mL of falcon tubes were used for the optimization of eluent type, eluent concentration, pH, sample amount, eluent volume and application time where optimum conditions for the removal of Cr⁶⁺ and Cd²⁺ metal ions were determined.

Standard experimental procedure is as follows:

50 mg of nanoflower was placed in 50 mL falcon tube where 10 mL deionized water containing 0.25 mL (50 ppm) heavy metal ion and 1 mL of buffer solution (pH: 6.0) was added. Solution pH was set to pH: 6.0 by adding 0.01M NaOH and 0.01 M HCl. The solution was topped up with ultra-pure water and set to 25 mL. After 10 mins of sonication, the solution was centrifuged at 9000 rpm for 10 mins. Liquid phase was kept for analysis; 5 mL of acid solution was added to the solid phase. Samples were sonicated for 10 mins and centrifuged at 9000 rpm for 10 mins. The second liquid phase was also kept. Each step was repeated for Cr⁶⁺ and Cd²⁺ heavy metal ion concentration.

For the eluent optimization steps of 0.1-1-2-3 M HNO₃ and 1M of HCl were studied. For pH optimization, pH values of 5, 5.5, 6, 6.5, 7, 7.5 and 8 were studied. For adsorbent amount, 50 mg, 100 mg, 150 mg and 200 mg of Co₃O₄ nanoflower amounts were studied. For the fluent volume study, activity in 5 mL, 10 mL, 20 mL and 30 mL pure water was assessed. For the optimization of sonication duration, 5 mins, 10 mins, 30 mins and 60 mins were studied.

2.3.1 Analysis of real samples: NRC-CNRC certified sea water was assessed for the validation of SRM (standard reference material) where standard addition method was used in the assessment. Before the analysis, 0.5 g of solid sample was taken and 5 mL of HNO₃:H₂O₂ (2:1, h/h) were added on them. Wet samples were placed in shaker water bath and kept at 50°C until the samples get dry. For liquid phase samples, samples were centrifuged at 9000 rpm for 20 mins liquid phase was evaporated until samples totally dry. 4.5 mL standard sea water and 0.5 mL HNO₃ solutions were dried at shaker water bath at 50°C.

Table 2. The chemical properties of synthetic natural water.

Concentration	
pH	8.0
Zn	0.200 ± 0.003
Na	9.00 ± 0.01
Ca	40.9 ± 0.3
Mn	0.200 ± 0.001
K	7.50 ± 0.02
Fe	0.200 ± 0.001
Cu	0.050 ± 0.002

2.3.2 Validation of Method-Analytical Performance: RSD (relative standard deviation), LOD (limit of detection), calibration equation, LOQ (the limit of quantification) and linear regression were defined. Determined values were illustrated in Table 3. The LOD and LOQ were calculated as three times the standard deviation (S.D.) (3σ) and (10σ) of the blank signal. The applied method had been confirmed by NRC-CNRC SRM (NASS-6) (Table 5). The method was also employed to the real seawater (see the Table 6). Moreover, the EF (enrichment factor) was assessed by the formula below [22–25] :

$$EF = \frac{Q_T}{Q_M} \cdot \frac{Q_T^0}{Q_M^0} \quad (1)$$

Table 3. Optimum conditions for Cr^{6+} and Cd^{2+}

	Cr^{6+}	Cd^{2+}
Eluent type,	3 M HNO_3	3 M HNO_3
Correlation coefficients (R2)	0.9985	0.9991
Linear regression ($y=ax+b$)	$0.0229x - 0.0006$	$0.0187x - 0.002$
LOD, $\mu\text{g/L}$	0.6	1.8
LOQ, $\mu\text{g/L}$	2	6
RSD%	0.2-9.7	0.7-9.2
Amount of nanoflower, mg	150	100
Sonication time, min	60	30
Enrichment factor, fold	6	2
Sample volume, mL	30	10
pH	6.5	6.0

3. Results and Discussions

3.1. Characterization of Co_3O_4 nanoflowers

Co_3O_4 nanoflowers were produced using hydrothermal synthesis, nanoparticles were then analyzed using FTIR, XRD, FESEM, and EDS methods. Figure 2 illustrates FTIR spectrum of Co_3O_4 nanoflowers between 400 and 4000 cm^{-1} . Straight line illustrating the band between 665 and 575 cm^{-1} illustrate $\nu(\text{Co-O})$ tension graph occurs due to Co_3O_4 structure. The large band observed 3400 cm^{-1} belongs to O-H tension vibration of hydroxyl groups originated from adsorbed water molecules [20].

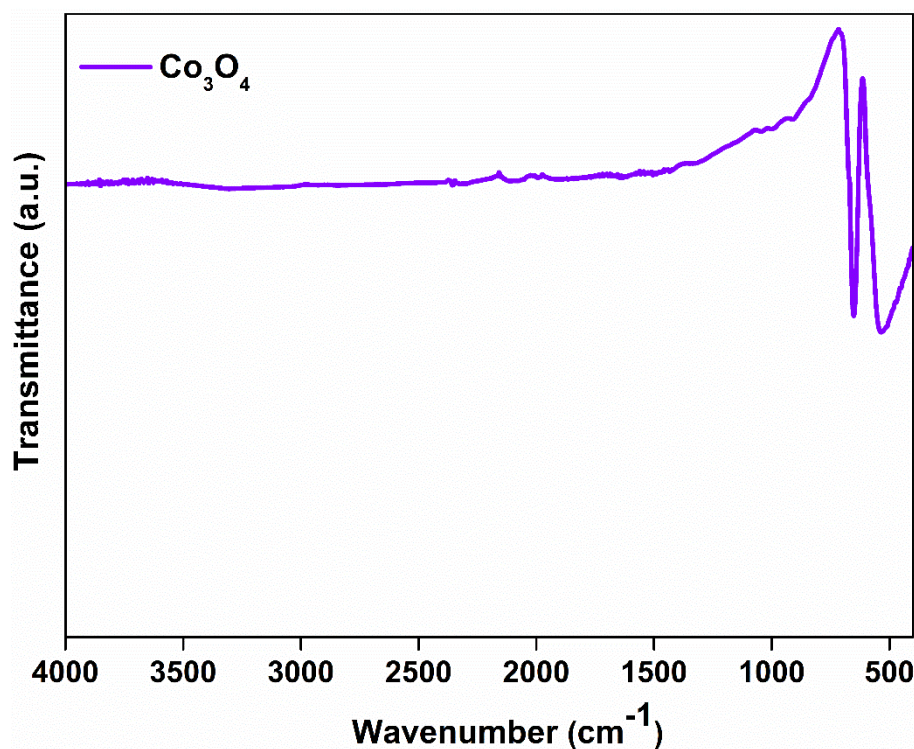


Figure 2. FTIR spectrum of Co_3O_4 nanoflowers.

XRD patterns of Co_3O_4 nanoflowers were presented in Figure 3 where diffraction pattern was plotted in purple color. It was seen that there are various peaks which indicate different types of crystal formations. Peaks at 19.0° , 31.3° , 36.8° , 38.5° , 44.8° , 55.6° , 59.4° , 65.2° , 77.3° degrees were observed; such peaks are corresponding to face centered cubic crystal structures in (111), (220), (311), (222), (400), (422), (511), (440) orientation. Sharp peaks observed in crystal diffraction pattern correspond to face centered cubic crystal formation [20]. It illustrates that the production method can

produce pure crystals in stable crystal type. Therefore, no different types of crystal formation were observed.

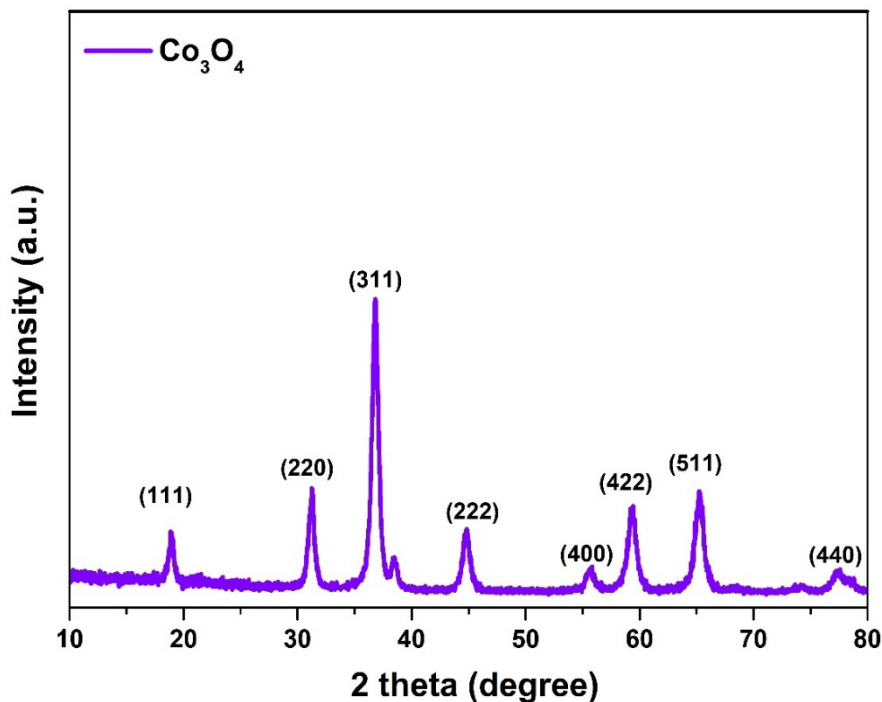


Figure 3. XRD diffraction pattern of Co_3O_4 nanoflowers

FESEM images of nanoflowers were illustrated in Figure 4. In Figure 4, different images were presented. The image on the left illustrates a larger scaled version where different nanoflowers can be seen all of which are in flower form. In the image in the right zoomed version was presented. Co_3O_4 nanoflowers contain fiber like structures that come together and form a dandelion like structure. Nanofibers in the nanoflowers are pointing out such a case enhances the surface area/surface volume rate and porosity. Such a case enables us to obtain enhanced adsorption capacity with outstanding electronic and catalytic activity.

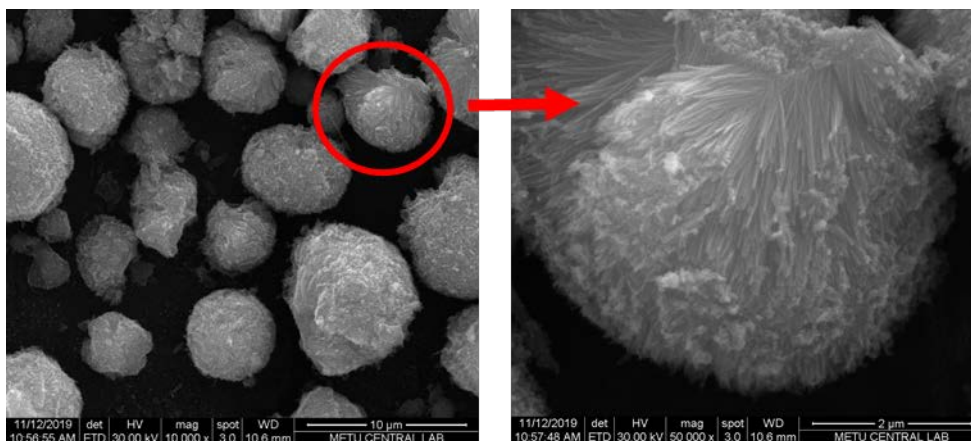


Figure 4. FESEM images of Co_3O_4 nanoflowers.

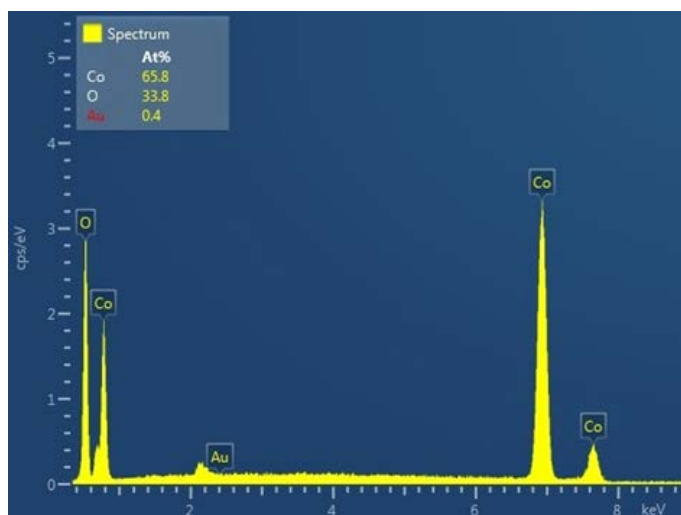


Figure 5. EDS spectra of Co_3O_4 nanoflowers [20].

EDS spectra were presented in Figure 5. Elemental analysis was performed using EDS apparatus of FESEM. Apparent Co and O related peaks could be addressed in the spectra. EDS spectrum confirmed that nanoflowers consisted of Co and O atoms where no residual distortion peaks were seen in the spectra.

Surface area of the nanoflowers were investigated using BET analysis. The surface area of the nanoflowers was measured as $50.73 \text{ m}^2\text{g}^{-1}$. The average pore volume was found to be 168.9913 \AA and the average pore width was determined as 165.819 \AA . Measured surface area was found to be consistent with the results reported for Co_3O_4 nanoflowers in the literature [26, 27]. N_2 adsorption – desorption BET isotherms were presented in Figure 6.

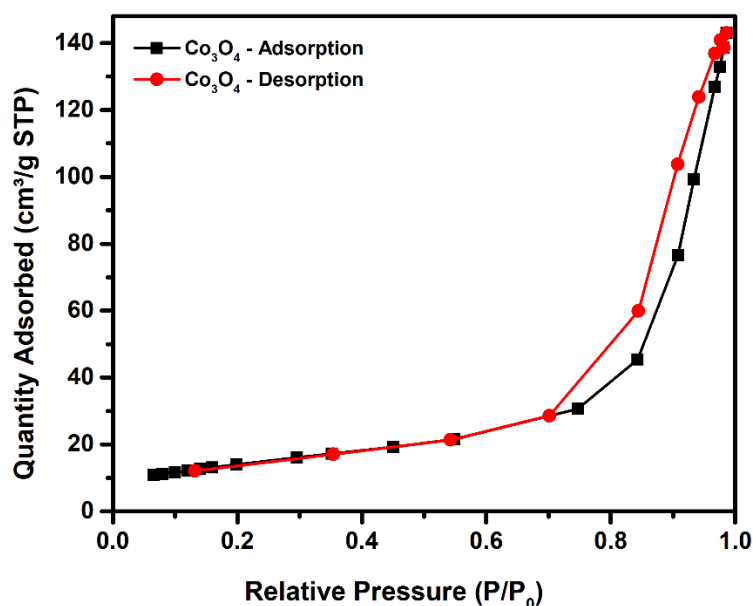


Figure 6. N_2 adsorption – desorption BET isotherm plots of Co_3O_4 nanoflowers.

3.2. Removal of heavy metal ions (Cr^{6+} , Cd^{2+})

3.2.1 Effect of eluent type: To promote the influence between Co_3O_4 nanoflowers and Cr^{6+} , Cd^{2+} heavy metal ions in aqueous media, sonication was employed to the solution. Samples were sonicated at room temperature for 10 mins. After the sonication, centrifugation process was held at 9000 rpm for 10 mins. To assess the Cr^{6+} , Cd^{2+} content, AAS investigation was employed to the filtered supernatants. Eluent type influence for the Co_3O_4 nanoflowers based recovery of Cr^{6+} , Cd^{2+} metal ions were investigated for 1 M HCl and 0.1 M HNO_3 , 1 M HNO_3 , 2 M HNO_3 , and 3 M HNO_3 . Results

were illustrated in Figure 7. Co_3O_4 nanoflowers successfully recovered the 99.7% and 92.8% for 3 M HNO_3 for Cr^{6+} and Cd^{2+} respectively.

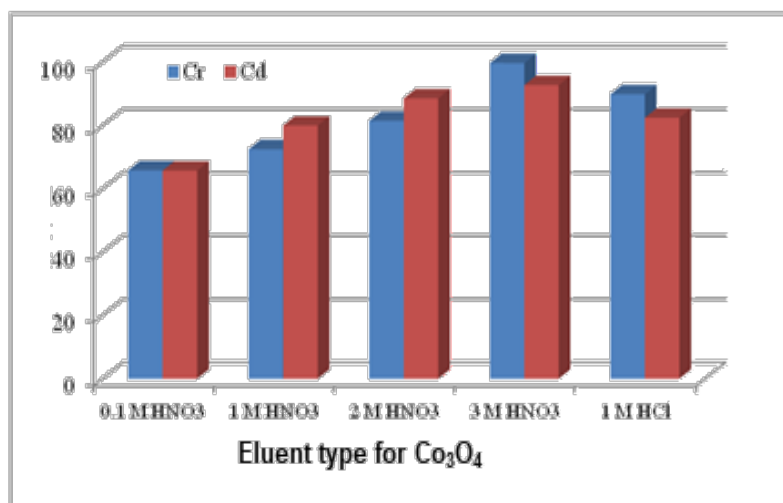


Figure 7. The effect of eluent on Cr^{6+} , Cd^{2+} ion removal.

3.2.2. Effect of pH: pH value has a significant effect on metal ion solubility. Therefore, pH is an important parameter affecting the recovery rate of heavy metals. Thus, pH is an essential parameter that addressed in the recovery studies. Hence, effect of pH on Cr^{6+} , Cd^{2+} heavy metal ion removal in the existence of Co_3O_4 nanoflowers was investigated. pH related Cr^{6+} , Cd^{2+} metal removal rate was illustrated in Figure 8. By scanning between pH 5.5 and 8.0, the pH value with maximum recovery was determined as 6.5 and 6.0 optimum for Cr^{6+} and Cd^{2+} , respectively. Removal percentage starts to decrease by pH 6.0 and 6.5 for Cr^{6+} and Cd^{2+} , respectively. Maximum removal rate for Cr^{6+} and Cd^{2+} were obtained as 97.8% and 93.6%, respectively. We concluded that Cr^{6+} and Cd^{2+} metal ions prefer a soft acidic condition for optimum recovery process.

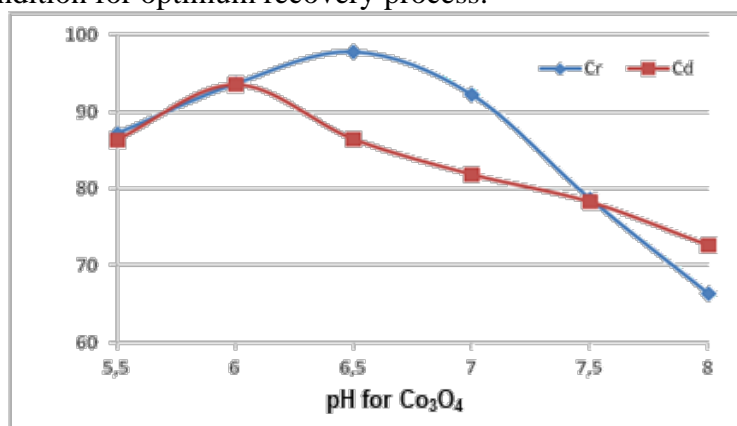


Figure 8. The effect pH for the removal of Cr^{6+} , Cd^{2+} ions

3.2.3. Effect of adsorbent amount: Optimization of Co_3O_4 nanoflower adsorbent amount is a critical parameter for not to overuse the adsorbents. The graph presented below shows recovery percentage of Cr^{6+} and Cd^{2+} ions. Heavy metal ions removal rate depending on nanoflower concentration was illustrated in Figure 9. The best recovery rates for Cr^{6+} and Cd^{2+} were achieved as 99.0% and 96.3% with 150 mg Co_3O_4 and 100 mg Co_3O_4 , respectively.

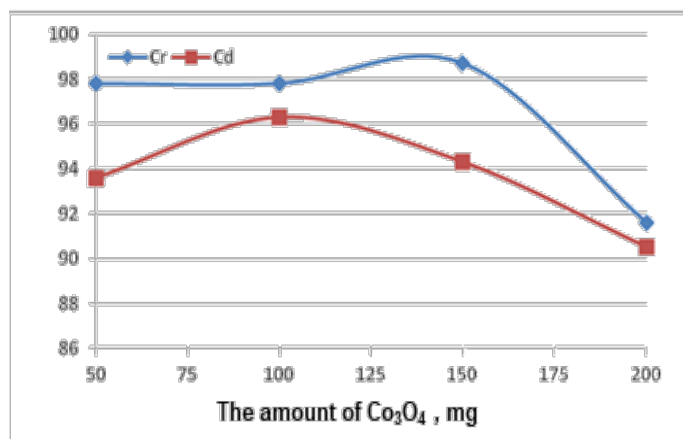


Figure 9. The effect of nanoflower dosage on Cr^{6+} , Cd^{2+} heavy metal ion recovery.

3.2.4. Effect of solvent volume: The plot in Figure 10 illustrates the solvent volume effect on removal rate of Cr^{6+} and Cd^{2+} in the presence of Co_3O_4 . To investigate the influence of solvent volume on removal rates, different volumes 5 mL, 10 mL, 25 mL, 20 mL and 30 mL were studied. The max removal rate for Cr^{6+} and Cd^{2+} were found to be 99.0% and 97.8% with 30 mL and 10 mL, respectively.

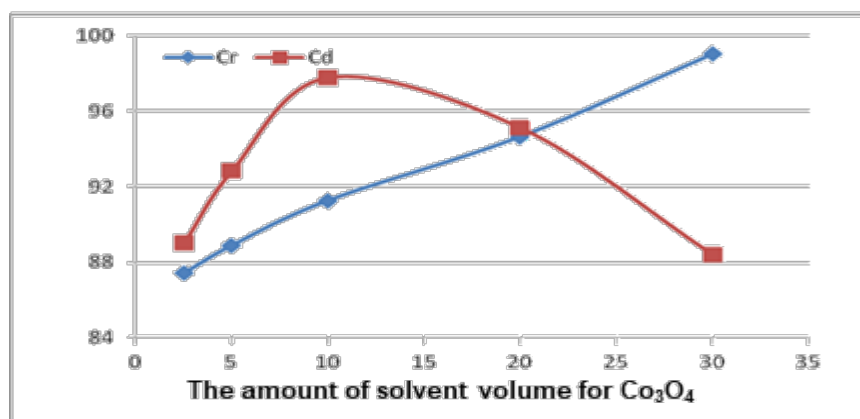


Figure 10. The effect of solvent amount for the removal of Cr^{6+} , Cd^{2+} ions

3.2.5. Influence of sonication duration: To speed up the nanoflower adsorption of metal ions, sonic vibration was applied to samples. To assess the sonication effect on the removal rate of Cr^{6+} and Cd^{2+} , various sonication time periods were studied like 5 mins 10 mins, 15 mins, 20 mins, 30 mins, and 60 mins. Plots showing the effect of sonication duration on removal rate of Cr^{6+} and Cd^{2+} were illustrated in Figure 11. The graph shows that the optimum removal duration was obtained at 30 mins. The recovery percentage increased gradually till 30 mins of sonication, after that recovery percentage starts to diminish. Removal percentages at 30 mins of sonication is 98.6% and 98.7% for Cr^{6+} and Cd^{2+} , respectively.

3.2.6 Repeatability: In the extraction time optimization, the last remaining solid phase was washed several times using pure water. The optimum conditions were repeated 6 times and the residue was analyzed using FAAS. Results were presented in Table 4. The table clearly illustrates that matrix ions affect the recovery of heavy metal ions. All in all, recovery rates were found to be quite high. Therefore, the presented procedure is able to recover heavy metal ions from the aqueous media and could be used in enrichment applications.

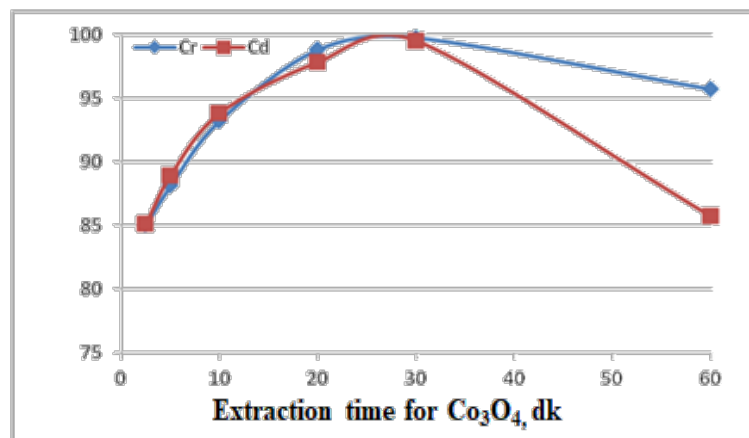


Figure 11. The effect of sonication time for the removal of Cr⁶⁺, Cd²⁺ ions.

Table 4. Influences of matrix ions on the recoveries of Cr⁶⁺ and Cd²⁺ (N = 3)

Ions	Added as	Concentration (mg/L)	Cr ⁶⁺	Cd ²⁺
Na ⁺	NaCl	500	97 ± 2	97 ± 3
K ⁺	KCl	150	95 ± 3	95 ± 3
Ca ²⁺	CaCl ₂	150	96 ± 2	96 ± 2
Mg ²⁺	MgCl ₂	100	97 ± 3	99 ± 1
Na ⁺	NaCl	500	97 ± 2	97 ± 3
Cu ²⁺	Cu(NO ₃) ₂	5	97 ± 3	97 ± 3
Fe ³⁺	Fe(NO ₃) ₂	0.5	98 ± 3	97 ± 3
Mn ²⁺	Mn(NO ₃) ₂	0.5	99 ± 1	98 ± 3
Zn ²⁺	Zn(NO ₃) ₂	1	95 ± 2	96 ± 2
Ni ²⁺	Ni(NO ₃) ₂	0.2	97 ± 2	98 ± 2
Pb ²⁺	Pb (NO ₃) ₂	0.2	97 ± 1	97 ± 2

3.2.7 Reliability of the method and nanoflowers enrichment application on real samples: To check the reliability of the method, results obtained using certified reference material (CRM) were presented in Table 5. These values were quantitative, and it shows that the presented procedure could be applied for the preconcentration of heavy metal ions in real samples. Our results were compared with similar works in literature. Results comparing our work with similar works was presented in Table 7.

Table 5. Analysis result of certified reference materials (N=3).

		Cr ⁶⁺	Cd ²⁺
Sea Water (SRM)	Certified Value (µg/L)	0.118 ± 0.008	0.0311 ± 0.0019
	Result, µg/mL	0,116 ± 0,008	0.0301 ± 0.0019
	Recovery, %	98.3 ± 0.9	96.8 ± 0.5

Results obtained after the application of nanoflowers for real samples in optimum conditions were presented in Table 6.

Table 6. Cr⁶⁺ and Cd²⁺ levels before and after from enrichment in various samples (N=3)

Ions	Before		After	
Sample	Cr ⁶⁺ , µg/L	Cd ²⁺ , µg/L	Cr ⁶⁺ , µg/L	Cd ²⁺ , µg/L
Sea Water	35.0 ± 2.1	2.2 ± 0.1	196 ± 9	622 ± 8
Bottled Water	ND	ND	367 ± 2	618 ± 11
Tap Water	ND	ND	231 ± 6	620 ± 11
Soda	ND	3.1 ± 0.2	262 ± 5	634 ± 9

Enrichment factor was Cr^{6+} and Cd^{2+} was determined as 200 fold and 560 fold, respectively. The method is found to be successful on real samples. The method is rapid as compared with previously reported procedures for the enrichment of heavy metal ions. The method is successfully used in the assessment of the ingredient materials.

Table 7. Works reported in the literature used for the removal of heavy metal ions

Materials	Element	Amount of adsorbent	Time	pH	Apparatus	Ref.
ZnO nanoparticles	Cr^{3+} , Co^{2+} , and Ni^{2+}	0.5 g	1.5 mins - 180 mins	2	UV-Vis	[28]
ZnO nanoflowers	Cd and Pb	0.8 g/L	100 mins	6.0	AAS	[29]
MgO nanoparticles	Cd and Pb	2294 mg/g for Cd(II) and 2614 mg/g for Pb(II)	30 min and 15 min for the adsorption of Cd(II) and Pb(II), respectively	2.0 and 3.0	Voltammetry	[30]
Nano-HAP composites	Cr (VI)	20 mg	10 mins	5.0	FAAS	[31]
Mf (magnetite that the modified with triethylenetetramine)-graphene oxide	Cr(VI) and Cr(III)	50 mg	10 mins and 30 mins of Cr(VI) and Cr(III), respectively	2.0 and 8.0 of Cr(VI) and Cr(III), respectively	FAAS	[32]

4. Conclusions

Today, heavy metal ions threatening the natural water sources. Therefore, reliable, and affordable methods are important to fight against this problem. Nanoparticles may have high adsorption rates due to their structural properties and they can be mass produced using conventional methods. Hence, flower-like Co_3O_4 nanostructures were produced using hydrothermal synthesis method and heavy metal removal rates were checked in this work. Structural characteristics of the nanoflowers were assessed using different microscopic and elemental methods. Methods confirmed that nanoflowers consisted of well-ordered Co_3O_4 crystals which are consisting of Co and O molecules. There was not any contamination related signal in EDS spectra. Co_3O_4 nanoflowers were then used for the recovery of Cr^{6+} and Cd^{2+} heavy metal ions. Numerous factors affecting the recovery of heavy metal ions such as pH, eluent type, eluent concentration, adsorbent amount, solution volume and adsorption duration were studied. The optimum conditions to obtain max recovery rate were determined. It was seen that our nanoparticles managed to remove almost 99.0% of Cr^{6+} and Cd^{2+} heavy metal ions. The case was also tasted in real samples where sea water, bottled water, tap water and soda were used. It was seen that our nanoflowers perform similar characteristics where 99.2% of Cd^{2+} and 98.3% Cr^{6+} heavy metal ions were removed from real samples. Our result indicates that Co_3O_4 nanoflowers exhibit outstanding heavy metal removal performance for Cr^{6+} and Cd^{2+} metal ions. It illustrates that Co_3O_4 nanoflowers have potential to be used as a nanomaterial for the removal of heavy metal ions especially in aqueous media.

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