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Effect of annealing on the spectral and optical characteristics of nano ZnO: Evaluation of adsorption of toxic metal ions from industrial waste water

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ABSTRACT

The present work accentuates an unexploited and environmentally benign method of synthesizing ZnO nanomaterials using Sugar cane juice. The synthesized nanomaterials were characterized by XRD, SEM, TEM, BET, EDS and FTIR. UV–visible and photoluminescence studies were also carried out to understand the absorption properties of synthesized nanomaterial. From the adsorption studies, it would be clear that synthesized ZnO should be used as an effective adsorbent for Pb(II) and Cd(II) removal. The kinetic data followed the pseudo-second-order model. The equilibrium attained at 120 min and isotherm follows the order Sips > Langmuir > Freundlich. The adsorption–desorption studies conducted over 6 cycles illustrate the viability and repeated use of the adsorbent for the removal of Pb(II)and Cd(II) from aqueous solutions. The practical efficiency and usefulness of the adsorbent was tested using real industrial wastewater also. Cytotoxicity result shows that, ZnO was biocompatible at lower concentrations, and it was used as an ecofriendly nanoadsorbent for industrial and environmental applications.

1. Introduction

Toxic heavy metals like lead (Pb), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), silver (Ag), mercury (Mg) and zinc (Zn) in trace amount were present in natural constituents in earth crust. But human activities will enhance its concentration; these terrific increases of heavy metals are major concern in the field of water pollution (Radhakrishnan et al., 2015). The effects of acute lead and cadmium poisoning can cause serious health and environmental issues. Various technologies were developed for the effective removal of these metal ions from the aqueous solution, ion exchange, and adsorption are considered as basic purification methods for the treatment of industrial wastewater due to simplicity in practical application, high efficiency and economic nature (Shibi and Anirudhan, 2005). Recent adsorption techniques, based on the nanomaterial as adsorbent, has been hot spot due to significant higher surface area to volume ratio resulting higher adsorbent efficiency and spontaneous removal of toxic metal ions (Li et al., 2007). Nano metal oxides with multi-carboxyl fictionalization are reported to be effective for the removal of metal ions from the aqueous solution. The proposed profitability of the nanometal oxide is the availability of functional moiety covalently bonded to the inorganic matrix for binding metal ions due to higher surface area, highly-stable, non-toxic, economical approach, and facile synthesis (Goswami et al., 2012).

ZnO is a fascinating semiconducting material which has been much investigated in recent years due to its extensive important applications as catalysis, electrode materials, gas sensors and electrochromic films (Usman Ali et al., 2011). Recently, various chemical and physicochemical methods have been employed to produce ZnO nanomaterials including nanoparticles, nanorods, nanowires, and nanosheets. Among the various hierarchical structures, ZnOs remain of significance to chemists and material researchers due to their ability to form nanomaterials easily and role in device applications (Benxia and Yanfen, 2010). As an environmentally friendly material, ZnOs are promising candidate for contaminant removal and environmental remediation. Therefore, developing a facile and template-free method to prepare hierarchical ZnO structures is of scientific and practical importance. The use of green techniques for the synthesis of nanomaterials is a dynamic area of research in recent years. To utilize plants and fruit extract for the synthesis of nanomaterials could be more

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advantageous, because of the easy availability and produce no toxic industrial wastage (Tamuly et al., 2013). In this paper, we report for the first time the synthesis of ZnO nanomaterials using Sugar Cane juice, rich in hydroxyl groups and well-known for its excellent anti-oxidant properties. Sugar cane juice is used as therapeutic agent in treatment of cancer, jaundice, urinary tract infection, inflammation in the stomach or digestive tract etc. The nutrients present in sugar cane juice are beneficial for the smooth functioning of vital organs, such as the brain, heart and sex organs (Karthikeyan and Samipillai, 2010). We have investigated the adsorption efficiency of biogenic synthesized ZnO nanomaterials on the adsorption of Pb(II) and Cd(II) ions. We have also studied the toxicity of these nanomaterials to investigate its environmental applications. Studies revealed that Cytotoxicity of nanomaterials is higher as compared to their bulk counter parts. The size and shape of the nanomaterials have significant effect on cell viability and cytotoxicity (Bhuvaneshwaria et al., 2015). With the increasing demand of nanomaterials in the field of biological applications cytotoxicity of nanomaterials becomes a major concern, especially ZnO nanomaterials. ZnO nanomaterials are widely used in cosmetics, sunscreens, foot care, and ointments etc. Here we investigated a short term *in vitro* cytotoxicity, determined by Trypan Blue exclusion method by using Dalton Lymphoma ascites (DLA) tumor model in Swiss Albino mice.

2. Materials and methods

$ZnCl_2.xH_2O$ was procured from Sigma Aldrich. Sugar cane were collected locally and crushed it to obtain fresh concentrated juice. All the solutions for the synthesis of Zinc Oxide nanoparticles were freshly prepared using demineralized water.

2.1. Synthesis of nano ZnO

Sugar Cane (sc) is crushed to get 20 ml of fresh concentrated juice. The juice is then made up to 20 ml using deionised water and filtered. The filtrate is slowly mixed with 0.25 g zinc chloride ($ZnCl_2.xH_2O$) salt dissolved in 25 ml of demineralized water with constant stirring for 30 min. Then the solution was microwave-heated by a 100 W domestic microwave oven for 10 min to obtain a turbid white precipitate, which was cooled to room temperature, filtered, washed with water followed by drying in hot air oven at 90 °C for 24 h. The obtained product is then annealed for 2 h at 300 (denoted as Zn203), 500(denoted as Zn205) and 700 °C (denoted as Zn207) separately and cooled to room temperature.

2.2. Adsorption experiments: batch type contact method

Adsorption experiments were carried out in a thermostatic water bath shaker at 150 rpm rate at a particular temperature for a predetermined time intervals using 100 ml clean and dried Stoppard bottle. The metal ion concentrations in liquid phase were determined by atomic absorption spectroscopic studies. The amount of metal ions adsorbed in (mg/g) at equilibrium (qe) was calculated from the mass balance of initial and final metal concentrations in the aqueous phase. The amount of metal ion adsorbed at time q_e was calculated from mass balance equation (Anirudhan et al., 2013).

$$q_e = \frac{(C0-Ce)V}{m} \tag{1}$$

where q_e is the adsorbed metal ions per unit mass of adsorbent (mg/g) and V is the sample volume in L, m is the weight of the adsorbents.

The removal efficiency of various nanoadsorbents was calculated by using the equation,

$$\%\ \text{removal} = \frac{C0-Ce}{C0}\times 100 \tag{2}$$

where Co and Ce are the initial and the equilibrium concentrations of heavy metal ions.

The quantity of metal ions adsorbed at selected time intervals was determined and used for kinetic analysis. Through the batch adsorption experiments it is possible to collect the details of the applicability of adsorbent materials. But for studying the practical application in a bulk, continuous column studies are to be conducted in waste water effluents.

The adsorption conditions for the adsorbents were optimized by varying experimental parameters such as contact time, pH, initial concentration of adsorbate, temperature, adsorbent dose by batch method.

2.3. Cytotoxicity studies

The *in vitro* cytotoxicity studies of the synthesized nanomaterials were carried out using Daltons Lymphoma Ascites Cells [DLA]. The tumor cells aspirated from the peritoneal cavity of tumor bearing mice were washed thrice with Phosphate Buffer Saline (PBS), and the cell viability was determined by trypan exclusion method. Viable cell suspension (1×10^6 cells in 0.1 ml) was added to tubes containing various concentration of the nanoadsorbates and the volume was made up to 1 ml using PBS. Control tube contained only cell suspension. There assay mixture were incubated for 3 h at 37 °C. Further cell suspension was mixed with 0.1 ml of 1% trypan blue and kept for 2–3 min and loaded on a haemocytometer. Dead cells take up the blue color of trypan blue while live cells do not take up the dye. The number of stained and unstained cells was counted separately.

$$\%\ \text{Cytotoxicity} = \frac{\text{Number of dead cells}}{\text{Number of live cell} + \text{Number of dead cell}} \times 100 \tag{3}$$

2.4. Instrumentation

The XRD measurement was performed on an XPERT-PRO powder diffractometer with Cu-Kα radiation as the X-ray source in the 2θ range of 10–90°. The surface morphology was measured by a scanning electron microscope (SEM) of model JED-2300 system. The size and morphology of the samples were obtained from Transmission electron microscopy (TEM, Philips CM200). FTIR spectra recorded using Perkin-Elmer FTIR Spectrophotometer in the wavenumber range of 400–4000 cm^{-1} by KBr disc method. UV–visible studies were carried out using JASCO V 650, UV/Vis spectrophotomer. The synthesized ZnO nanomaterials were optically analyzed using Horiba Jobin Yvon Flourolog (III) Spectroflourometer equipped with 450 W Xenon lamp and Hamatsu R928-28 photomultiplier. The sample was excited with a wave length of 325 nm in the region of 350–600 nm. Adsorption studies were carried out using GBC-AAS spectrometer having lamp current 5 mA and a wave length 270 nm.

3. Results and discussion

3.1. XRD analysis

The XRD of the synthesized ZnO (Fig. 1) shows broad peaks at 2θ values of 31.8, 34.4, 36.2, 48.01, 57.3, and 62.7 which are typical