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REMOVAL OF Cr (VI) FROM WASTE WATER USING NiO NANOPARTICLES

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Abstract: The synthesis of NiO nanoparticles was done by sol-gel method. Nickel Acetate Tetrahydrate ($(CH_3COO)_2$ $-Ni{\cdot}4H_2O$) was dissolved in ethanol with constant stirring to obtain a clear and light greenish sol. Oxalic acid solution was used to obtain a thick green gel, then dried in an oven to get dried gel and was then grinded into fine powders and calcined for different time periods to obtain nanocrystalline NiO. The final product obtained was fine black powder. Nanoparticle powder formed was characterized using scanning electron microscope, X-ray diffraction spectrometer and Energy Dispersive X-ray diffractometer. Parameters studied were pH, nanoparticle dosage, Chromium ion concentration and contact time. Optimization of the process was done using Response Surface Methodology and ANOVA analysis.

Keywords: NiO nanoparticles; characterization; optimization, RSM; ANOVA.

1. Introduction

Removal of heavy metals released into the environment is essential. Many conventional processes have been synthesized for the removal of heavy metal ions from the wastewater. The nanoparticles because of very high adsorption efficiency due to very large surface area have attracted interest in the scientific community [1-2]. Chromium is very harmful for aquatic species as well human life and is known as potential carcinogenic. Chromium enters the environment by the industrial processes, such as leather tanning, electroplating, manufacturing of dye, paint and paper etc. Hexavalent chromium modifies DNA transcription process and is considered a very powerful carcinogenic agent by the International Agency for Research on Cancer [3-7]. The hexavalent form is 500 times more toxic than the trivalent form. The maximum permissible limit for hexavalent Chromium in wasterwater is 0.05 mg/L [8-14].

As the new field of nano-science and nano-technology has emerged during the last decade, the researches have been initiated to study the unique properties of nanoparticles for solving

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the environmental problems [15-18]. The objective of this work is to optimize the removal of Chromium(VI) by nickel oxide nanoparticles.

2. Materials and Methods

2.1. Chemicals and reagents

Potassium Dichromate (Merck, India), Nickel Acetate Tetrahydrate (S D fine Chemical Limited, India), Oxalic Acid, Ethanol, NaOH and H_2SO_4 (analytical grade)

2.2. Synthesis of NiO nanoparticles

The synthesis of NiO nanoparticles was done by sol-gel method. Nickel Acetate Tetrahydrate ($(CH_3COO)_2$ –Ni·$4H_2O$) was dissolved in ethanol with constant stirring for around 1 h at 40-45 ^oC to obtain a clear and light greenish sol. Oxalic acid solution (0.23 M in ethanol) was then added slowly to the warm sol to obtain a thick green gel. This thick green gel was then refluxed at 80-90 ^oC for 24 h under vigorous stirring with the magnetic stirrer in the air atmosphere. It was then dried in an oven by heating at 110 ^oC for around 14-16 h. Dried gel was grinded into fine powders and calcined in a furnace between 300 ^oC to 700 ^oC for different time periods to obtain nanocrystalline NiO. The final product obtained was fine black powder [19].

2.3. Characterization

The characterization of nanostructured NiO was carried out employing Scanning Electron Microscope (7500X and 12000X), X-Ray Diffraction (using Cu-K radiation, with operating voltage 45 kV and current of 40 Ma) and Energy Dispersive X-Ray spectroscopy to determine crystalline phase of NiO nanoparticles.

2.4. Liquid phase adsorption experiments

Batch experiments were carried out for adsorption of Chromium using NiO. 10-100 ppm of Cr(VI) solution was taken in the flask. 0.1-1.0 g of NiO nanoparticles was added to 500 mL flasks containing 25 mL of heavy metal ion solution. The flasks were agitated at 250 rpm in an orbital shaker for varying time periods and pH. The samples taken at different time intervals were analyzed in spectrophotometer for residual metal concentration in the aqueous solution [20].

2.5 *Modelling*

Describing RSM would be like a combination of mathematical and statistical techniques that can be further used for developing, improving and optimizing the processes to finally evaluate the relative significance of various process parameters even in the presence of complex interactions. The prime objective is to determine the optimum operational conditions of the process. This method is widely used chemical engineering and applied sciences. RSM usually contain three steps: (a) design and experiments, (b) response surface modelling through regression, (c) optimization [21-22]. A higher order polynomial such as the quadratic model will be used, if there is a curvature in the system, $Y = C_o + \Sigma C_i X_n + \Sigma d_i X_i^2 + \varepsilon$

2.6 *Experimental design for optimization of parameters*

Four factors i.e. effect of contact time, pH, adsorbent dose and initial ion concentration were studied. Various experiments were conducted and percentage adsorption was obtained accordingly. The optimum values of the four variables under consideration were obtained by solving the regression equation and by analyzing the response surface contour plots. The variance in dependent variables was explained by the multiple coefficients of determination, R2 and the model equation which was used to predict the optimized value within the specified range, and then finally explains the interaction between the factors.

3. Results and Discussions

3.1. Structural and morphological characterization of NiO nanoparticles

The XRD pattern of the nanoparticles obtained after calcining for 2 h has been depicted in Fig. 1. The peaks of synthesized NiO nanoparticles were identical to the NiO cubic structures. Corresponding lattice parameters of the synthesized one were a = 4.1790A°, b = 4.1790A°, c = 4.1790°, Z = 4, α = 90 Å, β= 90 Å, γ= 90 Å and space group Fm-3m. The SEM image is illustrated in Fig. 1 showed that nanoparticles are perfectly spherical with size in nano range.

3.2. Adsorption experiment

The effect of initial Cr(VI) concentration on removal efficiency was investigated in the range of 10-100 mg/L for Cr(VI). It is observed that the removal efficiency increased with increasing concentration of Cr(VI) ions in the solution. As the concentration was increased, active sites of NiO were surrounded by more number of metal ions resulting in increase of uptake of the ions. After reaching the equilibrium the uptake of ions became constant.

3.3 Adsorption isotherm

3.3.1. Langmuir Isotherm

The equation for the Langmuir isotherm is $Q_e = \frac{Q_m b C_e}{1 + bC_e}$

Where Q_e=x/m, the amount of solute adsorbed x per unit weight of adsorbent m (mg/g), C_e=Equilibrium concentration of the solute (mg/L), Q_m=Amount of solute adsorbed per unit weight of adsorbent (mg/g), b = Constant related to the heat of adsorption.

The comparison of the various parameters obtained for Cr(VI) is listed in Table 1.

3.4 RSM and ANOVA analysis

The relationship obtained between the independant variables and response is according to the equation.

$$Y = -291.373735289773 + 89.7950556108608*X_1 + 0.0195077427673519*X_2 + 2.82619383129666*X_3 - 6.24096929702280*X_1^2 - 2.37729807001921e\text{-}05*X_2^2 - 0.0277149383129666*X_3^2$$

To evaluate the goodness of the model, the coefficient of variation and F-value tests has also been performed. The F distribution is a probability distribution used to compare variances by examining their ratio. The F value in the ANOVA table is the ratio of model mean square (MS) to the appropriate error mean square. The larger the ratio, the larger the F value and the more likely that the variance contributed by the model is significantly larger than random error. The results of ANOVA are given in Table 2.

4. Conclusion

Studies were performed for removal of Cr(VI) from wastewater using NiO nanoparticles. Further the optimum process conditions were explored, using response surface methodology. This approach further proved to be very effective and time saving, hence reducing the total number of experiments to be performed. The optimum conditions obtained for Cr(VI) were synchronized well with the experimental data.

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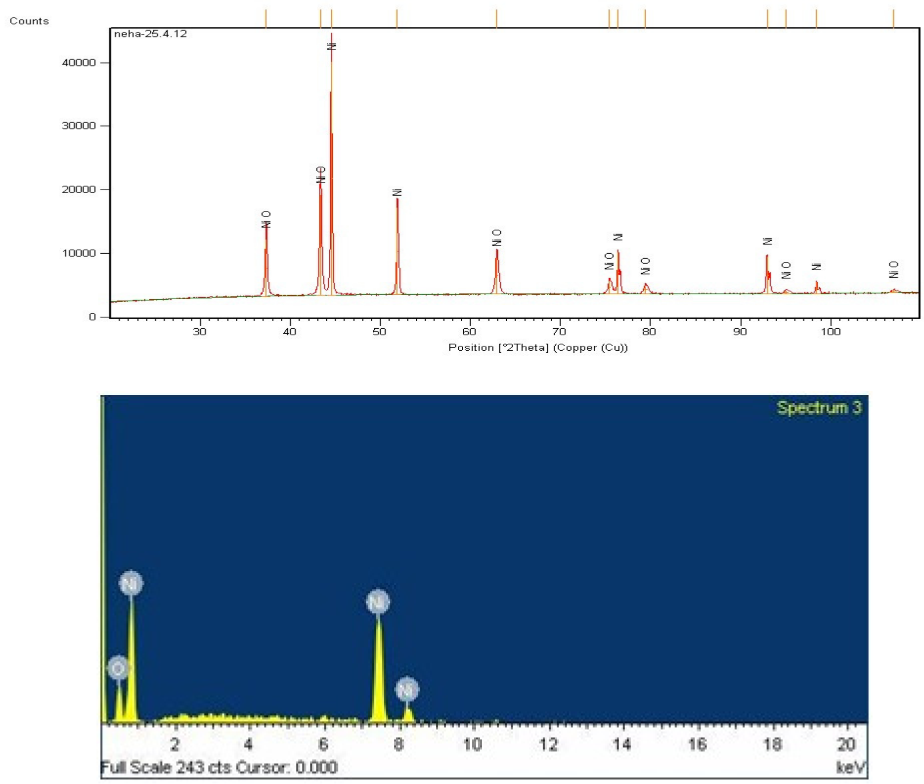

Fig. 1. XRD analysis and EDX analysis of NiO nanoparticles

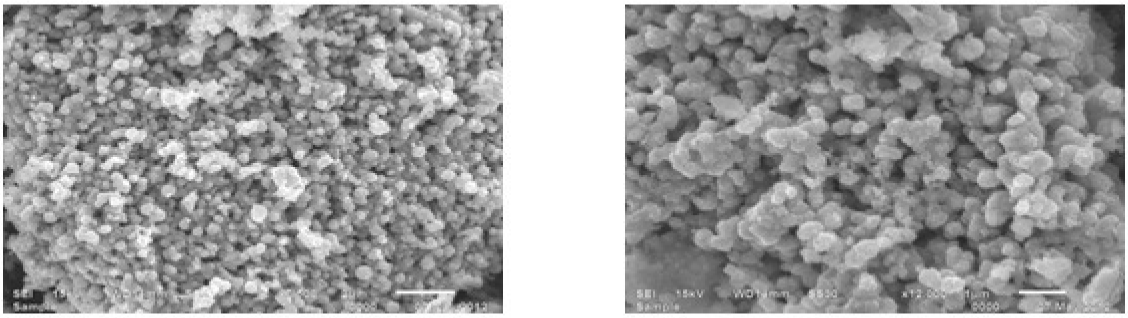

Fig. 2. Scanning electron photomicrograph of nickel oxide nanoparticles at 7500 X and 12000 X magnification showing highly uniform sample

Table 1. Comparison of the various parameters obtained for Cr(VI) for Langmuir isotherm

Parameters	Cr(VI)
$1/Q_m$	0.005
B	0.178
Qmax	200
R^2	0.896

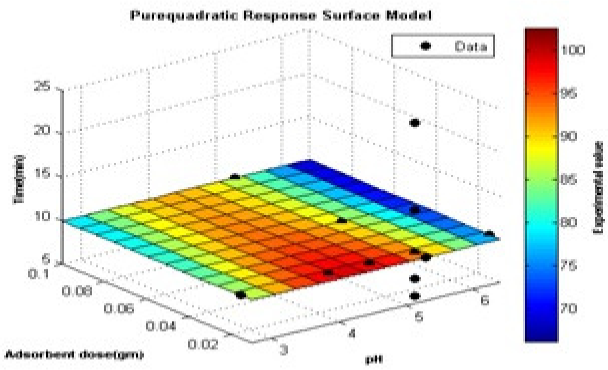

Fig. 3. 3-D plot showing effect of pH, time and adsorbent dose on % removal

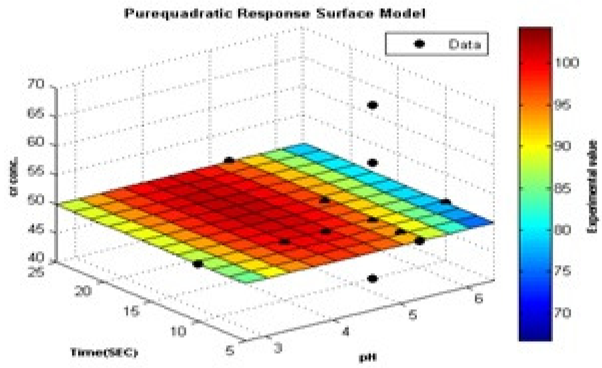

Fig. 4. 3-D plot showing effect of pH, time and initial concentration on % removal

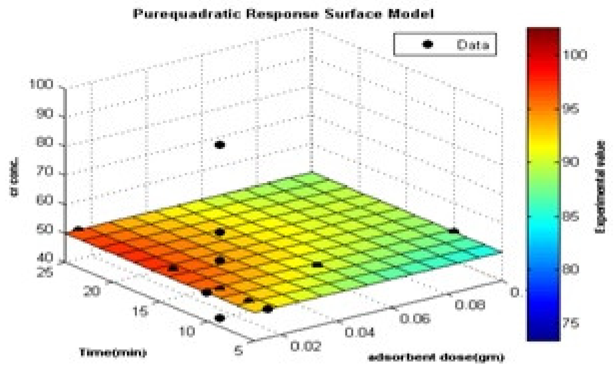

Fig. 5. 3-D plot showing effect of adsorbent dose, time and concentration on % removal

Table 2. ANOVA Table for Cr(VI)

Source	Sum of Square	df	Mean Square	F	Probabilty>F
Column	6.28	2	3.1405	0.07	0.928
Error	1384.8	33	41.9636		
Total	1391.08	35			