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Synthesis and characterization of [Ni-Al-Fe] nanocomposite and its application for the removal of cadmium(II) and zinc(II) ions

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The applicability of [Ni-Al-Fe] trioxide nano composite for the selective removal of toxic metals from wastewater has been investigated. The [Ni-Al-Fe] nanocomposite of 10 nm size has been synthesized via solution combustion route using aqueous solutions containing aluminum nitrate, iron nitrate and nickel nitrate as oxidizers and glycine as fuel. The calcined composite oxide has been characterized by powder x-ray diffraction, scanning electron microscope and transmission electron microscope. The surface area of the nanocomposite is determined to be 91 m^2/g using Brunauer-Emmett-Teller method. Batch experiments carried out to determine the adsorption kinetics and the efficiency of removal of trace metals such as zinc and cadmium under different experimental conditions show the process to be highly *p*H dependant, which makes the nanocomposite selectively adsorb these two metals. The adsorption of the two metals reached equilibrium within 35 min; the adsorption data well fitted with Langmuir and Freundlich isotherms.

Keywords: Nanocomposites, Oxides, Trioxides, Adsorption, Nickel, Aluminium, Iron, Cadmium, Zinc

Heavy metals are the most important constituents among toxic compounds in waste waters and surface waters[1]. Exposure to heavy metals even at a trace level is believed to be a risk for human beings[2-5]. Adsorption is a conventional but efficient technique to remove trace metals from aqueous solutions. Many kinds of adsorbents have been developed and commercialized for water treatment[6,7]. In many cases, these adsorbents are highly porous materials, providing adequate surface area for adsorption. However, the existence of intraparticle diffusion may lead to decrease in the adsorption rate and available capacity, especially for macromolecules. Thus, developing an adsorbent with large surface area and small diffusion resistance is of great significance. In recent times, nanotechnology is considered to have wide applications in the remediation of environmental pollutants and a great deal of attention has been focused on the synthesis and application of nanostructure materials as adsorbents or catalysts to remove toxic and harmful substances from water sources Many attempts have been made in literature to address the synthesis of metal oxides by using hydrothermal method precipitation method[8], sol-gel process[9], solvothermal route[10], etc. Even though efficient, these methods are time consuming, expensive and complex. Solution Combustion Synthesis (SCS) provides a simple, low cost fast process, with energy and time saving to produce pure nanopowders[11]. The parameters that influence the combustion reaction includes the type of fuel, fuel-to-oxidizer ratio, use of excess oxidizer, ignition temperature, and water content of the precursor mixture. Literature survey reveals the use of various types of nano oxides[12-14] as adsorbents for successful removal of trace metals. Most of the nanoparticles used in these processes are made up of the relevant metal only. In the present study, an attempt has been made to synthesize a composite metal oxide [Ni-Al-Fe] by solution combustion method by carefully controlling the desired parameters. This quick, straight forward process can be used to produce homogeneous, high-purity crystalline oxide. The synthesized metal oxide has been used to study the extent of adsorption of metals such as cadmium and zinc in aqueous solutions.

Experimental

All the chemicals used in this study are of analytical grade. Aluminum nitrate, iron nitrate and nickel nitrate have been used to prepare the composite solution. In this procedure, glycine (CH_2NH_2COOH) was employed as the fuel due to its more negative heat of combustion of −3.24 kcal g^{-1}. This mixture was well stirred and heated on a hot plate at 200 °C until the solution volume was considerably reduced to a syrupy state. The contents were transferred in to a porcelain dish and calcined at 350 °C for 3 h. The thus formed powdered sample was ground in a mortar to get the fine crystalline powder.

The surface morphology of the nanocomposite was analyzed by scanning electron microscopy at different magnifications (ZEISS-Make).2kev-30keV

in combination with FEG-SEM. X-ray diffraction studies of the [Ni-Al-Fe] nanocomposite were carried out on PANalytical XPert Pro X-ray diffractometer (PXRD) with generator settings of 40 kV and 30 mA at room temperature. Morphology and microstructure of the [Ni-Al-Fe] nanostructure was studied using high resolution transmission electron microscope (TEM) with resolution 0.23 nm and a voltage of 200 kV.

Results and discussion

The purity and crystalline nature of the as-synthesized (Ni-Al-Fe) nanocomposite were examined by using powder X-ray diffraction (XRD) as shown in Fig. 1. It can be seen that the diffraction peaks are low and broad due to the small size effect and incomplete inner structure of the particle. The peaks appearing at 2θ is 37.22°, 43.43°, and 62.89°, corresponds to the (311), (400) and (440) planes which were attributed to the formation of [Ni-Al-Fe] composite spinal structure in the calcined material. The diffraction peaks of the particles matched with the diffraction data from the JCPDS files 10-0339 and 44-1485. The crystallite size calculated by using the Scherer equation, $t = K\lambda/\beta\cos\theta$, is found to be in the range of 100 to 10 nm. No characteristic peak related to any other impurity was observed.

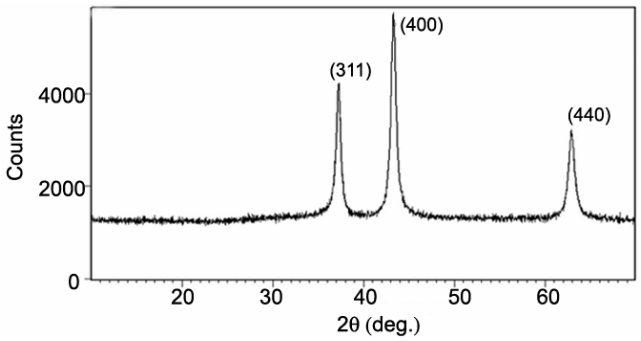

Fig. 1 – Powder XRD pattern of Ni-Al-Fe composite.

SEM provides detailed high resolution images of the sample to visualize the microstructure of the sintered sample (Fig. 2). SEM images show the formation of agglomerates in the form of flakes containing fine particles with irregular shape . These findings may be attributed to the release of large amounts of gases during combustion process. An energy dispersive X-ray (EDX) analyzer was also used to provide elemental identification and quantitative compositional information (Fig. 3).

In order to further confirm the morphology, HR-TEM studies were carried out. The TEM micrographs of the as-fabricated Ni-Al-Fe nanocomposite shows homogeneous and uniform distribution of these particles in the powder composite sample (Fig. 4). The particles comprised some regular and irregular polyhedrons with mean size of about 10 nm.

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. The specific surface area (SBET) was calculated to be 91 $m^2 g^{-1}$

Adsorption studies were conducted with known concentrations of synthetic samples of Cd and Zn metal ion solutions. A stock solution of zinc nitrate (1000 ppm) was prepared by dissolving 2.895 g of 99% $Zn(NO3)_2$ in 1 L of distilled water, while 1000 mg/L of cadmium stock solution was prepared by dissolving 1.6308 g of cadmium chloride in 1 L distilled water. Equilibrium isotherms for zinc and cadmium were obtained by carrying out batch adsorption studies. Solutions of concentrations ranging from 0.1 ppm to 1.0 ppm were adjusted to optimum *p*H values and adsorbent doses ranging between 0.1 and 0.5 g were added to solutions. The adsorbed heavy metal amount (*q*e) per unit absorbent mass was calculated as follows: $q_e = [(C_0 - C_e) \times V]/W$, where C_o is the initial heavy metal concentration (ppm), C_e is the concentration of heavy metal at

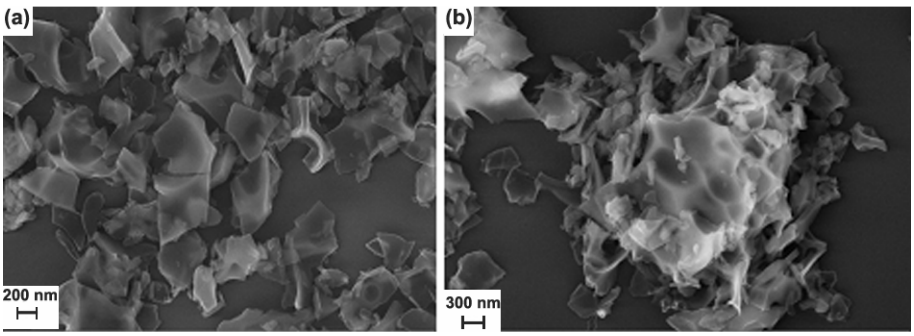

Fig. 2 – SEM images of Ni-Al-Fe composite at different magnifications.

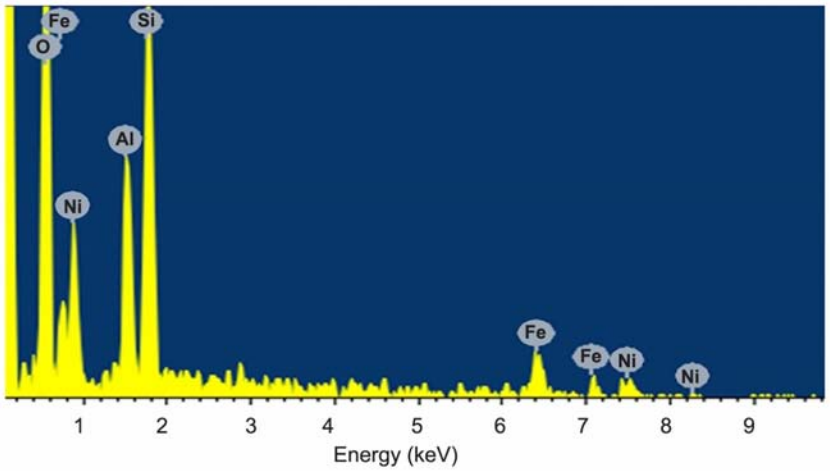

Fig. 3 – EDX pattern of [Ni-Al-Fe] composite.

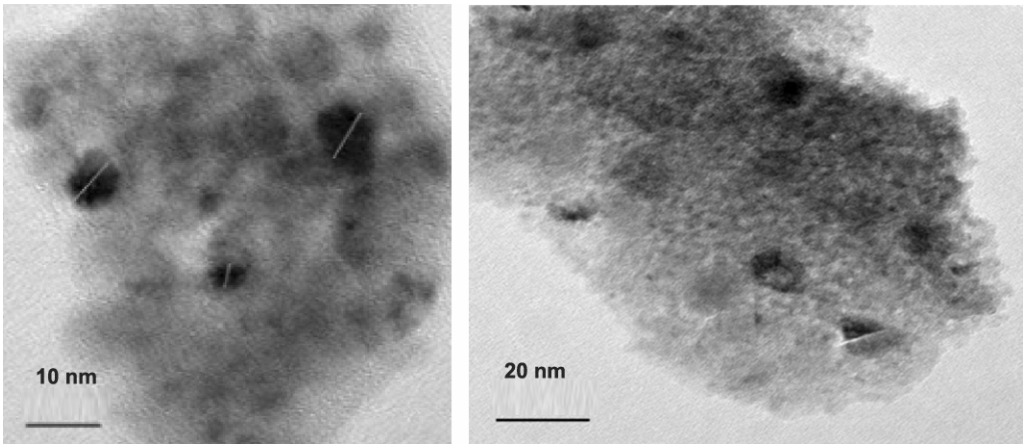

Fig. 4 – TEM images of Ni-Al-Fe composite at different magnifications.

equilibrium (ppm), *W* is the adsorbent dosage (mg) and *V* is the solution volume (L).

The effects of experimental parameters such as *p*H, adsorbent dosage, initial metal ion concentration and contact time were studied to optimize the conditions for effective adsorption in a batch mode operation.

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage was studied on cadmium and zinc ions from aqueous solutions by varying the amount of metal oxide, while keeping other parameters such as *p*H, agitation speed, temperature, initial concentrations of Cd(II) and Zn(II) and contact time, constant.

In this study the percentage removal of metal ions was gradually increased with the addition of metal oxide from 0.1 g to 0.5 g. The optimum amount of metal oxide for the effective removal of both metal ions was found to be 0.35 g.

One of the important parameters for adsorption of heavy metals is *p*H. The adsorption experiments were carried out in a series of 100 mL flasks containing 0.1 g [Ni-Al-Fe] composite and 0.1 ppm Cd(II) ions or Zn(II) ions in separate solutions at serial *p*H values from 2.0 to 10.0. The prepared samples were shaken with a mechanical shaker for 35 min. Then the solid/liquid phases were separated by filtration. The concentration of the Cd(II) ions and Zn(II) ions before and after adsorption was determined using ICP-MS. The results showed that the removal of Cd increased significantly as the *p*H increased from 0.0 to 4.0 and approached a plateau at the *p*H range of 4.0–9.0, while the removal of Zn(II) increased significantly as the *p*H slightly increased from 0.0 to 4.0 and then reached a plateau at *p*H 6.0 to 10.0.

The concentrations of the heavy metals were determined at different time intervals, varying between 10 and 40 min. The percentage of metal removal (%) was calculated using the equation: Removal (%) = C_0–C_e/C_0×100, where C_o is the initial concentration and C_e is the concentration at equilibrium, after treatment with the nanocomposite. The percent removal (%) for the metals reached maximum, i.e. above 95% in 35 minutes, for Cd(II) and Zn(II),

Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. The experimental data obtained in the present work was tested with the Langmuir and Freundlich models.

The theoretical Langmuir sorption isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. R^2 values for both metals were found to be 0.998 and 0.997 respectively which are very close to 1.

On applying the Freundlich model, which is applied to adsorption on heterogeneous surfaces with interaction between adsorbed molecules, R^2 values for both metals were found to be 0.997 and 0.998 respectively.

In the present study, metal oxide composite of [Ni-Al-Fe] has been synthesized, using the solution combustion technique. The synthesized composite was characterized by powder XRD, SEM, HR-TEM and BET surface area analyses. It was used as potential adsorbent for the removal of Cd(II) and Zn(II) from aqueous solution. The rate of uptake of the Cd(II) and Zn(II) was rapid in the beginning and the time required for equilibrium adsorption was 35 min. It was found that the composite has efficient adsorption capacity for both Cd(II) and Zn(II). The time of equilibrium was found to be independent of initial concentration. The results showed that the removal of Cd(II) was significant at a *p*H 6.5 while the removal of Zn(II) proved to be significant at *p*H 9.0. The study revealed that [Ni-Al-Fe] composite can be a promising adsorbent for the removal of Cd and Zn from waste water. The adsorption of Cd(II) and Zn(II) onto [Ni-Al-Fe] nanocomposite followed the Langmuir and Freundlich isotherms.

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