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Synthesis and characteristics of polyaniline/zirconium oxide conductive nanocomposite for dye adsorption application

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ABSTRACT

The organic–inorganic hybrid nanocomposite of polyaniline/zirconium oxide was synthesized through the chemical method, using the ammonium persulfate as an oxidant. The developed adsorbent was characterized using various analytical techniques such as scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. The developed nanocomposites i.e. polyaniline modified with ZrO_2 and polyaniline were used as effective adsorbents for the rapid removal of methylene blue from the solvent phase. The effects of different system variables such as initial dye concentration, temperature and contact time were well studied and investigated. From the optimized parameter results obtained it was found that as contact time increases, the dye removal efficiency also increases. Additionally as the temperature increased the amount of adsorption also increased. The results indicated that the polyaniline modified with ZrO_2 and polyaniline nanocomposite have considerable potential for the removal of methylene blue from aqueous solution. The adsorption capacities (qmax) of polyaniline modified with ZrO_2 ($PANI/ZrO_2$) and polyaniline (PANI) for methylene blue in terms of monolayer adsorption were 77.51 and 192.30 mg/g, respectively.

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1. Introduction

About 30 years ago polymers were considered as a conductor and also polymers and plastics that had electrical conduction power were meaningless. After discovery of some polymers that were conductive and electrical by nature, this idea changed. PANI has properties such as good environmental stability, cheap synthesis procedure, air and moisture stability, and high flexibility. It has a great variety of potential application including anti-corrosion coating [1–3], batteries [4] and sensors [5,6], full-cells, and computer chips [7–9].

It is estimated that approximately 40,000 tons of dyes out of roughly 450,000 tons in total production is not used but discharged into wastewaters. A large variety of dyestuffs is available under the categories of acid, basic, reactive, direct, disperse, sulfur and metallic dyes [10]. Dyes are synthetic aromatic compounds, which have various functional groups [11]. Some dyes and their degradation products may be carcinogens and toxic, and consequently their treatment cannot depend on biodegradation alone [12]. High amount consumption of methylene blue leads to several cardiovascular diseases like hypertension and precordial pain, in dermatological diseases it leads to staining of skin and necrosis, in gastrointestinal diseases it leads to fecal discoloration, nausea, and abdominal pain while in hematological disease it leads to anemia and in genito-urinary problems it leads to bladder irritation. The discharge of this colored noxious waste not only is damaging the esthetic nature of receiving streams, but also is toxic to the aquatic life [13]. Adsorption is one of the most effective physical processes for the removal of color and treatment of textile effluents. Currently, activated carbon is the most effective adsorbent, but it suffers from two major disadvantages: high cost and difficulties in regeneration. These include phosphate [14], bagasse pith [15,16], sunflower [17], fly ash [18], peat [19], saw dust [20], marine algae [21], fungal biomass [22], wasted activated sludge [23], digested sludge [24], red mud [25], coir pith [26], Neem leaf [27], waste organic peel [28] and tree fern [29]. However, the adsorption potential of most of these low cost adsorbents is generally low [30–48].

The objectives of this study were: (i) to synthesis of PANI and $PANI/ZrO_2$; (ii) to determine the appropriate dosage of PANI and $PANI/ZrO_2$ to adsorb MB; (iii) to measure the effect of various factors such as contact time, initial concentrations and temperature on the removal efficiency of PANI and $PANI/ZrO_2$ were also studied; and (iv) to measure the coefficients of Langmuir and Freundlich for adsorption of MB.

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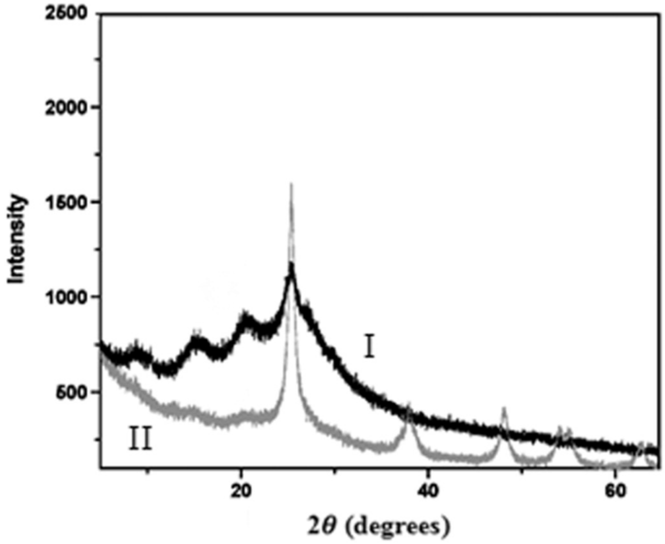

Fig. 1. X-ray diffractometer (XRD) spectra of (I) PANI and (II) $PANI/ZrO_2$.

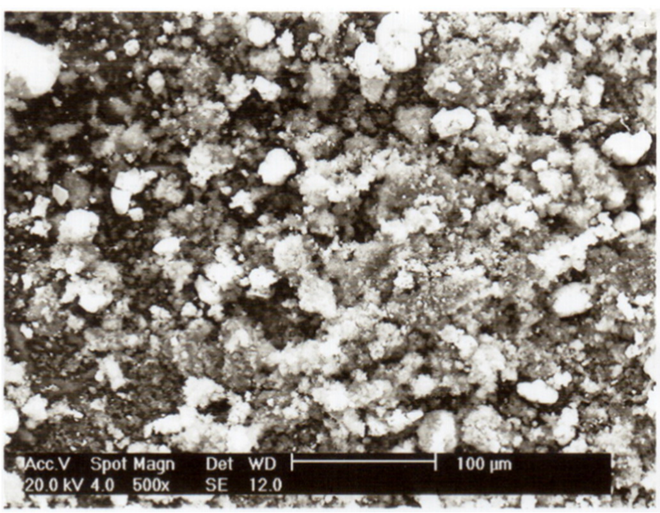

Fig. 2. Scanning electron microscopy (SEM) spectra of $PANI/ZrO_2$.

2. Materials and methods

2.1. Reagents

Aniline 99.5% (that was distilled water two times), hydrochloric acid and ammonium persulfate ($(NH_4)_2S_2O_8$) were purchased from the Merck. Zirconium oxide and methylene blue (CI 52015) were supplied by Merck.

2.2. Synthesis of polyaniline and $PANI/ZrO_2$ composite

2.2.1. Synthesis of polyaniline

In a typical experiment, 50 ml of 1 M HCL solution was added to 1 ml of aniline and mixed for 15 min in an ice bath. 2.45 g ammonium persulfate was added to 10 ml of 1 M HCL solution. The resulted colorless solution was added to the first solution drop by drop. At first, the color of solution becomes light pink and after 24 h in an ice bath, it changed to dark green. The resulted solution is Emeraldine salt. Then it was filtered and washed with acetone and ethanol several times and then dried in oven at 60 °C for 1 h.

2.2.2. Synthesis of $PANI/ZrO_2$ composite

1 g polyaniline (prepared according to the procedure reported earlier) was dissolved in 0.5 M HCL and added to 25 ml from this solution to 0.3 g zirconium oxide. After that sonication for 30 min the solution was filtered and washed with distilled water and ethanol, then dried at 70 °C for 45 min.

2.3. Adsorbent characterization

Fourier transform infrared (FT-IR) spectrophotometer model Nicolet 380, X-ray diffractometer (XRD) Philips X'Pert and scanning electron microscope (SEM); JEOL JSM-5600 Digital Scanning Electron Microscope were employed.

2.4. Batch adsorption studies

For isotherm studies, the effect of the initial MB concentration (10 and 40 mg/L) was investigated by adding 0.01 g of PANI and $PANI/ZrO_2$ into 20 ml of each MB solution, and the mixtures were agitated at 1000 rpm for 10 min. For the effect of contact time, the experiments were conducted by adding 0.01 g of PANI and $PANI/ZrO_2$ into 20 ml of the MB solutions (30 mg/L) and agitated for varying contact times (5 min to 60 min) at room temperature. The effect of temperature

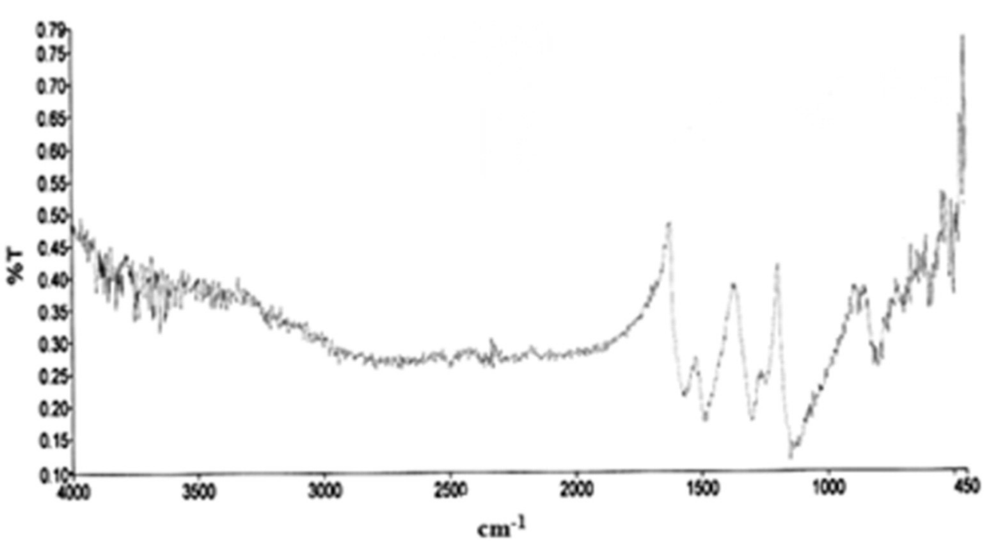

Fig. 3. Fourier transform infrared (FTIR) spectra of $PANI/ZrO_2$.

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