

# Adsorption of Cr(VI) from Aqueous Solution on Mixed Oxide Nano Fe-Al nanoparticles

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Mixed oxide nanoparticles of iron and aluminium (FeAlO) were synthesized by combustion process and evaluated for the removal of chromium by adsorption from aqueous solution. The FeAlO were characterized for various physico-chemical properties using x ray diffraction, particle size, SEM, TEM, FTIR analysis. The adsorbent was evaluated to study the effect of different parameters like dose, pH and interference of other ion on removal efficiency. The data was fitted in Langmuir and Freundlich adsorption parameters were computed to determine adsorption capacity. The adsorption isotherm was best fitted for Freundlich adsorption model and adsorption capacity was 0.824mg g<sup>-1</sup> for Cr (VI). The FeAlO has good potential for the removal of Cr(VI) from water and wastewater.

## Introduction

Chromium is an important and highly soluble metal pollutant having wide applications in metal and chemical industries. It is mainly used in stainless steel, on iron alloy, electroplating, development of pigments and for leather processing [1]. Chromium is mostly present in aqueous solution in mainly Cr (III) and Cr (VI) oxidation states. The chromium is a heavy metal that can be very frequently found in high proportion in wastewater discharges from different industries. The widespread use of chromium and the incorrect disposal of the by-product and waste from industrial activities have created serious environmental pollution [2].

As per the report of Tata Environmental Research Institute, India, (TERI) out of 7.2 million tons of hazardous waste is generated from industries every year in India and 5.2 million tons is improperly disposed off. Kanpur is a hub of tanneries and the industries manufacturing basic chrome sulphate [3,4]. The high concentration of chromium with low biodegradability in tannery water is a serious environmental challenge [5]. The BIS has set maximum contamination level for total chromium in drinking water as 0.1 ppm.

Many methods have been used for removal of Cr (VI) from water and wastewater which include chemical precipitation, ion-exchange, membrane separation, etc.

However, these methods have some limitations and less efficiency. Adsorption is one of the most proven physical processes reported for Cr(VI) removal from water and wastewater [6].

Various adsorbents have been reported for the removal of chromium by adsorption such as zeolite [7], dolomite [8], activated carbon, bio-materials, minerals, polymer resins etc. But they have limited adsorption capacity and reusability [9].

Several studies revealed that nanoparticles and nanostructured materials have better efficiency for removal of metal ion pollutants from aqueous solutions [10]. They have attracted considerable attention in recent years because they exhibit useful and unusual properties compared to conventional materials. During past few years considerable efforts have been made in synthesizing, and functionalization of nanostructured and nanoporous materials for the remediation of heavy metals from water [11].

In particular, gold, iron, aluminum and copper-based nanomaterials have potential applications in removal of hexavalent chromium from water [12,13]. Iron nanoparticles are known for their unique optical, mechanical, magnetic and catalytic properties [14].

The applications of nano-metals for the removal of Cr (VI) from water and waste water were reported using iron oxide nanoparticles which showed a good adsorption capacity [15]. Also, they can be produced in a different nanosize range by surface modifications [16].

In this study, mixed oxide iron-aluminium nanoparticles (FeAlO) were synthesized, characterized and evaluated for the removal chromium (VI) from water. The metal oxide nanoparticles were thoroughly characterized using advanced characterization techniques. Attempts were made to study adsorption mechanism and effect of pH and co-ions on removal efficiency.

## Experimental

### Synthesis of FeAlO

FeAlO nanoparticles were synthesized by combustion method taking equimolar concentrations of nitrate salts of Fe and Al in required quantity of DI water. The solution was heated at controlled temperature up to 80-90°C. The material was dried, washed and calcined at 550°C

temperature. In order to study Cr (VI) removal efficiency dose studies were conducted with  $5\text{mg l}^{-1}$  concentration of chromium nitrate aqueous solution. The study on individual iron and aluminum nanoparticle was also conducted using similar concentration.

### Methods of characterization

FeAlO nanoparticles were characterized to determine the structure, composition and morphology of adsorbent by using techniques namely XRD, BET, SEM and FTIR. The XRD patterns were obtained using benchtop X-ray diffractometer. The sample was powdered and scanned for  $2\theta$  ranges from  $10^\circ$  to  $80^\circ$ . Scanning Electron Microscope images were captured by field emission SEM (JEOL). Fourier Transform Infrared spectroscopy (FTIR) was used to study the mechanism and interaction of Cr on adsorbent sites.  $\text{N}_2$  adsorption method was used to determine BET surface area and pore size.

### Batch adsorption study

Batch adsorption study was carried out to see the optimum adsorption w.r.t. contact time. The desired dose of synthesized adsorbent was taken in 250 ml flask and Cr(VI) solution was added with different dose of adsorbent. The flasks were placed in orbital shaker at ambient temperature. After desired time interval, sample were withdrawn and analyzed for residual Cr concentration. The concentration of residual Cr(VI) in water was estimated by inductively coupled mass spectroscopy (ICP-MS). The concentration of Cr in samples at different pH, in presence of co-ions in filtrate were determined by using similar method. All the experiments were repeated twice and thrice if discrepancy in two results were observed.

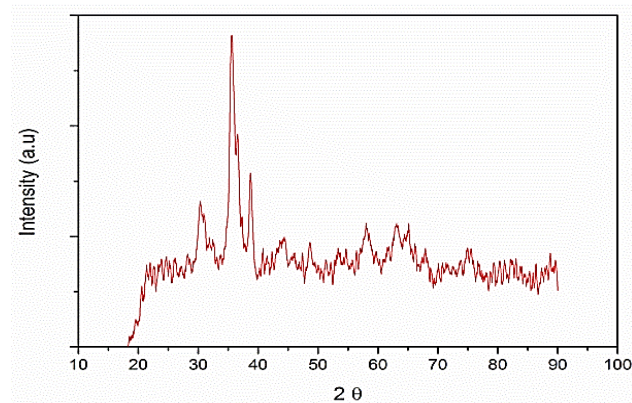


Fig. 1. XRD of FeAlO.

## Results and discussion

### Characterization of FeAlO

The XRD pattern of FeAlO is presented in Fig. 1. In this figure two most prominent peaks were observed at  $33.2^\circ$  and  $35.5^\circ$  corresponding to presence of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$  phases respectively. These two peaks are matching with standard JCPDS data card no. 33-0664 and no.39-1346 of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$ . The next peak is observed at  $41.9^\circ$  which confirm the presence of FeO phase matching

with JCPDS data no.6-0615. The peak obtained at  $36.96^\circ$  corresponds to the presence of  $\text{Al}_2\text{O}_3$  phase as per JCPDS data card no. 4-0877. The FeAlO has cubical crystal system. The surface area analysis shows that FeAlO has high surface area with highly porous nature. The BET surface area of FeAlO is  $42.2\text{m}^2\text{g}^{-1}$  and pore volume is  $0.072\text{cm}^3\text{g}^{-1}$ .

SEM results represent local and near-surface structures and morphology of particles. The higher magnification observation shows that bright region believed to be Fe and dark  $\text{Al}_2\text{O}_3$  matrix. The shape of particles is irregular with the presence of individual nodular shaped particles shown in Fig. 2(b). The average diameter of particles is about 200-300 nm in size. Fig. 2(a) shows that the FeAlO has highly porous structure and the Fe-Al nanoparticles are adhering on porous support in agglomerate form. The pores and voids can also be attributed to the gases liberated during the calcinations and partial combustion.

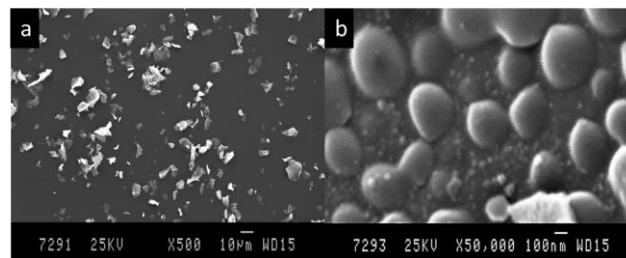


Fig. 2. SEM of FeAlO.

The FTIR spectra of FeAlO before and after adsorption of chromium is shown in Fig 3. The possible interaction of Cr(VI) and FeAlO were identified with the help of FTIR spectroscopy. The spectra were obtained in the range of 400 to  $4000\text{cm}^{-1}$  with resolution of  $1\text{cm}^{-1}$ . The FTIR of FeAlO before and after adsorption were carried out to study the possible interaction between the Cr adsorption and functional group present on surface of FeAlO. The major peaks were obtained at 571, 1364, 1508, 2343, 2389 and  $3701\text{cm}^{-1}$ . The peak intensity is almost similar except the reduction in peak intensity at 1364 and 2343 which may due to adsorption of Cr on FeAlO. The peaks obtained at 1634 and 1508 may be assigned to Fe-Al bonding which is normally peaks of metal oxide.

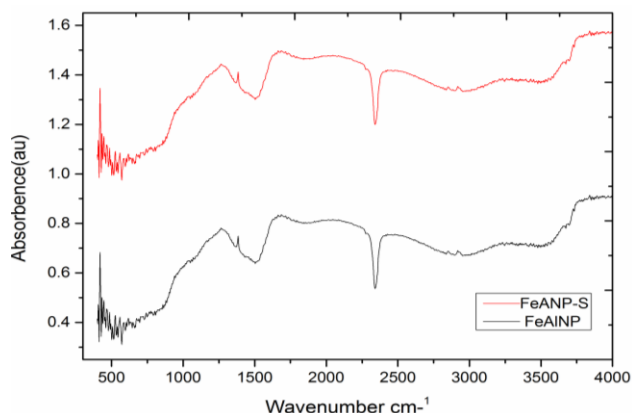


Fig. 3. FTIR spectra of FeAlO.

### Adsorption study

The batch adsorption studies were carried out to study the maximum adsorption at optimum dose with respect to contact time [17]. The FeAlO in required quantity was taken into flask of 250 ml capacity with 50 ml of Cr (VI) solution of desired concentration at 28-30°C. The flasks were kept on orbital shaker at 150±5 rpm. The flasks were taken out at pre-determined time intervals and contents were centrifuged to separate sorbent and filtrate. The residual chromium concentrations were determined in the supernatant. Experiments to study the effect of contact time on adsorption were carried out with initial chromium concentrations of 5 mg l<sup>-1</sup>.

The effect of adsorbent dose was investigated by taking the different dose of FeAlO from 1 to 10g.l<sup>-1</sup> for initial chromium concentration of 5mg.l<sup>-1</sup>. The adsorption isotherms obtained from dose study are presented in Fig. 4. All the experiments were conducted at room temperature 28-30°C. All experiments were duplicated with experimental error limit ±2% and average values are reported.

The experimental data of adsorption of Cr (VI) on FeAlO for Langmuir and Freundlich adsorption isotherm is presented in Fig. 4(a) and Fig. 4(b). The Langmuir adsorption model is as follows [18].

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad [1]$$

The Freundlich adsorption model in linear form is as follows.

$$\log(q_e) = \log k + \frac{1}{n} \log(C_e) \quad [2]$$

where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent (mg g<sup>-1</sup>),  $K_L$  is the Langmuir constant,  $q_m$  is the maximum adsorption capacity (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration (mg l<sup>-1</sup>),  $k$  and  $n$  are the Freundlich constant, which indicates the adsorption intensity [19].

On comparison of the fitness of these isotherms, it is evident that for chromium the experimental data were well fitted to Freundlich model than the Langmuir model signifying the multilayer adsorption of Chromium on heterogeneous surface. The values of adsorption capacity for FeAlO obtained from the Freundlich model was 0.824 mg g<sup>-1</sup>.

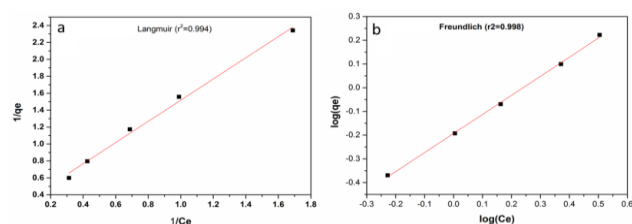


Fig. 4. Langmuir and Freundlich adsorption isotherm.

### Adsorption kinetics

The adsorption study was conducted with respect to time using different Cr (VI) concentration solution at different time interval. Two kinetic models are commonly used to

determine different kinetic parameters of the adsorption system. Both the models are reaction based models and diffusion based models. The kinetics of reaction was studied by pseudo-first-order and pseudo-second-order models. To study the kinetic profile of Cr (VI) sorption onto FeAlO from aqueous solution batch kinetic studies were conducted using initial Cr (VI) concentrations of 10 mg.l<sup>-1</sup>. The two mathematical models were used namely first order and pseudo second order model. The linear plots of pseudo-first-order (Eq.1) and pseudo second-order (Eq.5) models for Cr(VI) are presented in Fig. 5(a) and Fig. 5(b) respectively.

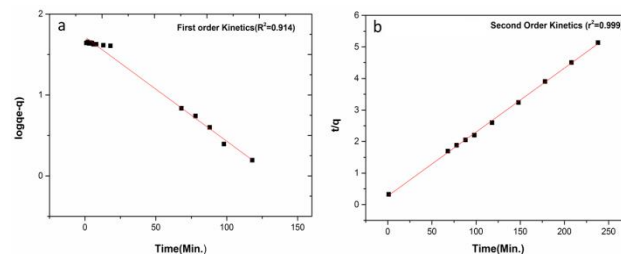


Fig. 5. Pseudo first order and second order kinetics.

A simple pseudo-first-order kinetic model is represented (Lagergren equation) as follows [20].

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \quad [3]$$

where  $q_t$  is the amount of Chromium adsorbed at time  $t$  (mg.g<sup>-1</sup>) and  $k_{ad}$  is the equilibrium rate constant (min<sup>-1</sup>).

The linearised plots of  $\log(q_e - q_t)$  versus  $t$  will give the rate constants.

The pseudo-second-order model is frequently used to study the kinetic parameters. The linear equation can be given as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad [4]$$

It was observed from the correlation coefficients given in Table 1 the pseudo-second-order model is better as compared to pseudo-first-order model.

Table 1. Kinetic parameters for chromium(VI) adsorption.

Pseudo first order		Pseudo second order		
$K_{ad}$ ( $min^{-1}$ )	$R^2$	$K$ ( $g\ mg^{-1}\ min^{-1}$ )	$H$ ( $mg\ g^{-1}\ min^{-1}$ )	$R^2$
0.0276	0.914	0.0014	3.6630	0.999

### Effect of pH

The adsorption of Cr(VI) on FeAlO was studied at different pH range from 3 to 10 by taking 10 g.l<sup>-1</sup> of adsorbent dose and the results are presented in Fig. 6(a). The pH of the solution before addition of sorbent was maintained using 0.1N NaOH or 0.1N HCl within a range of 3–10. All the experiments were conducted at room temperature of 28-30°C. The maximum removal of Cr(VI) was found between pH 3-5 after which slight reduction in adsorption was observed. At higher alkaline pH, adsorption is decreased and found lower than the adsorption occurs at



normal pH to 10. The pH study shows that the adsorption efficiency of FeAlO is almost stable in wide range of pH.

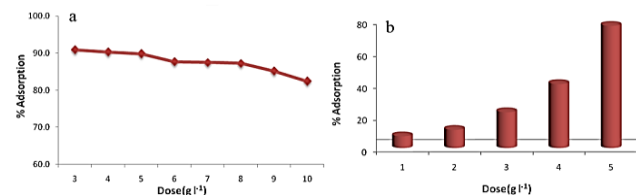


Fig. 6. Effect of pH and Co-ion.

### Effect of presence of other co-ion

The adsorption study was carried out to see the effect of co-existing anions such as phosphate, sulphate, nitrate, carbonate and bicarbonate which are normally present in water and compete in adsorption process. The initial concentration of chromium was maintained at 5 mg l<sup>-1</sup> and the concentrations of phosphate, sulphate, nitrate, carbonate and bicarbonate used were 50, 100, 50, 100 and 100 mg l<sup>-1</sup> respectively. The effect of these anions on Cr(VI) removal at different adsorbent doses is presented in Fig. 6(b). It was observed that removal of Cr(VI) at optimum dose value is least affected by the presence of co existing ions in water. The maximum removal efficiency in presence of all possible co-ions was found to be slightly affected by the presence of these anions. The maximum adsorption was 76% in presence of co-ions.

### Conclusion

The study has proved that FeAlO can effectively used for removal of Chromium (VI) which showed good adsorption efficiency 90%. The values of BET show the FeAlO has very high surface area with highly porous nature. The effect of pH shows that the removal capacity is maximum at pH 3 to 5 and slightly reduced after pH 6, hence the FeAlO is considered as efficient adsorbent at wide range of pH. Adsorption isotherm data was well fitted to Freundlich model signifying multilayer adsorption and the adsorption capacity was found to be capacity 0.824 mg g<sup>-1</sup>. The kinetic studies confirm the applicability of second order kinetic model which is based on chemisorption as prevailing mechanism. The FeAlO is suitable for field job and ability to remove chromium(VI) from water and wastewater.

### Keywords

Chromium, iron oxide, nanoparticles, aluminum oxide nanoparticles, adsorption.

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### Graphical abstract

