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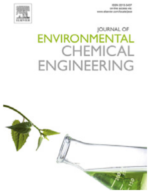

Nickel doped Zinc oxide as a potential sorbent for decolorization of specific dyes, methylorange and tartrazine by adsorption process

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ABSTRACT

Nickel doped zinc oxide ($Ni_{0.05}Zn_{0.95}O$) nanoparticles were tested as a possible potential adsorbent for the removal of specific dyes, methylorange and tartrazine, from an aqueous solution. The adsorbent was synthesized by forced hydrolysis conducted in polyol medium and characterized by X-ray diffraction (XRD), nitrogen adsorption/desorption isotherms, UV–vis spectroscopy and TEM images. Experiments showed that Ni doped ZnO nanoparticles were very efficient for the removal of TA and MO dyes and quasi-equilibrium reached in 30 min. The removal efficiency was found to be dependent on the initial dyes concentration and there is no significant effect of temperature on the adsorption process of dyes. Maximum adsorption capacity of dyes was achieved at pH 4 and 6 respectively for TA and MO. The adsorption capacity decreases proportionately to adsorbent dosage. Both the right match and accurate prediction of q_e indicate that the pseudo second-order kinetic model better describes the adsorption of MO and TA dyes on Ni doped zinc oxide. The equilibrium data were analyzed by the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich and intra-particle diffusion, mass transfer models, which revealed that Freundlich and Temkin isotherms were more suitable for describing MO and TA dyes adsorption than the other two isotherm models. Thermodynamic study showed that the adsorption was a physisorption, spontaneous and endothermic process.

Introduction

Methylorange (MO) and tartrazine (TA) anionic azo dyes are the most commonly used substances for dyeing cotton, wood, and silk [1]. These substances are usually present in the effluent water of many industries, such as textiles, leather, paper, printing, foodstuffs and cosmetics. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies [2]. Although methylorange is not considered to be very toxic, it can cause some harmful effects such as vomiting, increased heart rate, diarrhea, shock, cyanosis, and tissue necrosis in human beings [3]. Contrary to MO, tartrazine (known as E102) is considered to be mutagenic and carcinogenic and can also cause some allergic problems [4,5]. Consequently, the wastewater containing these dyes with various concentrations (ranging from mg L^{-1} to few tens of mg L^{-1}) should be treated before discharge. There are several methods to remove dyes including physical and chemical process. Among them, adsorption has been considered an attractive process due to its many advantages such as low cost, simplicity of design, ease of operation, insensitivity to toxic pollutants and smaller amounts of harmful substances [6]. Various adsorbents, such as fly ash [7], swelling clays [8], sawdust [9], pineapple leaf powder [10], activated carbon (AC) [11], and carbon nanotubes [12,13], have been studied for adsorption of dyes from aqueous solutions. Among the above-mentioned adsorbents, AC seems to be the best, because of its large specific surface area, low density, chemical stability, variety of structural forms, and the ability to modify the pore structures [14]. However there are still some disadvantages such as, firstly, high costs due to the added cost of activated carbon regeneration, and secondly, long adsorption time and the inconvenience of separation, as any regeneration process results in a loss of carbon with a potentially slightly lower adsorption capacity. Many researchers are therefore working hard to develop alternative adsorbents which may replace activated carbon in pollution control. In the last ten years, attention has been focused on nanoparticles of various oxides. Indeed thanks to the nanometer size, such oxides can be easily dispersed in solution and thus are likely to present high surface contact with pollutants. Furthermore, these oxides may present physical properties which can be of great help for depollution process. In this context, magnetic iron oxide (Υ-Fe_2O_3) has been used as adsorbent for methylorange dye. Its ferromagnetic character enables it to easily remove pollutants from contaminated water by simply applying a magnetic field into the reactor [15]. The system CuO–ZnO is another example from these new classes of nano-adsorbent. Here, the photoluminescence of these materials enables to achieve photo-catalytic degradation of Acid Red 88 impregnate on the

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nanoparticles of the adsorbent [16]. Nanoparticles of the perovskite compounds $SrFeO_3$ have shown good efficiency in degradation of organic pollutants under dark ambient conditions [17].

The present work concerns nanoparticles of Ni doped ZnO, a material belonging to the spintronic class. Some of it's uses have been shown in a recent work that this nanomaterial presents both interesting magnetic and photo-luminescent properties [18]. Most of the studies reported in the literature dealt with the removal of dyes or organic compounds by a photo-catalytic process in the presence of Ni doped zinc oxide thin films, nanopowders and nanorods [19–22]. This work lies within a more general goal we are presently developing, which pertains to propose a depollution process including several steps based on the multifunctional of such material (high surface/volume, ferromagnetic and photo-luminescent characters). Indeed, to our knowledge there is no study which compared the adsorption process of dyes onto nickel doped zinc oxide nanoparticles of small size and a low specific surface area.

MO and TA with large and complicated structures were selected as model dyes because of their well -known kinetic and isotherm analysis in materials such as activated carbon, zeolithe and ash, etc.

In this paper, the comparison is made for the adsorption behavior of MO and TA (some tens of mg L^{-1}) on nickel doped zinc oxide nanoparticles as a possible sorbent for the removal of dyes from aqueous solutions. The objective of this study is to investigate the adsorption properties, based on equilibrium adsorption capacity, pH effect, concentration effect, adsorbent dosage, temperature and contact time on the adsorption process. Kinetics studies have been performed and the results have been analyzed by applying conventional theoretical methods. The physico-chemical properties of the material were also discussed here.

Experimental part

Adsorbent synthesis

Nickel doped zinc oxide nanoparticles (NP) were synthesized by forced hydrolysis in polyol media according to the previous work reported by Balti et al. [18]. All chemicals, of the highest quality available, were ordered from Sigma–Aldrich. Ni doped ZnO NP were prepared by refluxing zinc acetate dihydrate and nickel acetate tetrahydrate, using PEG (1,2-propanediol) as a solvent. In a typical procedure, zinc acetate dihydrate (0.5 M), nickel acetate tetrahydrate (0.025 M), ground in a mortar, were introduced into a three-neck round-bottomed flask and then dissolved in PEG (100 mL). Sodium hydroxide (4.3 g) and purified water (17 mL) were also introduced. The three-neck round-bottomed flask was slowly heated to reflux (189 °C) and kept at reflux for 4 h. After cooling down to room temperature, the particles were separated from the liquid polyol by centrifugation and then washed repeatedly with ethanol three times and finally once with acetone. The obtained product was placed in an oven for 24 h at 60 °C to produce the $Ni_{0.05}Zn_{0.95}O$ powder. The same procedure was used for the synthesis of un-doped ZnO nanoparticles.

Adsorbent characteristics

The morphology and surface structure of Ni doped ZnO ($Ni_{0.05}Zn_{0.95}O$) and un-doped ZnO nanoparticles were examined using a JEOL JEM-2010 transmission electron microscope (TEM). X-ray diffraction (XRD) was also used to determine the crystal phase of the obtained powder by means of an INEL X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å). The band gap of nanoparticles was determined by the maximum wavelength through optical absorption spectroscopy. Nitrogen adsorption isotherms at 77 K were determined in a Micrometric ASAP 2000 apparatus. The surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) equation, the adsorption average pore width (4 V A^{-1} by BET) (L) was determined by the Barrett–Joyner–Halenda (BJH) method.

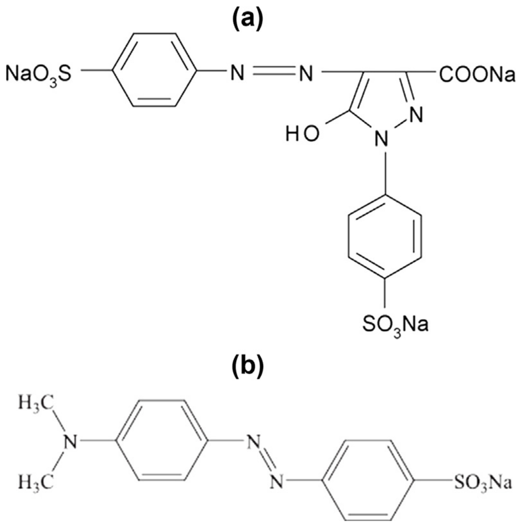

Fig. 1. Chemical structures of tartrazine (a) and methylorange (b).

MO and TA solutions

MO (C.I. no: 13,025, FW = 327.33) and TA (CI. no: 19,140, FW = 534.36), of the highest quality available, were supplied from Sigma–Aldrich and were used without any further purification. A mother-solution of 1500 mg L^{-1} for MO and TA was prepared by dissolving an accurate amount of dye in a liter of ultrapure Millipore Milli-Q water with a resistivity of 18.2 MΩ cm and less than 10 p.p.b of organic carbon. The experimental solutions were prepared by diluting the mother-solution of MO and TA to the desired concentration. The pH of each solution was adjusted in acidic and basic media by solution of HCl or NaOH (0.1 M) respectively. The chemical structures of TA and MO are shown in Fig. 1(a) and (b) respectively.

Adsorption process media

Batch adsorption experiments were performed using a 100 mL glass conical beaker in a homemade thermostated batch. In a typical procedure, 0.1 g of adsorbent was added to a glass beaker containing 25 mL of dye solutions in a concentration varying from 19 to 98 mg L^{-1}. The beaker was then placed in the batch media and stirred at 100 rpm for the desired time and temperature throughout the experiments. At the end of the equilibrium period, the suspensions were separated by centrifugation at 5000 rpm for 10 min, for later analysis of the dye concentrations. The concentration of the dyes in the solution was measured using a UV–vis spectrophotometer 6705 multi Cell Changer Jenway at 465 and 425 nm respectively for MO and TA. The contact time was varied from 0 to 30 min, the adsorbent dosage from 0.025 to 0.5 g, the temperature from 307 to 337 K and finally, the pH of the solutions from 2 to 12.

Some specific terms were defined here in order to evaluate the potential adsorption of Ni doped zinc oxide nanoparticles.

The removal efficiency (RE) was defined as follows:

$$\mathrm{RE}\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

where C_0 and C_t were respectively the concentration of dyes before and after adsorption.

The amounts of the dyes adsorbed on Ni doped ZnO at any time, t, were calculated from the concentrations in solutions before and after adsorption. At any time, the amount of MO and TA adsorbed, q_t