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Comparison of nickel doped Zinc Sulfide and/or palladium nanoparticle loaded on activated carbon as efficient adsorbents for kinetic and equilibrium study of removal of Congo Red dye

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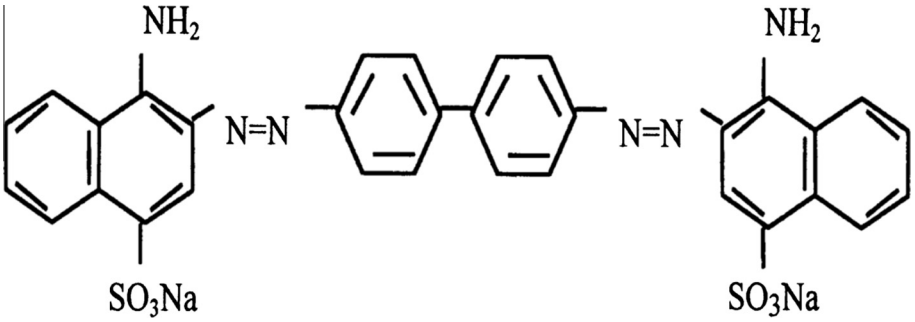
HIGHLIGHTS

- A novel nanoparticle has been used as reusable support for removal of dye Congo Red.
- A high efficiency removal technology is proposed for fast removal of dye.
- Removal of dye can be significantly enhanced under application of nanoparticles.
- The novel sorbent was characterized by SEM and TEM analysis.
- This model is applicable for rapid removal of large quantity of this dye.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the efficiency of nickel doped Zinc Sulfide nanoparticle loaded on activated carbon (Ni-ZnS-NP-AC) and palladium nanoparticles loaded on activated carbon (Pd-NP-AC) for the removal of Congo Red (CR) from aqueous solution was investigated. These materials were fully identified and characterized in term of structure, surface area and pore volume with different techniques such XRD, FE-SEM and TEM analysis. The dependency of CR removal percentage to variables such as pH, contact time, amount of adsorbents, CR concentration was examined and optimum values were set as: 0.03 g Ni-ZnS-NP-AC and 0.04 g of Pd-NP-AC at pH of 3 and 2 after mixing for 22 and 26 min for Ni-ZnS-NP-AC and Pd-NP-AC, respectively. Subsequently, it was revealed that isotherm data efficiency can be correlated Langmuir with maximum monolayer adsorption capacities of 286 and 126.6 mg g^{-1} at room temperature for Ni-ZnS-NP-AC and Pd-NP-AC, respectively. Investigation of correlation between time and rate of adsorption reveal that the CR adsorption onto both adsorbents followed pseudo second order and interparticle diffusion simultaneously.

Introduction

Generally waste water of most industries containing toxic colors and other pollutants that leads to production of non-safe and turbid medium. The chemical reactivity and stability of dyes molecules significantly depend on variables such as pH, electrolyte and content of, heavy and transition metal levels [1–4]. Congo Red (CR) has not been easily biodegradable and simply metabolized to benzidine (known human carcinogen) and its exposure to organism causes an allergic reaction. This complex chemical structures (high molecular weights) namely as sodium salt of

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benzidinediazo-bis-1-naphtylamine-4-sulfonic acid (Fig. 1) due to presence of various reactive center and charge nature seems to be very toxic agent in terms of their resistance to heat, chemical reagent and ability to generate cancer and mutagens. CR leads to health hazards such as difficulties in breathing, vomiting, diarrhea and nausea. Protocol including coagulation and flocculation [5], membrane separation [6] and adsorption using conventional and nanoscale adsorbent [7–13] are applicable for dyes removal that permit achievement of safe and low toxicity environment. A successful design and development of adsorption process can be achieved by appropriate operational conditions and adsorbents. The non toxic, low cost and easily available adsorbents benefit from high surface area and reactive centers are (good criterion for appropriate selection of adsorbent) which totally achieved by application of distinct nano-scale materials [14] that have smaller size and higher surface area. Activated carbon (AC) due to the presence of various reactive sites such as OH, COOH, C=O and amine groups is good support for fixing nano-scale materials. Possible loading various nanomaterial cause extensive increase in their application in removal and adsorption of different pollutants. In this technique, application of two nanoscale materials enhances the removal percentage and adsorption capacity of AC toward CR. These adsorbents are applicable for removal of high amount of CR in a very short contact time with high adsorption capacity.

Experimental

Instruments and reagents

All chemicals including Congo Red (CR), NaOH, HCl and KCl with the highest purity available were purchased from Merck (Darmstadt, Germany). The stock solution (1000 mg L^{-1}) of CR [CI = 22,120, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, FW = 696.7] was prepared by dissolving 100 mg of CR in 100 mL double distilled water (Fig. 1). The pH measurements were carried out using Metrohm 692 pH/Ion meter (Metrohm, Switzerland, Swiss) and the CR concentration was determined using UV–Vis spectrophotometer (Make: Jusco, model: V-570 Japan) at a wavelength of 423 nm. The morphology (FE-SEM; Hitachi S-4160, Japan and TEM Hitachi H-800, Japan, analysis) of the Pd-NP-AC and Ni-ZnS-NP-AC was monitored at specified conditions via instruments mentioned in our previous publication [7,9,10].

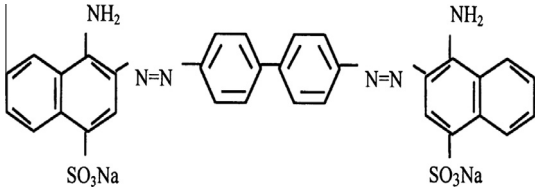

Fig. 1. The structure of Congo Red.

Measurements of dye uptake

The CR concentration was determined according to well known protocol via calibration carve obtained at maximum wavelength obtained at previously optimized condition. The efficiency of CR removal was determined at different time intervals (0.5–40 min) and revealed that mixing the solution for 26 and 22 min permits to achieve equilibrium for Pd-NP-AC and Ni-ZnS-NP-AC. The effect of pH on the CR removal onto 0.02 and 0.03 g of Pd-NP-AC and Ni-ZnS-NP-AC in the pH range of 1–8 after 30 min was investigated and optimized. The equilibrium of adsorption system was investigated over 10–40 mg L^{-1} of CR, while its removal percentage and equilibrium adsorption capacity (q_e (mg g^{-1})) was using equation presented in literature [3]. The Pd nanoparticles (Pd NP) were synthesized in a one-step reduction in the presence of ultrasound according to our previous publication [7,9]. The Ni-ZnS-NP-Ac were synthesized based on recommended protocol in literature in the presence of ultrasound as mixing power [10].

Results and discussion

Characterization of Ni-ZnS-NP-AC

The influence of various parameters including ultrasound power and times, pH, reaction time, order for addition of reactant and temperature were investigated. It was found by rising the time until 2 h lead to increase in amount of produced nanoparticles, while higher time lead to aggregation of nano-scale material. On the other hand, the increase in the concentration of reagents leads to increase in the size of nanomaterial. The best order of addition of reagent is final addition of thiol acetamide. Elevating temperature till 65 °C cause enhance in amount of nano-scale material and at higher temperature due to aggregation and fast settling of material lead to growth of nanomaterials. The magnitude and size of nano-scale material depend significantly to the pH. The amount of Ni in the ZnS:Mn nanoparticles evaluated by EDX measurements (Ni/Zn atomic percent ratio) was around 8%, while produced material has absorption edge about 325 nm, while energy band gap was estimated via following relation [15]:

$$(\alpha h\upsilon)^2 = A(E_g - h\upsilon) \quad (1)$$

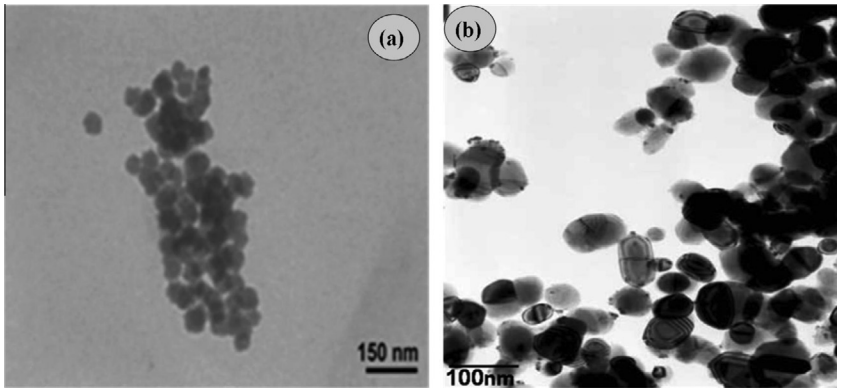

Fig. 2. (a) Typical TEM image of the ZnS:Ni nanoparticles and (b) Typical TEM image of the starch-stabilized Pd nanoparticles.