NiO-UF Modified Nanocomposite and its Application in High Efficiency Removal of Cr(VI)

Dr.NATHALIE JOHN

[1]Dada Ramchand Bakhru Sindhu Mahavidyalaya. Nagpur India
[2,3]Department of Chemistry RTMNU Nagpur University Nagpur India

Keywords: Heavy metals, Nanomaterial, Nanocomposites, Isotherms

Abstract. Effective removal of dyes and toxic heavy metals from wastewater using newly fabricated nano adsorbents is one of the embattled areas of research. Cr(VI) is well known highly toxic metal, considered as priority pollutant. The aim of present work is to prepare and characterized NiO nanomaterial using sol-gel method to remove the Cr(VI) from the water samples. Nanocomposite of NiO was prepared using urea-formaldehyde in 1:2 ratio. Characterization and formation of NiO and NiO-UF were done by using FT-IR, XRD, BET, FESEM and EDX. The studies on adsorption of hexavalent chromium on nanocomposite NiO-UF was conducted by varying parameters such as concentration of adsorbate, amount of adsorbent, contact time and pH. It was found that, Freundlich adsorption isotherm was best fitted in order to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be dependent on adsorbent doses, which was good in acidic pH. Adsorption was found to increase with increase in dose of adsorbent NiO-UF then it became constant. It was found that the synthesized material has capacity of about 95 % removal of Cr(VI) from its solution with optimum doses of 0.150 g at concentration 75mgL^{-1}.

Keywords: Heavy metals, Nanomaterial, Nanocomposites, Isotherms.

Introduction

Various heavy metals exist in surface water such as Cd, Cu, Zn, Ni, Cr. Cr(VI) is one of the most toxic and heavy metal which polluted the aquatic environment. Chromium occurs in nature in two different stable oxidation state viz trivalent Cr(III) and hexavalent Cr(VI). International Agency for Research on Cancer (IARC) categorized Chromium as group I Carcinogen [1]. Effluents coming out from leather, textiles, metallurgy, paints industries contains Cr(VI) [2]. As per report of World Health Organization (WHO), allowable chromium in industrial waste water and potable water is 0.05 ppm and 0.1 ppm, respectively [3]. Ionic species containing Cr(VI) such as $CrO4^{2-}$ or $HCrO_4^-$ are highly soluble and mobile than Cr(III). Thus Cr(VI) containing species pass through cell membranes readily, whereas Cr(III) species are poorly cell-permeable [4]. Cr(VI) causes Cancer, epigastric pain, mutagenic abnormalities, severe diarrhoea, tumours in lungs, vomiting, nausea [5]. Most normally used technique for Cr(VI) removal is adsorption, ion-exchange, membrane separation, coagulation, chemical precipitation, extraction, dialysis and electrochemical separation are employed for the removal of heavy metal ions, including hexavalent chromium from waste water [6-18]. Among these different methods, adsorption was found to be most effective, economically feasible, environmentally sustainable, and technologically promising processes [19-20]. Recently, a variety of adsorbents such as activated carbons, iron-based metal oxides, metal-organic frameworks, polymeric and biomass-based materials [21-25] have been used for Cr (VI) removal. In particular, polymeric materials have been shown to be more efficient in adsorbing Cr (VI) and their highly branched structures can be readily functionalized to selectively adsorbed and removal of different heavy metal ions [26,27].

From the literature survey it was observed that, various metal oxides and their polymeric materials are applicable for the removal of Cr(VI) from water and waste water. In current work Nickel oxide is taken as base for study because of its catalytic, electronic and magnetic properties [28-30]. Properties of NiO improved by encapsulation in other materials [31]. Among various techniques available to synthesized desired material Sol-gel method is selected because it allows homogeneous mixing, better crystallinity, uniform particle distribution and nanosized material of interest [32].

Mohammad Behnajady et.al. synthesized mesoporous NiO by using nickel nitrate hexahydrate [$Ni(NO_3)_2.6\ H_2O$] and NaOH used it for the adsorption of Cr(VI) by variation in parameters like concentration, dosages, pH, contact time. It has been found that at PH range 4 to 5 there are nearly 95% removal of Cr(VI) from its sample [33]. N. K. Shrivastava et.al prepare NiO by sol-gel method using Nickel Acetate Tetrahydrate ($(CH_3COO)_2$ –Ni·$4H_2O$) as a precursor, ethanol as solvent using oxalic acid as reducing agent. The NiO was applicable for removal of Cr(VI) by variation in parameters concentration, dosages, pH, contact time. However, due to difficulty in their separation from the aqueous phase after adsorption, it is not feasible to use nanoparticles for metal removal. In order to overcome these limitations, polymeric organic-inorganic nanocomposites/composites or synthetic adsorbents have been used as matrix to anchor the nanoparticles which can be applied in the field of desalination technology for the removal of toxic metal ions from waste water or aqueous solutions [34,35]. In this work sol-gel method is employed for the synthesis of NiO using Nickel Acetate Tetrahydrate ($(CH_3COO)_2$ –Ni·$4H_2O$) as a precursor, ethanol as solvent and citric acid in ethanol as reducing agent. The synthesized material NiO was encapsulated on urea- formaldehyde polymer. Study of adsorption of Cr(VI) on NiO-UF carried out by changing parameters such as initial concentration, dosages, contact time and pH are interpreted on the basis of it. The purpose of this work is to produce a novel adsorbent for the removal of Cr(VI) from water sample and study the effect of above different variables on the adsorption process.

To the best of our knowledge this is the first attempt to apply NiO-UF for the removal of Cr(VI) using batch experiments.

Materials and Methods.

Chemicals and reagents

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

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 hour at 40-45°C to obtain a clear and light greenish sol. Citric 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°C for 24 hours with vigorous stirring with the magnetic stirrer in the air atmosphere. It was then dried in oven at 100°C for about 14-16 hour. Dried gel was then grinded into fine powder and calcined at 500°C in a furnace between for different time periods to obtain nanocrystalline NiO. The final product obtained was a fine black powder.

Preparation of NiO-UF Resin

To make composite of NiO on urea formaldehyde, 20 ml of 40% formaldehyde and 10g of urea in standard molar ratio 2:1 in 250 ml beaker stirred magnetically for uniform mixing. To this homogeneous clear mixture 100 mg of NiO was added and 0.5 ml of concentrated H_2SO_4 with continuous stirring. There was a formation of NiO-UF nanocomposite having white colour with black spots. NiO-UF nanocomposite was dried in oven at 100°C for 12 to 14 hours.

Characterization.

The characterization of nanostructured NiO and NiO-UF was carried out by using Bruker ALPHA-E FTIR Spectrometer in Department of Organic Chemistry RTM Nagpur University Nagpur, Scanning Electron Microscope JEOL Model No. JSM7610FPLUS (75000X and 8000X) equipped with Energy Dispersive X-Ray spectroscopy at RUSA Manipal University Jaipur, Rigaku Mini Flex 300/600 Benchtop X-Ray Diffractometer (using Cu-K radiation, with operating voltage 45 kV and current of 40 Ma with range of 2Θ 10 to 70 degrees) at RUSA RTM Nagpur University Nagpur, BET Analysis at Department of Analytical Chemistry Nagpur using Quantachrome Nova 2200e.

FT-IR spectra

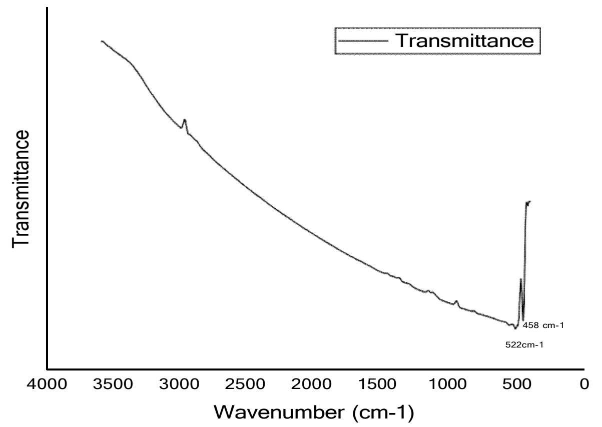


Fig. 1. FT-IR of NiO

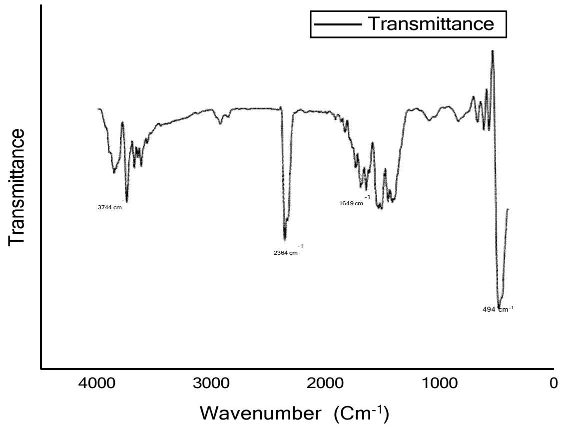


Fig. 2. FT-IR of NiO-UF

A) NiO: Peaks at 458cm^{-1} and 522 cm^{-1}confirmed that Ni-O bond is present, without any impurity [36,37]

B) NiO-UF: Shifting of bands at higher wavenumber indicates that there is formation of composite. Sharp peak at 494 cm^{-1}of Ni-O bond, Carbonyl group peak is shifted to 1649 cm^{-1}, C-N bond peak appear at 2164 cm^{-1}, N-H peak get shifted to 3744 cm^{-1}.

X-ray diffraction studies.

A) NiO: In XRD studies existence of strong and sharp diffraction peaks at 2Θ values 37.25, 43.30 and 62.90 corresponding to crystal planes (111) (200) and (220) shows that product NiO is single phase with cubic structure. Any impure peak was not observed in the XRD pattern. The typical XRD pattern of NiO nanoparticles obtained after heat treatment at 773 K is presented in Figure. The nature and positions of the above diffraction peaks are characteristic of cubic nickel oxide phase as cited in other report [38] and JCPDS card file number 4-0835.

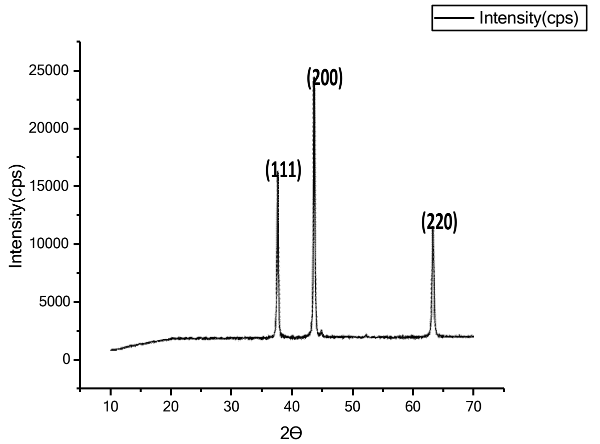


Fig. 3. XRD Pattern of NiO nanoparticles

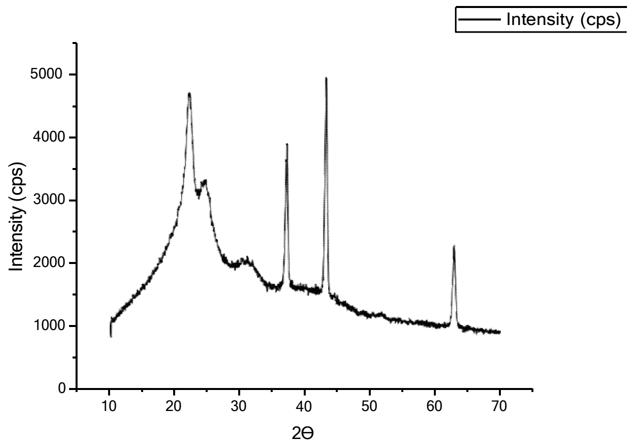


Fig. 4. XRD pattern of NiO-UF Nanocomposite

B) NiO-UF: In XRD spectra of NiO-UF shows that it consists of individual nm thick layer suspended in urea formaldehyde polymer matrix exfoliated with well order encapsulation of metal oxide on urea formaldehyde. and are a result of extensive penetration of the polymer and delamination of the layer structure. The d-spacing between the layers is significantly expanded beyond which the interaction forces between the layer structures diminished. The separation distance between the layers is typically 10 nm or more apart. Due to exfoliation properties of the material are found to be dramatically increases than normal way of traditional nanocomposites. As ordered exfoliation, the ordered and parallel arrangement of nano-layers is preserved and a homogeneous morphology with individually separated layers exists throughout the entire matrix

SEM(Field Emission Scanning Electron Microscopy).

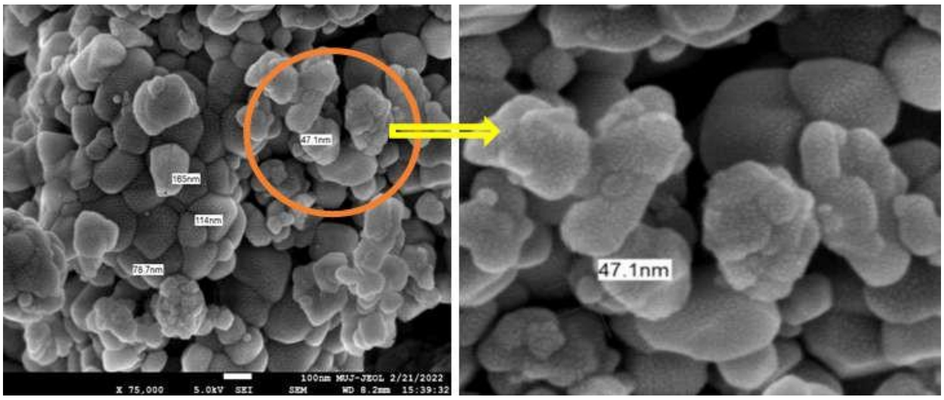


Fig . 5. FESEM of NiO at 75000 X

A) NiO: Structural morphology of synthesized NiO observed by SEM images under low and high magnification.it was found that irregular spherical particles are aggregated with presence of microspheres to form 3D structures with rough surface and porous structure.[39]

The aggregates have irregular spherical.The spherical particle have diameter in range of 47 to 165nm.

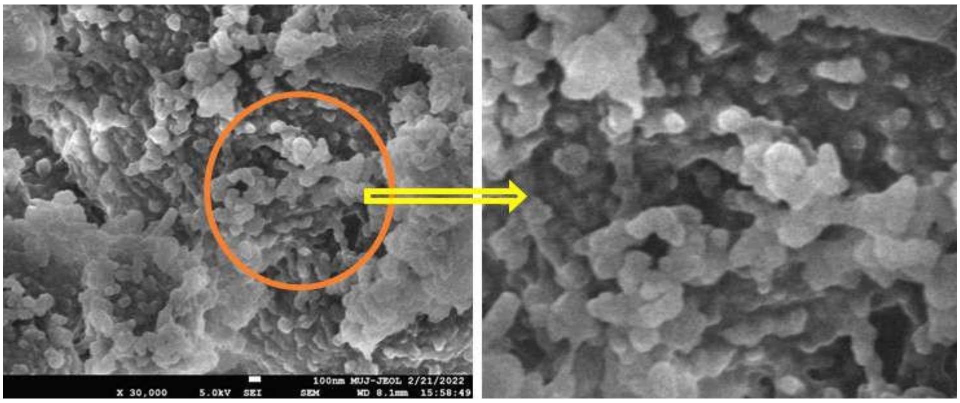


Fig. 6 .FESEM of NiO-UF at 30000X

B) NiO-UF: Nanoparticles are well Homogeneously encapsulated in framework of urea formaldehyde resin without agglomeration.It get uniformly distributed on resin of urea formaldehyde. Due to incarporation of NiO on urea formaldehyde surface to volume ratio increases.

EDX(Electron Diffraction X-rays).

In electron diffraction xrays analysis gives details regarding percentage of elemental compositions in synthesized materials.

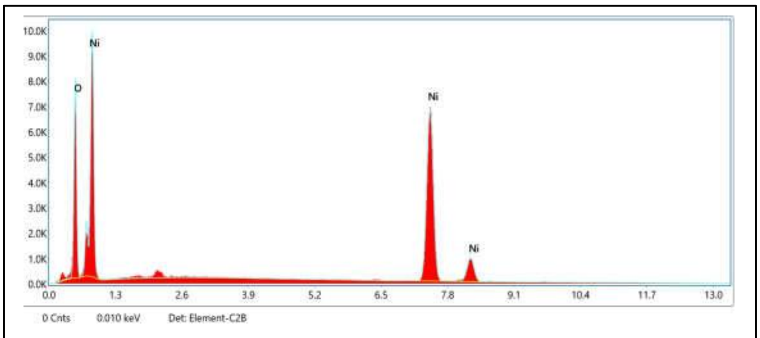


Fig.7. EDX of NiO Nanoparticles

A) NiO:

Element	Weight %	Atomic %	Error %
O K	24.8	54.7	7.5
Ni K	75.2	45.3	1.9

Table 1 - EDX Data of NiO

Table 1 show results obtained from EDX characterization suggested that NiO powder has good purity (Nickel Content-75.38%;Oxygen Content-24.8%) with less impurities.

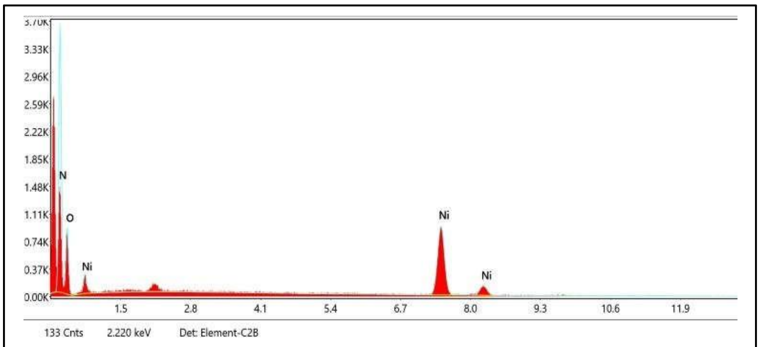


Fig. 8. EDX of NiO-UF

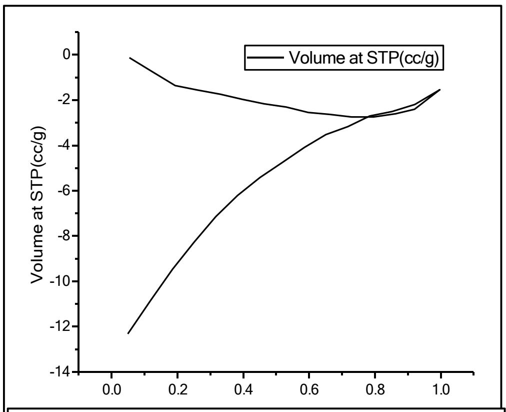
B) NiO-UF:

Element	Weight %	Atomic %	Error %
C K	30.5	39.9	7.7
N K	39.9	38	10.9
O K	17.7	17.3	11.9
Ni K	17.9	4.8	3.1

Table 2 - Nanocomposite NiO-UF

Weight Percentage of Ni,O.N and C are found to be excellent with minimum error.

BET Studies



A) NiO : In this case concave nature of adsorption curve P/P_0 proves that $P/P_0 << 1$ NiO is mesoporous and follows Langmuir adsorption isotherm. The adsorption was chemisorption and deviation of desorption confirmed that is was irreversible. From the multipoint BET data surface area of the synthesis metal oxide is 32.736 m²/g. From BJH method Total pore volume = -2.381e-03 cc/g for pores smaller than 2943.9 Å (Radius) at P/Po = 0.99674. Average pore size of the synthesized material was found to be -1.45437e+00 Å.

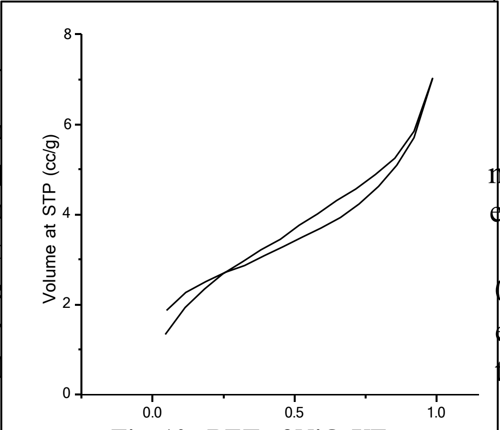


Fig. 10 . BET of NiO-UF

B) NiO-UF: The reversible nature of adsorption and desorption curve indicates that material is nonporous with micropore in it. Up to the knee point adsorbent follows a eviates from Langmuir type of adsorption. Nature of curve n. From the multipoint BET data surface area of the synthesis e. NiO-UF is 8.638 m²/g. The decrease in surface area of kes place.Total pore volume is 1.086e-02 cc/g for pores 0.98557.Decrease in surface area shows that the metal oxide ehyde resin. The adsorbed volume increases dramatically in to 1) which is feature of textural porosity and indicates the presence of pores within the sample. Due to increase in porosity adsorption behaviour drastically increases.

Liquid phase adsorption experiment.

Batch experiments were carried out for adsorption of Chromium using NiO using NAVYUG(India) Rotary Shaker. The experiments were performed in a batch reactor with a wide range of stirring speed 100 to 500 rpm. A known weight of NiO-UF 0.1g was in contact with 25ml of 10-100 ppm of Cr(VI) solution was taken in different flask. The sample was filter after shaking by using Whatman filer paper No.40.To the sample 1-5 diphenyl carbazide, orthophosphoric acid, was added to develop colour. The amount of Cr in sample was estimated by using Shimadzu UV-1800 Spectrophotometer. To obtained the adsorption capacity, the amount of chromium adsorbed per unit mass of NiO-UF (qe)was calculated by using following equation.

where, C_0 is the initial metal ion concentration (mg.L^{-1}), C_e the equilibrium metal ion concentration (mg.L^{-1}),V is the volume of the aqueous phase in liter and m is the weight of adsorbent used in gram. The adsorption percentage of metal ions from aqueous solution is computed as follows:

Adsorption Study.

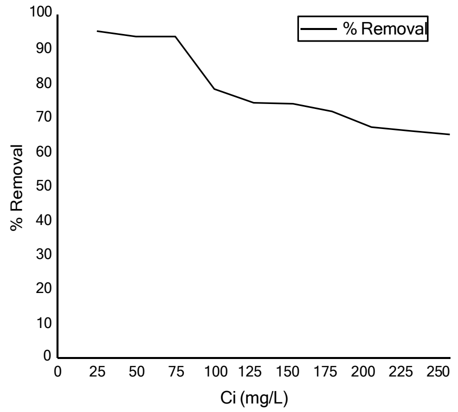


Fig. 11. Initial Concentration Vs Percentage removal

With increase in concentration there occur decrease in adsorption.This was to be done by taking 0.1g of nanocomposite (NiO) dosage and pH was 4.7 and contact time of 120 minutes.Optimization of concentration was done by selecting lowest concentration and maximum removal of Cr (VI).Effect of other parameter like dosages, contact time, pH was done by selecting concentration of 75 ppm.

B) Effect of Adsorbent dosages: The dosages of nanocomposites NiO-UF changes from 0.50 g to 2.50 g with increase in dosages percentage of adsorption will be increases from 80% to 96%. This is due to increases in active binding sites also increase in surface area. The minimum dose with maximum adsorption is taken as 0.150 g with 95% adsorption of Cr.

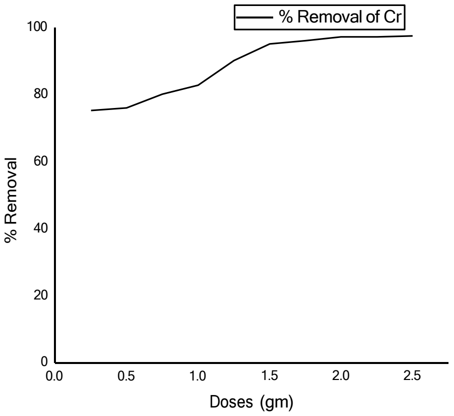


Fig. 12. Dosages of adsorbent Vs Percentage removal

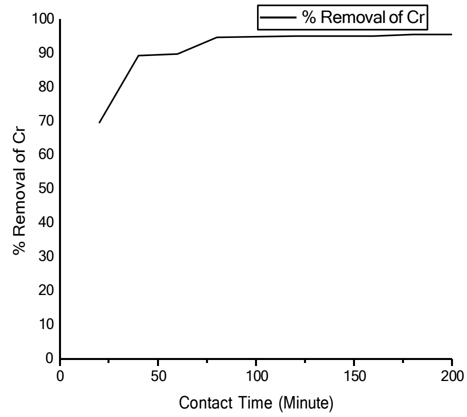


Fig. 13. Contact Time Vs Percentage removal

C) Effect of Contact Time: Percentage of adsorption increases with time upto certain constant time after that it has been found that there will be no increase in rate of adsorption. At optimum time all the active sites for adsorption of adsorbent get blocked and no vacant side available for adsorption of heavy metal Cr. The minimum time with maximum adsorption 94% was 80 minutes further increase in time period to increase in adsorption.

D) Effect of PH:The adsorption capacity decreases with increase in PH. This due to increase in OH^- ions in solutions leads to repulsive interaction with NiO-UF nanomaterials.

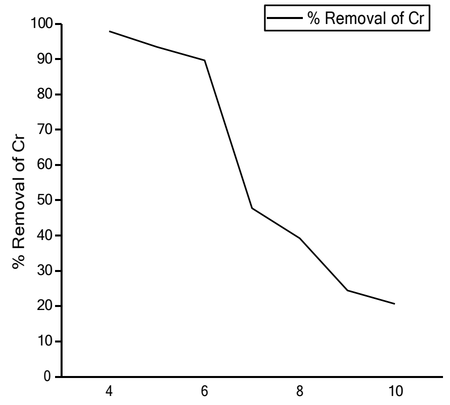


Fig 14. pH Vs Percenta^{P}g^{H}e removal

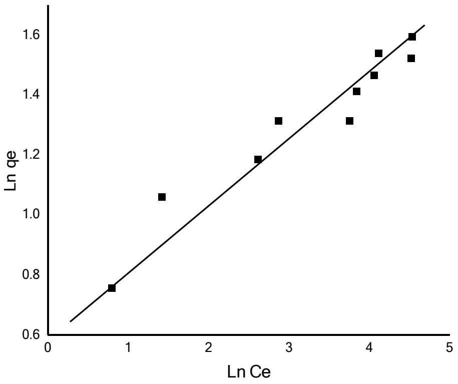


Fig .15. Ln qe Vs Ln Ce

Results and discussion.

Formation of NiO and nanocomposite was confirmed from the data obtained from characterization technique FT-IR, XRD, SEM, EDX and BET. The results of the adsorption find out by applying various adsorption isotherm. It has been found that adsorption of Cr (VI) on the surface of NiO-UF obey multilayer adsorption ie Freundlich Adsorption Isotherm. This type of adsorption take place on heterogeneous surface which was best complementary to applied material NiO-UF for adsorption.

The Freundlich adsorption equation was employed for the adsorption of Cr (VI) on NiO-UF

The equation is

slope	Intercept	K	R^2
0.4315	-0.3391	0.712418	0.9537

Conclusion.

NiO synthesized using simple sol-gel method. Its nanocomposite prepared by in situ encapsulation of NiO on urea formaldehyde in ratio 1:2. The nanocomposite NiO-UF provides economically cheap, fast, efficient, environmentally friendly approach for the adsorption of Cr (VI) from sample. The current work shows that due to binding of NiO on urea formaldehyde the properties and applications of parent materials drastically changes and it was applicable to water remediation technique. There found to be decrease in surface area of nanocomposites as comparable to nanomaterials but due to presence of amine groups on synthesized NiO-UF it shows the excellent affinity for the adsorption of Cr (VI). The mechanism is agreement and good fitting with the experimental data with Freundlich adsorption isotherm which is best applicable for heterogeneous adsorbent.

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