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Original Research Paper

Heulandite/polyaniline hybrid composite for efficient removal of acidic dye from water; kinetic, equilibrium studies and statistical optimization

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ABSTRACT

Heulandite/polyaniline (HU/PANI) composite was prepared by mechanical mixing from natural heulandite and synthesized polyaniline. HU/PANI was characterized by XRD, SEM, TEM, FT-IR, and UV–Vis spectroscopy. The product is of polycrystalline nature with an average crystallite size of 25.7 nm and optical band gap of 1.69 eV. HU/PANI shows higher efficiency in the removal of light green SF dye than natural HU or PANI in the dark and under artificial illumination. The equilibrium time was attained after 360 and 480 min in the dark and under illumination, respectively. The results fitted well with pseudo second order and Elovich kinetic models. The adsorption isotherm in the dark fitted well with Langmuir isotherm model and the calculated q_{max} was 44.6 mg/g. Using illumination, the data fitted better with the Freundlich and Temkin model than with the Langmuir model. Based on response surface analysis, the predicted conditions for maximum removal of light green SF dye in the dark (70.9%) were 5.5 mg/L, 24 mg, 3, and 430 min for dye concentration, HU/PANI dose, pH, and contact time, respectively. Whereas, under light illumination (97%) at operating conditions of 15 mg/L, 15 mg, 3, and 589 min, respectively. The composite also shows high efficiencies in the removal of other types of acidic and basic dyes.

1. Introduction

There continuous pollution of fresh water resources under the extensive industrial and non-environmental agricultural activities which reduce the quality of water supplies for the human communities as well as their ecosystems [1,2]. Industrial and agricultural wastewater effluents are loaded by different pollutants as metals, dyes, pesticides, fertilizers, organic matters and suspended particles which have negative effect on the water quality and the ecosystem [3].

Dyes are natural or synthetic coloring materials with a complex aromatic chemical composition [4], which may be anionic, cationic or non-ionic (disperse) [5]. Dyes are widely used in several industries such as pigments, leather, printing, rubbers, textile, and paint [6]. The annual production of synthetic dyes in the world range from 7×10^5 to 1×10^6 tons [7,8]. There is about 10–15% from the produced synthetic dyes are discharged into our environment and surface water bodies as untreated effluents causing severe environmental problems [9]. Occurrences of such toxic and non-degradable pollutants in natural water impede the light penetration, which upset the photosynthesis of aquatic plants [10,11]. Also, dye contaminants can reduce the water quality and cause several diseases as skin irritation, cancer, dysfunction of liver and kidney; and allergy [12].

Several techniques are used to eliminate synthetic dye pollutants from water bodies. The commonly used techniques are photocatalytic degradation, Fenton's oxidation, photo Fenton's oxidation, membrane filtration, flocculation, ion exchange, electrochemical destruction, electrokinetic coagulation, ozonation, adsorption and biodegradation [9,13,14]. Adsorption by minimal effort and efficient materials gave off an impression of being all the more encouraging methodology and prescribed for the removal of heavy metals and dyes from water [15,16]. The adsorption process is simple, cheap, and easy to handle, less maintenance; and the amount of produced sludge is smaller than the other methods [15].

Among adsorptive materials, natural and synthetic zeolite minerals were introduced as brilliant materials for efficient removal of organic and in organic contaminants from wastewater [17,18].

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Zeolites are aluminosilicate minerals of microporous structure and their crystal structure composed of a three-dimensional network of SiO_4 and AlO_4 tetrahedrons [19]. Ionic substitution of Si^{4+} ions by Al^{3+} ions commonly occur in the crystal lattice of zeolite minerals forming a net negative charge [20]. Thus, several alkali cations as Na^+, Ca^{2+} or K^+ are usually present to balance charges in the crystal lattice. In addition, these ions are exchangeable with other cations in solution which appears to be promising for the removal of dissolved water pollutants. However zeolites are groups of natural minerals, they can be synthesized in the laboratory. About 45 species of natural zeolite minerals were recorded in the world as clinoptilolite, heulandite, mordenite, phillipsite, and chabazite [21]. Natural zeolite minerals are environmental, cheap and available materials with the exceptional surface area, adsorption, chemical stability, and mechanical strength and ion exchange properties [22]. However, the adsorption capacity of zeolites can be enhanced through several surface modification processes or by forming of composites with other materials [23]. Recent studies revealed that zeolite-polymer composites exhibited unique properties for several advanced applications such as superior adsorptive products [24].

Composites, in general, are materials composed of minimum two components. Such mixed materials show different physical or chemical characteristics which are superior to those of the individual materials [25,26]. In the case of the zeolite-polymer composite, the polymeric part is incorporated inside the cavities of zeolite and also outside the channels [27]. In recent years, conducting and semiconducting polymer nanostructures have attracted particular attention in the fields of water treatment due to its ability to remove contaminations. This can be ascribed to their adsorption and photocatalytic behavior [28]. One of the most important polymers is the nanostructured polyaniline, which has enthused research interest because they have good redox properties, high surface area/volume ratio, low toxicity, low cost, excellent environmental stability, and can be readily synthesized in bulk quantities [29]. Thus, it is expected that, production of composite from natural zeolite of low cost and high availability; and conductive polymers will result in hybrid material of higher adsorption capacity and semiconductor properties for photocatalytic removal of organic pollutants as compared to the individual components.

It was reported that heulandite zeolite is of higher cation exchange and adsorption properties than other natural zeolite minerals [30]. Therefore the aim of this paper is to synthesis heulandite/polyaniline composite of enhanced adsorption capacity and exhibits photocatalytic properties for efficient removal of acidic dye (light green SF dye) from water. The adsorption properties were investigated based on several uptake parameters and the operating mechanisms were studied through different kinetic and equilibrium models. Moreover, Response Surface Methodology (RSM) and statistical Central Composite Rotatable Design (CCRD) were used to study the interactive effect of the studied variables and the ideal optimum conditions for maximum removal light green SF dye by the composite. Finally, the composite was used for the removal of different acidic and basic dyes (Safranin dye, methylene blue dye, Congo red ye and methyl orange dye).

2. Material and methods

2.1. Materials

Natural Heulandite zeolite sample was obtained from zeolite mine Located southwest of Taiz city, Yemen. Aniline was purchased from Rankem Company, India. Light green SF (LGSF) dye was obtained from Lab-scan Company, Poland. $(NH_4)_2S_2O_8$ was purchased from Winlab company, UK. DMSO was purchased from Sigma-Aldrich, USA. NaOH and HCl were obtained from El Nasr pharmaceutical company, Egypt. All chemicals were of reagent grade and were used without purification.

2.2. Synthesis of polyaniline nanoparticles

PANI was prepared by sudden in situ chemical oxidative polymerization method. 0.1 M PANI was dissolved in 0.5 M HCl under the effect of ultrasonic waves. By the same method, 0.15 M $(NH_4)_2S_2O_8$ was dissolved well. And then $(NH_4)_2S_2O_8$ was added over the dissolved aniline suddenly. The solution let till the precipitation of green polyaniline powder which was then separated and washed several times with warm distill water.

2.3. Preparation of Heulandite/polyaniline (HU/PANI) composite

The composite was prepared via mechanical mixing; the natural heulandite (HU) was grounded to 50 μm. Then 2 g of the grounded HU was dispersed in 100 mL distilled water and the suspension was stirred for 2 h at 150 rpm. 1 g of the prepared PANI nanoparticles was dispersed in 50 mL water, and the suspension was stirred for 2 h at 150 rpm. Thereafter, the dispersed PANI solution was added slowly to the HU suspension under stirring. The HU/PANI solution was stirred overnight thereafter the composite was washed several times with distilled water and dried at the room temperature for 24 h (Fig. S1).

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2.4. Characterization

X-ray powder diffraction pattern for HU, PANI, and HU/PANI composite were measured using a Philips APD-3720 diffractometer with Cu Kα radiation, operated at 40 kV and 20 mA in the 2θ range of 5–70 at a scanning speed of 5°/min. Morphology of the prepared PANI and HU/PANI composite were studied by scanning electron microscopy (SEM) using a field emission-scanning electron microscope (JSM-6510, JEOL, and Tokyo, Japan) and Transmission Electron Microscope (JEOL-JEM2100, Japan). The Fourier Transform Infrared spectrometer (FTIR - 8400 S Shimadzu, Japan) was used to determine the chemical structural groups of HU, PANI, and HU/PANI composite. The UV–Visible absorption spectra were measured using a Shimadzu UV spectrophotometer (M160 PC) at room temperature in the range of 200–900 nm using dimethylsulfoxide (DMSO) as a solvent and reference.

2.5. Adsorption experiments

LGSF dye stock solutions were prepared by dilution of pre-prepared standard dye solution (1000 mg/l). The pH value was adjusted using sodium hydroxide solution (0.1 M) and HCL acid solution (0.1 M). The experimental tests were performed in the absence of light and under artificial visible light irradiations lamp (blended metal halide lamp 400 W) to test the photocatalytic performance of the composite. The UV–Vis spectrophotometer analyzed the remained LGSF solution at a wavelength of 630 nm.

2.5.1. Effect of pH

To explore the effects of pH value on the uptake of LGSF dye, 20 mg of HU/PANI composite was shaken with 100 mL (20 mg/l) LGSF dye solution at different pH values from 1 to 10 for 60 min at room temperature as separated tests. (0.1 M) sodium hydroxide solution and (0.1 M) HCl solution were used for pH adjustment. After each test, centrifugation was carried out to separate the remaining dye for analysis using a UV–Vis spectrophotometer.

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