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Adsorption of chromium (VI) on bismuth incorporated cobalt ferrite nanoparticles

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Abstract: CoFe₂O₄ and CoFe_{1.9}Bi_{0.1}O₄ nanoparticles are prepared by combustion method utilizing glycine. Pure phase formation is affirmed from the X-ray diffraction and Fourier transform infrared spectroscopy. From the Scanning electron microscopy and Energy Dispersive X-ray spectroscopy, morphology and presence of respective elements in the synthesized compounds are analyzed. Decrease in average crystallite size and increase in lattice parameter is observed due to bismuth substitution. The adsorption capability of CoFe₂O₄ and CoFe_{1.9}Bi_{0.1}O₄ are tested for one of the toxic environmental pollutants chromium (VI). The adsorption efficiency with respect to adsorbent quantity, concentrations of adsorbate and pH are studied. The substitution of the bismuth increased the adsorption capability of cobalt ferrite nanoparticles.

1. Introduction

Cobalt ferrite (CoFe₂O₄) is significant due to interesting properties like high coercivity, chemical stability, catalytic activity and saturation magnetization [1]. Generally, the spinel oxides are represented by the formula AB₂O₄. Spinel oxide may be a normal spinel or inverse spinel depending on the occupancy of the ions in various sites (A - tetrahedral or B - octahedral). Cobalt ferrite is an example of inverse spinel, in which Co²⁺ ion occupies only B site, whereas both B and A sites are equally occupied by Fe³⁺ ions [2].

Cobalt ferrites are synthesized by several methods [3-7]. Recently researchers are envisioned on the combustion method of synthesis. This method has advantages such as, high purity, chemical homogeneity and crystallinity of the ferrites [8]. Exclusion of harmful metal ions such as chromium, cadmium, mercury and lead from the industrial waste water is one of the worldwide research interests because of the severity. Among these toxic metal ions, chromium induces the most severe environmental problem because of its release from electroplating, leather tanning and metal finishing industries into water. Among the two oxidation states of chromium metal ion, hexavalent chromium is more toxic than trivalent chromium [9] because the former is carcinogenic to living organism.

Hence, the removal of Cr (VI) - a toxic metal ion from wastewater is a crucial issue. Many methods are reported in the literature like ion-exchange, photocatalysis, filtration, electrochemical treatment techniques for the elimination of toxic metal ions from waste water [10]. Among these methods, adsorption is widely used methods due to its easy operation procedure and flexibility in design [11]. Adsorption executes on the basis of ion-exchange between chromium (adsorbate) and ferrite (adsorbent). Larger surface area, catalytic nature of nanomaterial, pore size and volume make them appropriate for adsorption. Many adsorbents such as chitosan, activated alumina, activated carbon, and zeolite are



reported for the removal of chromium (VI). But, the common problem associated with these catalysts is the separation of the catalyst from the solution which may enhance the operation cost. This problem can be avoided with the help of the magnetic adsorbent. Magnetic separation is the simple technique of removal of the adsorbent using the external magnetic field [12].

An enhanced magnetic property is reported for the bismuth substituted cobalt ferrite [13]. Cobalt ferrite, bismuth incorporated cobalt ferrite are studied as a catalyst for the conversion of 4-nitrophenol to 4-aminophenol recently [14]. Lanthanum doped and gadolinium doped cobalt ferrite are studied for adsorption of dyes from waste water [4,15]. However, bismuth incorporated cobalt ferrite has not been reported as an adsorbent for the elimination of Cr (VI) from wastewater. The objective of the current work is to prepare CoFe_2O_4 and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ by solution combustion method and to study their adsorption capacity for Cr (VI).

2. Experimental

2.1 Chemicals

Cobalt nitrate hexahydrate (97%), bismuth nitrate (98.5%), glycine (99.5%) from S.d. fine and ferric nitrate nona hydrate from HIMEDIA (98.0%).

2.2 Synthesis of bismuth substituted cobalt ferrite

Cobalt ferrite and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ were prepared by solution combustion method. Stoichiometric quantities of the reactants were weighed and dissolved in water. To the aqueous solution of cobalt nitrate, ferric nitrate and bismuth nitrate, aqueous solution of glycine (fuel) was added and heated on a hot plate. The concentrated solution mixture was kept in the preheated furnace (500°C) to undergo spontaneous combustion. The obtained fluffy product was ground well and calcined at 700°C for 2 h.

2.3 Characterization

Purity of the product was examined by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) (Bruker Advanced D8). Scherrer's formula was used to calculate the mean crystallite sizes of the samples and Fourier transform infrared (FTIR) spectra were recorded by KBr pellet method (Thermonicolet Avator 330 USA model) in the range $400\text{-}1500 \text{ cm}^{-1}$. ZESIS EVO18 SEM instrument was used to analyze the Surface morphology and Energy Dispersive X-ray spectroscopy (EDAX) of the compounds.

2.4 Adsorption of chromium (VI) from water

Batch mode studies were carried out to analyze the adsorption of Cr (VI) by CoFe_2O_4 samples. Stock solution of 1000 ppm of Cr (VI) solution was prepared by dissolving needed amount of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Double distilled water was used as the solvent. 0.2 g of the adsorbent was dispersed in 10 ml of 25 mg/L of chromium (VI) solutions which was adjusted to the acidic pH and alkaline pH using 0.1M HCl and dilute NaOH solution respectively. A UV-vis spectrometer was used to quantify the chromium (VI) concentration at 370 nm. The effect of quantity of the adsorbent, concentration of the adsorbate and effect of pH was studied. The Cr (VI) removal efficiency (R %) was calculated from the formula [16]

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

Co – Initial Cr (VI) concentration and Ce – Equilibrium concentration of Cr (VI)

3. Results and discussion

3.1 XRD analysis

Figure 1 shows the typical XRD pattern of prepared unsubstituted and bismuth incorporated cobalt ferrite. All diffraction peaks can be indexed to pure cubic phase of CoFe_2O_4 (JCPDS # 96-591-0064). No impurities are observed, which indicates the high purity crystalline cobalt ferrite formation⁴. The average crystalline size is calculated using Debye-Scherer formula [17]

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad (2)$$

Where $\lambda=0.15406 \text{ \AA}$, β is the full width half maximum, θ is the Bragg angle. The lattice parameter was calculated using this formula

$$a = d (h^2 + k^2 + l^2)^{1/2} \quad (3)$$

Where, a is lattice parameter, d is inter planner distance and hkl are miller indices. The calculated average crystalline size and lattice parameters are given in the Table 1. Decrease in the particle size and increase in the lattice parameter is observed by the incorporation of bismuth. The slight increase in lattice parameter by the substitution of bismuth content can be described on basis of the ionic radii. Bismuth ionic radius (1.03 \AA) is larger than iron (Fe^{3+}) (0.64 \AA). Therefore, the incorporation of Fe^{3+} by Bi^{3+} may cause the expansion of unit cell.

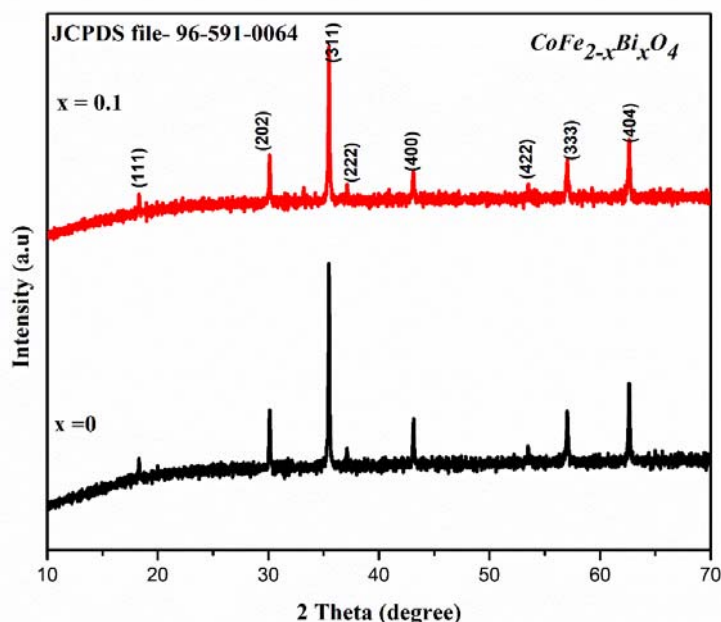


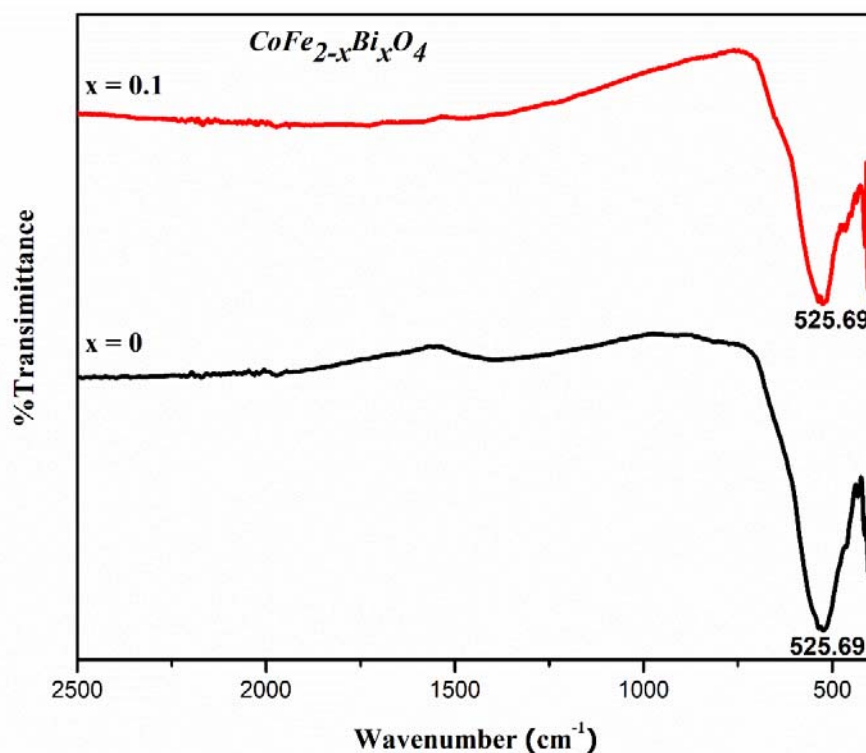
Figure 1. XRD diffraction pattern of $\text{CoBi}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0, 0.1$) nanoparticles

Table 1. Average Crystallite size and Lattice parameter of the synthesized $\text{CoFe}_{2-x}\text{Bi}_x\text{O}_4$

Sample (x)	Average Crystallite Size (nm)	Lattice parameter (\AA)
0	85.1040	8.3815
0.1	62.2400	8.3916

3.2 FT-IR analysis

FT-IR spectra of the compounds are given in Figure 2. The spinel structure is confirmed from the bands in the range $400\text{--}600\text{ cm}^{-1}$. The intrinsic stretching vibrations (ν_1) of the tetrahedral complex are observed in the range $529\text{--}536\text{ cm}^{-1}$. The stretching vibrations of octahedral complex (ν_2) are observed in the range $404\text{--}406\text{ cm}^{-1}$ are characteristic band of spinel structure [18]. Not much shift in the frequency is noted by the substitution of bismuth.

**Figure 2.** FTIR spectrum of $\text{CoBi}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0, 0.1$) nanoparticles

3.3 Morphological studies

The SEM micrographs and EDAX of CoFe_2O_4 and bismuth incorporated cobalt ferrite are given in Figure 3. Flakes like structure with large pores are noticed in both CoFe_2O_4 and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$. The chemical composition analyzed by EDAX is presented in Figure 3. EDAX shows the presence of the elements Cobalt, iron, bismuth and oxygen without any additional impurities.

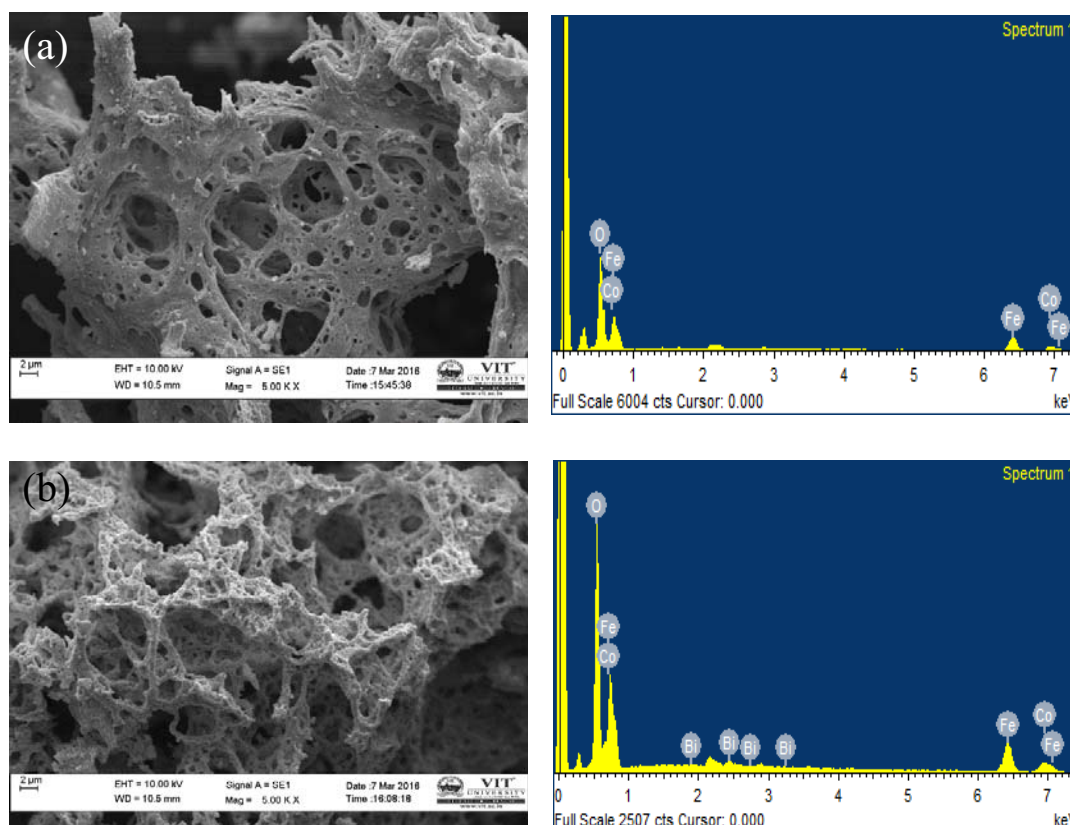


Figure 3. SEM-EDAX of a) CoFe_2O_4 b) $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ nanoparticles

3.4. Adsorption studies

3.4.1 Adsorption property of $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$

The theory of adsorption lies across the ion exchange between adsorbent and adsorbate. The adsorption efficiency of adsorbent depends on surface area of nanomaterial, pH, temperature, agitation time, concentration of the adsorbate and quantity of the adsorbent. From the literature, it is observed that adsorption efficiency of cobalt ferrite is lesser than another ferrite. A preliminary study is carried out to enhance the adsorption efficiency of cobalt ferrite by substituting bismuth ion. The parameters such as quantity of the adsorbent, pH, concentration of the adsorbate is optimized for both parent and bismuth substituted cobalt ferrite.

3.4.2. Effect of amount of adsorbent

Various amounts of CoFe_2O_4 and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ (25, 50, 100, 150 and 200 mg) are shaken well with 10 ml of 25 ppm Cr(VI) solution for 1 hour at 250 RPM in order to study the effect of the adsorbent. After the magnetic separation of the ferrite particles, the solution was examined for Cr(VI) by means of UV-spectrophotometer at 370 nm. Removal of Cr(VI) increases with increase of quantity of adsorbent in both the cases (Figure. 4 and Figure. 5). Maximum adsorption efficiency is observed with 200 mg of the adsorbent. This could be due to the more number of available adsorption sites [19]. The adsorption capacity of cobalt ferrite is enhanced by the incorporation of bismuth.

3.4.3. Effect of pH on adsorption

The percentage removal of Cr(VI) ions by CoFe_2O_4 and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ samples are tested at different pH. From the results (Table 2) it is observed that adsorption efficiency of both unsubstituted and bismuth incorporated cobalt ferrite is found to be higher at pH 2 when compared to neutral and alkaline condition. This could be due to the protonation of the surface of the adsorbent at acidic pH which attracts the anionic species ($\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- and CrO_4^{2-}) of Cr(VI) [20]. But at higher pH the adsorption of Cr(VI) decreases because of weakening of protonated surface. Similar results are observed by Tewari et al [21]. Hence acidic pH is suitable for adsorption of Cr(VI) by this adsorbent. It could be drawn from the results (Table 2) that the removal of Cr(VI) is enhanced by bismuth substitution.

Table 2. Removal efficiency of chromium (VI)

S.No	pH	%R of CoFe_2O_4	%R of $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$
1.	2	22.3	70.0
2.	7	19.3	45.0
3.	10	5.3	24.4

3.4.4. Effect of various concentration of adsorbate

The effect of various concentration of adsorbate are carried out with 25, 50, 75 and 100 ppm of Cr(VI) solution (pH - 2) using 0.2 g of the adsorbent (CoFe_2O_4 and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$) and shaken well for 1 hour. Adsorption efficiency of adsorbents decreases with increase of adsorbate concentration. It shows that the adsorption of Cr(VI) is highly concentration dependent. This could be due to ratio of metal ions available to the adsorption sites of adsorbent is more at lower concentration than higher concentration [22]. The maximum adsorption of 78% and 14% is observed using bismuth substituted ferrite and unsubstituted cobalt ferrite respectively when the concentration of adsorbate is 25 ppm. From the result, it is understandable that bismuth substitution increased the adsorption efficiency of cobalt ferrite (Figure. 6).

The increase in adsorption of chromium (VI) by bismuth substituted cobalt ferrite could be explained based on its higher saturation magnetization than cobalt ferrite (Table 2). Higher magnetic property is an excellent key role for the good adsorption behavior of magnetic adsorbent [23]. Similar observation is noted in the present work too. Among CoFe_2O_4 and $\text{CoFe}_{1.9}\text{Bi}_{0.1}\text{O}_4$, the later one is good adsorbent proved from its higher saturation magnetization and lower crystallite size (Large surface area) also. The advantages of these magnetic adsorbents are easy separation from the solution using an external magnet compared to other adsorbents. Yang et al reported that higher the magnetization higher will be potential of nanoparticle for the magnetic separation of chromium in waste water [24]. Chromium (VI) removal efficiency of bismuth substituted cobalt ferrite (78%) is better compared to other ferrites such as manganese ferrite nanospheres [17] (% Removal of Cr(VI) is 35-40%) and cobalt substituted manganese ferrite nanoparticles¹⁹ (% elimination of Cr(VI) is 65%).

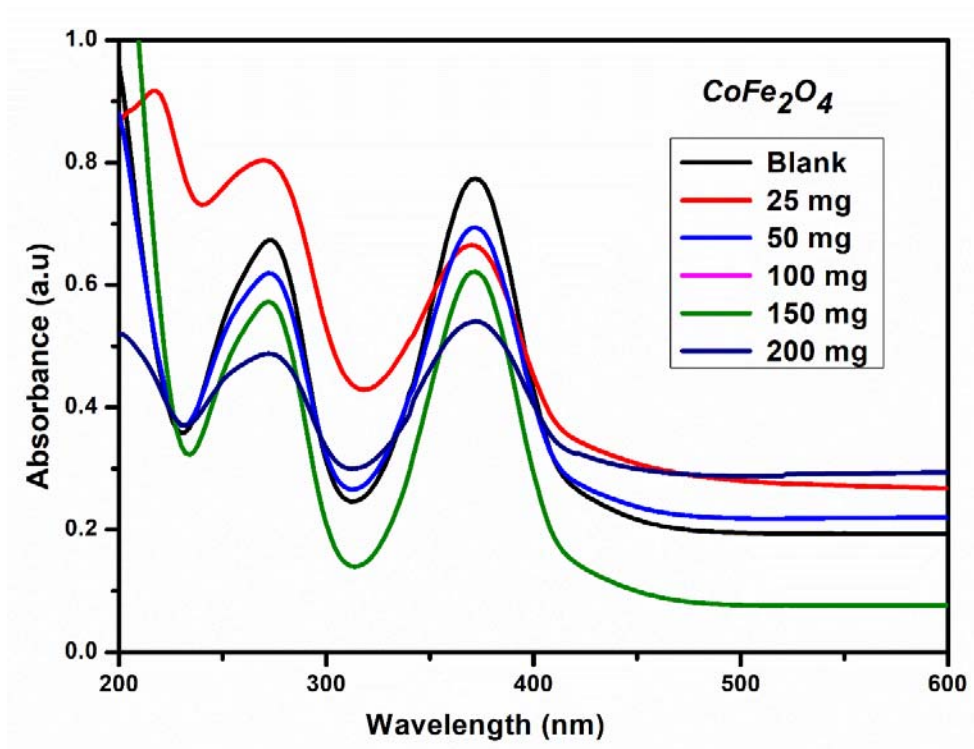


Figure 4. Effect of quantity (mg) of cobalt ferrite on the removal of Cr(VI)

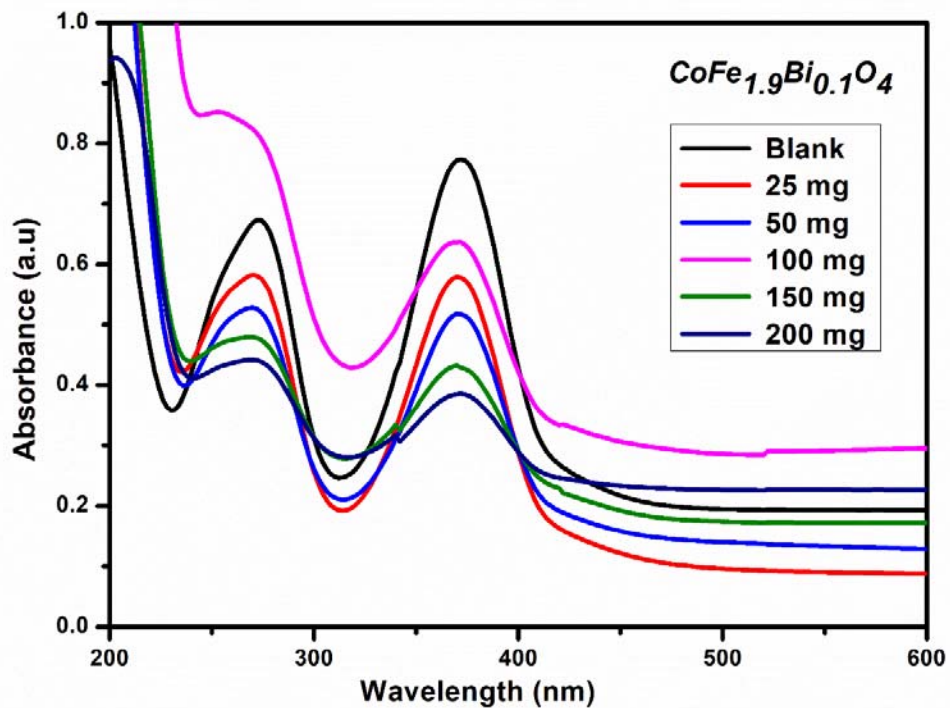


Figure 5. Effect of quantity (mg) of bismuth substituted cobalt ferrite on the removal of Cr(VI)

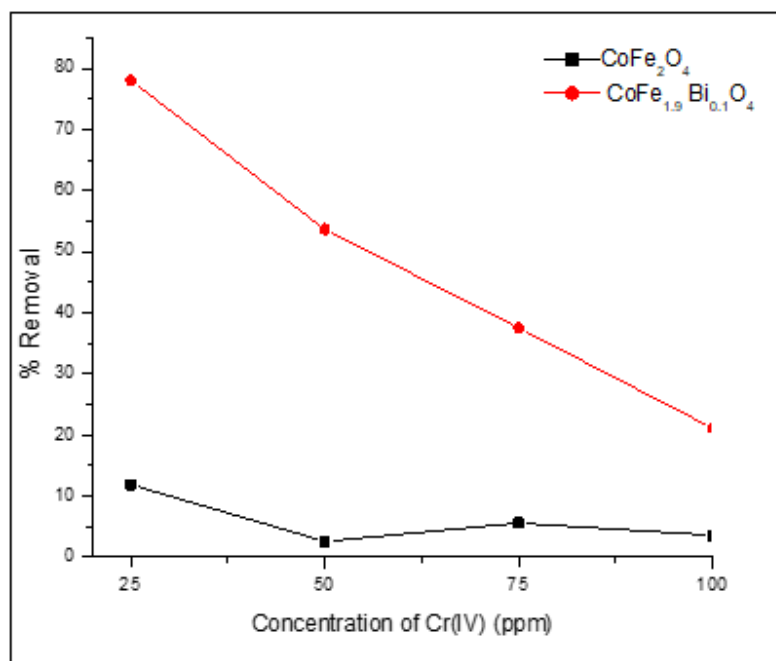


Figure 6. Removal of Cr(VI) at different concentration of adsorbate

4. Conclusion

CoFe₂O₄ and CoFe_{1.9}Bi_{0.1}O₄ spinel oxides are manufactured by solution combustion method. From the XRD and FTIR the pure phase formation was confirmed. The lattice parameter and average crystallite size are calculated from powder XRD. From the XRD pattern an enhancement in lattice parameter and reduction in particle size is noted. Adsorption efficiency of cobalt ferrite increases by the incorporation of bismuth. Maximum adsorption efficiency 78% is observed at acidic pH when the concentration of adsorbate is 25 ppm. The enhanced adsorption efficiency of bismuth incorporated cobalt ferrite could be due to its higher magnetic property.

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