SYNTHESIS, CHARACTERIZATION AND APPLICATION OF NiO/ZnO HETEROSTRUCTURED ADSORBENT FOR HEAVY METAL IONS

Dedhila Devadathan[1], Baiju V[2], Biju R[3], Raveendran R[4]

Nanoscience Research Laboratory, Department of Physics, Sree Narayana College, Kollam 691001,

Kerala, India

Abstract

In the present work heterostructured NiO/ZnO nanocomposite was prepared using co-precipitation method, analyzed using XRD and UV/Vis spectroscopy. For comparison purpose NiO and ZnO was also prepared. Comparison of XRD's of metal oxides with JCPDS confirmed the formation of heterojunctions. UV/Vis absorption studies confirmed the shift of the optical absorption towards the visible region. The batch type adsorption mechanism is utilized to study adsorption of heavy metal ions using synthesised samples as adsorbent in the present work. The factors affecting adsorption process such as contact time, pH, concentration of adsorbates, adsorbent dose, agitation speed and temperature were investigated and compared for the synthesized materials. Adsorption was found to be high in the case of nanocomposites than counterparts.

Keywords: Nanocomposite, Adsorbent

1. INTRODUCTION

Environmental pollution and its harmful effect on ecosystem have been studied intensively during the last decade. Heavy metals are very harmful for human beings, animals and plants. Industrial discharge of waste water containing elevated levels of heavy metals is a major environmental concern. Global and local agencies have established certain limits on the quantities of heavy metals being discharged into the environment. Adsorption is one of the conventional but efficient techniques used to remove heavy metals and organics from aqueous solutions. Presently nanotechnology is widely applied for purification and treatment of waste water. The novel properties of nanoparticles such as large surface area, potential for self assembly, high specificity, high reactivity and catalytic potential make them an excellent candidate for this application [1]. An expanding trend for nanomaterials is the fabrication of composite structures and devices with materials capable of enhancing the properties of the material [2]. In the present investigation, we report synthesis of NiO/ZnO heterostructured nanocomposite using the well known co-precipitation method. The nanocomposite has

been applied for the removal of Cd(II) from waste water. Heavy metal ion like Cd(II) was chosen as the metal ion adsorbate because of its toxicity and its wide existence in industrial waste water [3].

2 EXPERIMENTAL

AR grade chemicals obtained from Merck were used for the preparation of NiO/ZnO heterojunction. NiO/ZnO (NZF) were prepared by the co-precipitation method in presence of capping agent. NZF annealed at 500^0c for three hours, was used for analysis. XRD studies were carried out using XPERT-PRO model powder diffractometer (PAN analytical, Netherlands) employing Cu- K_α radiation ($\lambda = 1.54060A^o$) operating at 40kV, 30mA.The UV/Vis spectrum was obtained using JASCO V-650 UV visible spectrophotometer. Adsorption studies were carried out using GBC-AAS spectrometer having lamb current 5milli ampere and wavelength 270nm.

3 RESULTS AND DISCUSSIONS

3.1 XRD Analysis

X-ray diffractograms of NZF is shown in Figure 1. The well defined X-ray diffraction peaks in the case of NZF indicate that NiO/ZnO formed are crystalline in nature. Also, the diffraction peaks are notably broadened indicating the

smaller crystallite size. In order to confirm the phase purity of the samples prepared, the interplanar spacing (d_{hkl} values), 2θ values and relative intensity values corresponding to the observed diffraction peaks were compared with the standard values of NZF the observed diffraction peaks were compared with the standard values of NiO and ZnO as reported by JCPDS-International Centre for Diffraction Data. The data obtained for NiO/ZnO matched with JCPDS-ICDD pattern number #78-0423 of NiO and JCPDS-ICDD pattern number #79-0205 of ZnO separately. From JCPDS, NiO shows cubic system with FCC lattice and ZnO shows hexagonal system with primitive lattice. The variation observed in the d values of the crystal planes in case of NZF when compared to NiO and ZnO, confirms the formation of composites. This is also supported by the disappearance of the peak corresponding to (1 0 3) of ZnO in the XRD of the nanocomposite. The average crystallite size was calculated from the line broadening of the XRD pattern, making use of Scherrer formula. Average Crystallite size of NZF is 18.73± 3 nm.
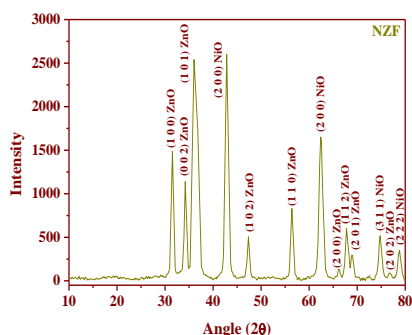
Fig.1 XRD of NZF

3.2 UV/Vis Spectrum Analysis

The UV/Vis absorption of NZF taken in the wavelength range 210 to 870 nm with 1 nm resolution is shown in the Figure 2. Presence of a weak absorption band was observed in the range 225 nm – 270 nm with λ_{max} situated at 256nm and also another strong absorption band in the range 260 nm – 400 nm with λ_{max} situated at 360 nm was also obtained. The second band can be attributed to the presence of ZnO which could be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band $(O_{2p} \rightarrow Zn_{3d})$ [4]. The absorption edge was found to be 3.44 eV for NZF.
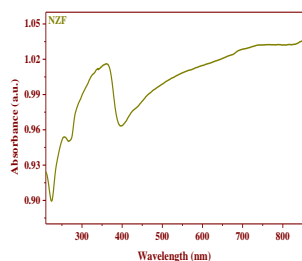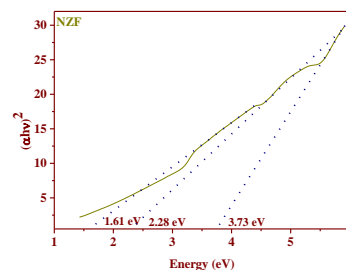

Fig.2 UV Absorbance spectrum of NZF

Fig.3 Tauc plot for NZF

From absorbance spectrum, Tauc plot was drawn and the corresponding energy gap was found. $(\alpha h\nu)^2$ vs hν was also plotted. The optical band gap determined from the absorption spectra using Tauc's relation for NZF is shown in Figure 3.

3.3 Adsorption Studies

Adsorption studies were performed by batch process by taking 0.1 gm of synthesized NZF in a 100 ml clean and dried stoppered bottle. Known concentration of 50 ml Cd^{2+} solution was added in the same stoppered flask. This flask was placed on a mechanical shaker at 160 rpm and the rate of adsorption of cadmium on NZF nanocomposite was studied. After desired time intervals [20, 40, 60, 80, 100 min etc], the solution was filtered using Whatman filter paper no. 41 and reserved for atomic absorption spectroscopy study. The factors affecting adsorption process such as contact time, pH, concentration of adsorbates, adsorbent dose, agitation speed and temperature were

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investigated. The adsorption capacity (q) and removal percentage are expressed as follows:

$$q = (C_0 - C_e)V / W \qquad (1)$$
$$\text{Removal (\%)} = ((C_0 - C_e) \times 100) / C_0 \qquad (2)$$

where q is the adsorption capacity of the adsorbate [$mg.g^{-1}$], w is the weight of adsorbent [g], V is the volume of solution[L], and Co [mgL^{-1}] and Ce [mgL^{-1}] are initial and equilibrium concentration of adsorbate in solution, respectively.

For Cd^{2+} adsorption, the removal efficiency of NZF after 120 min was found to be 77.08%. The pH of the solution was found to have a great effect on the adsorption of Cd^{2+} ions also. The adsorption increased sharply with pH and attained almost a constant value from pH 6 to 8 and then showed a decrease in adsorption level. The lower adsorption capacity observed at low pH may be explained on the basis of electrostatic repulsive forces between positively charged H_3O^+ and Cd^{2+} ions. At low pH values, the concentration of H_3O^+ is higher than that of Cd^{2+} ions and hence these ions are adsorbed on the active sites of activated adsorbents, leaving Cd^{2+} ions free in the solution. When the pH was increased, Cd^{2+} ions would replace with H_3O^+ ions. Competing effect of H_3O^+ decreased with increase of the pH, which increases the adsorption yield of the Cd^{2+} ions. As pH

increases the removal of Cd^{2+} takes place by adsorption as well as precipitation of Cd^{2+} ions in the form of $Cd(OH)_2$. The decrease in adsorption yield at alkaline conditions can be attributed to the formation of $Cd(OH)_3^-$ ions taking place as a result of dissolution of $Cd(OH)_2$ due to its amphoter characteristic. The hydrolysis and precipitation of metal ions affect adsorption by changing the concentration and form of soluble metal species those are available for adsorption. Depending upon the pH of the solution, various species of cadmium can be formed during the hydrolysis. The hydrolysis extent of Cd^{2+} ions is unimportant up to approximately pH 7.5 and cadmium is in the form of Cd^{2+} ions at this pH. For that reason it can be said that the adsorption mechanisms can be explained on the basis of H_3O^+–Cd^{2+} exchange reaction [5]. The amount of adsorption increased with adsorbent concentration from 0.025 g to 0.1 g and from 0.1 g onwards the adsorption percentage had attained an equilibrium level. The increase in concentration of Cd^{2+} resulted in increase of the amount adsorbed and decrease in percentage removal. To study the effect of temperature on the removal of Cd^{2+}, experiments were conducted at three different temperatures of 295, 300 and 305 K respectively. The results show that the amount of adsorption increased slightly with temperature for the adsorbent. The high driving force of attraction at higher temperature indicates the

higher mobility of ions. Results suggest that these adsorbents show endothermic nature of adsorption. The effect of agitation speed on the adsorption amount and percentage removal has been investigated. To study this parameter, the agitation speed (rpm) was varied from 50 to 200 rpm. There is increase in adsorption with respect to agitation speed with a maximum at 150 rpm. At 200 rpm the adsorption amount decreased. Hence the agitation speed was fixed at 150 rpm for studying the effect of all other factors on the adsorption process. The increase in agitation rate improves the diffusion of metal ions towards the adsorbent surface [6]. The diffusion rate of adsorbate ions (Pb^{2+}/Cd^{2+}) from the bulk liquid to the liquid boundary layer surrounding the particles becomes higher when the agitation rate is increased due to enhancement of turbulence and a decrease in the thickness of the liquid boundary layer. Thus, the external diffusion resistance can be neglected. A too vigorous agitation rate would result in more desorption of adsorbate from adsorbed sites.

4 CONCLUSIONS

Proper tuning can make NiO/ZnO heterostructured nanocomposite a good adsorbent for the removal of heavy metal ions.

5. REFERENCES

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