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Comparative performance of bare and functionalize ZnO nanoadsorbents for pesticide removal from aqueous solution

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ABSTRACT

The present study focus on the naphthalene adsorption from aqueous solution by using ZnO nanoparticles (NPs) synthesized via microwave methodology. This study reveals that the adsorption capacity depends not only on the textural features of the material but also on the functionalization of the nanoparticles. It was found that 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF-IL) functionalized Zinc oxide nanoparticles show maximum adsorption capacity (148.3 mg g^{-1}) towards naphthalene removal as compared with CTAB functionalized (89.96 mg g^{-1}) and bare ZnO (66.80 mg g^{-1}) nanoparticles. To obtain a good picture of the surface and best interpretation of the adsorption process various isotherms were applied. To find out the rate constant of adsorption process, the well-known kinetics models i.e. pseudo first order and pseudo second order model were applied as a function of time and it was found that pseudo-second order model fits best in the adsorption process. Further the adsorption studies were performed in real water samples and in different salts to ensure that nanoparticles work well in presence of real water samples and different ions respectively. Recovery technique of the nanoparticles using a simple methodology is also described.

1. Introduction

One of the most important problems faced by a lot of countries around the world is the deteriorating supply of clean water. The enhancement in the contaminants release from various industries such as heavy metals [1], dyes [2] pesticides [3] and pharmaceuticals waste [4] into the aquatic surroundings, which disturb the environment by effecting human health and also aquatic living organisms. One major concern is to protect contamination of water resources by using advanced technologies [5].

The widespread use of pesticides in farming is degrading soil and water quality. The majority of the pollutants are stable; small in size and non-biodegradable in the bionetwork hence there removal from waste water is the biggest concern [6]. Occurrence of the persistent pesticides in the water bodies can cause adverse health effects on public and environment [7]. It was found by WHO and UNEP that roughly 200,000 people dies and around three million are poisoned each year by use of various pesticides all over the world. India is home to approximately 16% of the total population, but has just less than 2% of the total landmass. Further the rapid growth of the population together with a high efficiency on achieving food grain self-efficiency has forced to use the pesticides [8].

There are various types of pesticides which are frequently used out of which polycyclic aromatic hydrocarbons (PAHs) are the most commonly used pesticides, which contribute towards effluents. PAHs compounds are considered as foremost contaminants because of their enduring persistence and extremely high solubility in the aqueous media [9]. These pesticides are well known toxic hazardous pollutants causing tumours [10], mutagenic effects [11,12] in the living organisms. Out of the various forms of PAH, naphthalene is one of the frequently used pesticide in domestic purpose etc. and there is an urgent need to remove this pollutant [13].

Many techniques generally employed to remove pesticides from the waste water effluents such as adsorption [14], chemical coagulation [15], photodegradation [16], electrochemical degradation [17], membrane filtration or phase separation [18], nanofilteration [19], ion exchange processes [20] and oxidation [21]. However it is not easy to search a distinct valuable method that can take out all the harmful pollutants from wastewater. Adsorption on nanoparticles is currently one of the most striking techniques for the removal of various pollutants from the water. The continually escalating demand for the waste water treatment has caused substantial attention to be focused towards reuse and recyclability of the method used for waste water treatment [22]. Nanoparticles usage for removal of pesticides could be advantageous as compared to other available materials, because of the unusual properties of nanoparticles such as low cost, ready availability, eco-friendly nature, and high effectiveness. Among a range of nanoparticles, ZnO possess an unusual place due to its unique properties and extensive

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applications [23–25]. Also functionalization with the suitable material on the surface of nanoparticles enhances the properties of nanoparticles [26–28]. Recently we have reported the role of 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF-IL) functionalized ZnO in the removal of various toxic dyes [29].

In this present study, the removal characteristic of naphthalene was investigated by using ZnO nanoparticles as an adsorbent. Due to fewer publications concerning about the adsorption of naphthalene we developed a simple microwave synthesis procedure for ZnO nanoparticles and used them for adsorption of naphthalene. The influence of various real water samples and interference of different salts/inorganic ions in the naphthalene removal was investigated and it was found that presence of ions does not alter the efficiency of ZnO. The present study is novel as functionalized ZnO resulted in better adsorption of naphthalene from aqueous solutions as compared to bare ZnO nanoparticles. The adsorption technique was valuable and cost effective for enhanced removal of naphthalene and other such pollutants from aqueous solution. Moreover a recovery system of the naphthalene from the nanoparticles surface using a simple process was also described.

2. Materials and methods

2.1. Chemicals

Sodium hydroxide (NaOH, 98%), cetyltrimethylammonium bromide (CTAB, 99%), 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF-IL,99%), zinc acetate dihydrate ($Zn(OAc)_2\cdot 2H_2O$), cadmium acetate ($Cd(CH_3CO_2)_2$, 98%), aluminium nitrate nona hydrate ($Al(NO_3)_3\cdot 9H_2O$, 98.7%), sodium acetate (CH_3COONa, 98%), sodium carbonate (Na_2CO_3, 98%), and naphthalene ($C_{10}H_8$, 99%) were purchased from Sigma-Aldrich, India. Ethanol was obtained from Changshu Yangyuan Chemical, China. All the chemicals were used without any further purification. Double distilled water is used for all the experiments.

2.2. Preparation of zinc oxide nanoparticles

ZnO nanoparticles were synthesized by using commercial microwave synthesis with different surface templates. For this synthesis, 0.11 g of Zinc acetate (10 mM) was taken in beaker containing 50 ml of double distilled water, then this solution was stirred for 10 min to obtain a clear solution. To the prepared solution 0.2 g of NaOH (0.1 M) was added drop wise till the solution turned into white precipitates. The formed solution mixture was micro waved for 10 min at 500 W (80 °C).

For functionalization after taking Zinc acetate (10 mM) salt in 50 ml of double distilled water, CTAB (0.8 mM) and BMTF-IL (20 mM) as capping agent was added respectively in separate beakers. Further the respective solutions were stirred for 10 min, to which 0.1 M solution of NaOH was added drop wise after that the reaction mixture was micro waved for 10 min at 500 W (80 °C) separately. After the completion of all the reactions white precipitates were separated by centrifugation, washed with ethanol and double distilled water, which were further dried at 50 °C to get ZnO nanoparticles.

2.3. Characterizations of synthesized ZnO nanoparticles

The microwave synthesis of nanoparticles was performed on Anton Paar (Multimode reactor) microwave reactor. To find out the structural, morphological, optical and compositional properties the formed ZnO nanoparticles were characterized through various techniques. Transmission electron microscopy (TEM; Hitachi-H-7500) was performed to obtain the size and dispersity of the nanoparticles. The crystallinity and X- ray pattern of the prepared powdered sample were performed at room temperature utilizing the X-ray diffraction (XRD; PANanalytical Xpert Pro.) utilizing Cu-Kα radiation ($\lambda = 1.54178$ Å) in the range of 0–90°. FTIR spectrum of prepared nanoparticles was carried on Perkin Elmer (RX1) FT-IR spectrophotometer in range of 400–4000 cm^{-1}. UV–Vis was examined on JASCO V-530 to find out the optical properties of synthesized nanoparticles. To find out the surface area of the functionalized nanoparticles BET (Branauer-Emmett teller) was performed using Quantachrome Instruments (version 3.01). AFM analysis was performed on Bruker AFM analyzer to see the morphology of the synthesized ZnO nanoparticles.

2.4. Adsorption studies

To understand the effect of three different types of ZnO nanoparticles on the removal efficiency of naphthalene, 25 ppm of naphthalene was dissolved in double distilled water. Due to less solubility of naphthalene in aqueous system it was sonicated for 1 h. before experimental trials. Batch experiments were performed to understand the mechanism of naphthalene adsorption. The pH of the solutions was adjusted with HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}) solution by using pH meter (Mettler Toledo digital pH meter). After stirring samples for definite interval of time, aliquots were withdrawn and centrifuged for 5 min. The supernatant was investigated by using UV–Vis spectrophotometer. Adsorption competence of naphthalene over different ZnO nanoparticles was computed by following equation (Eq. (1))

$$\text{Adsorption efficiency}(\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

where, C_o is the initial concentration of naphthalene and C_f is final concentration of the naphthalene after adsorption, respectively. Similarly, the desorption efficiency of naphthalene were calculated from the following equation:

$$\text{Desorption efficiency}(\%) = \frac{C_d}{C_0 - C_f} \times 100 \tag{2}$$

where, C_d is the concentration of naphthalene after desorption from ZnO nanoparticles surface.

3. Results and discussions

3.1. Structural and morphological analysis of ZnO templates

ZnO nanoparticles have been synthesized via a greener approach i.e. microwave synthesis using water as a medium. After the successful synthesis the nanoparticles were characterized by using techniques such as UV–visible spectra (UV–Vis), Photoluminescence (PL), X-ray diffraction (XRD), Fourier-transform infra-red (FTIR), transmission electron microscope (TEM) and field emission scanning electron microscope (FE-SEM) along with Energy dispersive X-ray spectroscopy (EDX). TEM images revealed that the ZnO nanoparticles were spherical in shape having size of 4–10 nm, 20–25 nm and 15-22 nm respectively for BMTF-IL functionalized, CTAB and bare ZnO NPs. Detailed characterization was reported earlier [26]. The synthesized ZnO nanoparticles were subjected for Nitrogen gas (N_2) physical adsorption-desorption studies at 77.350 K to analyze the pore structure and surface area. Using the well-known Barret-Joyner-Halendar (BJH) method N_2 adsorption/desorption isotherm and pore size distributions were obtained (Fig. 1). The surface area of BMTF-IL functionalized ZnO nanoparticles was found to be 21.971 m^2/g which is more than CTAB functionalized ZnO (17.164 m^2/g) and bare ZnO (14.782 m^2/g) nanoparticles which confirm that the BMTF-IL functionalized resulted in smaller sized nanoparticles and possess high surface area. The atomic force microscopy (AFM) was used to find out the morphology of the ZnO nanoparticles. It was observed that the particles were spherical in shape (Fig. 2).

To certify that the adsorption process does not modify the properties of nanoparticles, X-ray diffraction (XRD) and Fourier transform infra-