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Chitosan nanoparticles on a natural zeolite as an efficient adsorbent for Congo red

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Abstract. Congo red is a toxic synthetic dye that cannot be readily degraded by conventional methods, thus posing a risk to the environment. The increased use of this dye is mainly due to developments in the textile industry. A possible way to reduce the Congo-red waste is by performing the adsorption processes; therefore, in this study, we used a natural zeolite from Bayah and modified it using chitosan nanoparticles (Na-zeolite@chitosan) to increase its adsorption capacity. The obtained Na-zeolite@chitosan material, which was able to efficiently adsorb Congo red, was further characterized by ultraviolet–visible (UV–Vis) and Fourier-transform infrared (FTIR) spectroscopy as well as by transmission electron microscopy (TEM). A maximum of 98.019% of the Congo red was adsorbed at a concentration of 800 ppm and a pH of 5 for 60 min (the adsorption capacity was 0.00428 mmol/g). Our results exhibit that Congo red adsorption on Na-zeolite@chitosan follows the Freundlich adsorption isotherm and can be described using a pseudo-second-order kinetic model.

Keywords: natural zeolite, chitosan, adsorbent, congo red

1. Introduction

Today, textiles have become a major export commodity in several countries; however, their production exhibits a negative effect on the environment because it generates nondegradable, toxic, and stable synthetic dyes [1]. One of these dangerous dyes is Congo red, which can be barely decomposed in nature. This compound exhibits a complex aromatic chemical structure and is therefore physicochemically and thermally stable [2], and it exhibits carcinogenic properties [3].

Liquid dye wastes are treated by chemical, physical, and biological methods such as adsorption, coagulation, advanced oxidation, ozonization, filtration through membranes, and liquid–liquid extraction. Adsorption is an effective, efficient, and economical method for eliminating the contaminants from water [4–6]. Some of the adsorbents used to perform Congo-red adsorption from contaminated water are zeolites, montmorillonites, bentonites, chitosan hydrogels, fly ashes, activated carbon, and clay materials [7–10].

Zeolites exhibit unique ion-exchange and adsorption properties, and they have been extensively used in water-treatment processes, ammonia purification, and the elimination of heavy metals, radioactive substances, organic material, microorganisms, and anions during the desalination of seawater [11–13]. However, they should be modified to increase their adsorption capacity. This has been achieved by modifying them using hexadecyltrimethylammonium bromide (HDTMA-Br) [14], goethite [15], gold nanoparticles [16], hexamethylenediamine (HMDA) [17], and chitosan [18]. Among these modifiers, chitosan exhibits several advantages; it is nontoxic, biodegradable, and antibacterial [19].

Chitosan is a chitin deacetylation biopolymer that can be used as an adsorbent for heavy metals and dyestuff such as Congo red [20]. Other dyestuff adsorbents include cetyltrimethylammonium bromide



(CTAB), which also adsorbs Congo red [2] and chitosan nanoparticles, which can be used as adsorbents for acid orange and acid red [21, 22].

To the best of our knowledge, zeolites that were modified using chitosan nanoparticles have not been used as Congo-red adsorbents until now. In this study, we modified a zeolite with nanochitosan and tested it as a Congo red adsorbent by monitoring several parameters such as pH, reaction time, and dye concentration. We also determined the adsorption isotherm and studied the kinetics of the adsorption process.

2. Experimental

2.1. Materials and methods

Natural zeolite was obtained from Bayah (Lebak, Banten, Indonesia). NaOH, HCl, NaCl, AgNO₃, CH₃COOH, and Congo red (C₂₀H₁₂N₆Na₂O₆S₂) were purchased from Merck (Germany). Chitosan was collected from Bogor, West Java, Indonesia. Double-distilled water was used as a solvent.

2.2. Activation of natural zeolite

Natural zeolite was physically activated by washing in double-distilled water at 70 °C for 1 h. For chemical activation, NaOH and HCl were added to the natural zeolite, and the zeolite cation was uniformed by adding 1 M NaCl. The mixture was further stirred at 70 °C for 6 h and was then precipitated for 12 h. The precipitate was finally dried at 105 °C. The chloride ions of the zeolite were eliminated by washing in double-distilled water.

2.3. Synthesis of chitosan nanoparticles

Synthesis of chitosan nanoparticles was conducted by adding NH₃ and 0.01 M CH₃COOH solution to chitosan powder. The mixture was further stirred for 2.5 h. The formation of chitosan nanoparticles was detected by the appearance of a white colloid.

2.4. Modification of the zeolite with chitosan nanoparticles

The zeolite was mixed with the chitosan-nanoparticle solution. This mixture was then stirred for 2.5 h, centrifuged to form the precipitate, and dried using N₂.

2.5. Na-zeolite@chitosan nanoparticles as adsorbents for Congo red

The obtained material was tested by adding 10 mL of 800 ppm Congo red to 0.1 g Na-zeolite@chitosan nanoparticles at pH 5 and stirring the mixture several times for 60 min. Then, ultraviolet–visible (UV–Vis) spectroscopic experiments were performed between 200 and 800 nm. The kinetic model for Congo red adsorption was determined by monitoring the decrease in absorbance at 499 nm [23]. In addition, Langmuir and Freundlich isotherms were fitted to the experimental data to describe the adsorption processes at the equilibrium point.

2.6. Characterization

A Shimadzu 2600 UV–Vis spectrophotometer was used to obtain the absorption spectra describing the Na-zeolite@chitosan nanoparticle–Congo red adsorption activity. Identification of the functional groups present in the natural zeolite was accomplished by Fourier-transform infrared (FTIR) spectrometry (PerkinElmer) in the range of 4,000–400 cm⁻¹. A JEM 1400 transmission electron microscope was used to determine the structure and size of the Na-zeolite@chitosan nanoparticles.

3. Results and discussion

The uniformity of natural zeolite cation aims to homogenize the cations in zeolite pores. It can facilitate ion exchange in the Congo red adsorption process. The results of the FTIR characterization are presented in figure 1a. Both Na-zeolite@chitosan nanoparticles and Na-zeolite show different peaks at 3,624 cm⁻¹, corresponding to N–H stretching in chitosan. There is also a signal corresponding to the –OH group at 3,422 cm⁻¹. These are the two main functional groups of chitosan. The functional groups –NH₂ and –OH give the Na-zeolite@chitosan nanoparticles their adsorption ability. The obtained FTIR spectra show that Na-zeolite has been successfully modified with chitosan nanoparticles.

This result was confirmed by transmission electron microscopy (TEM) characterizations, as shown

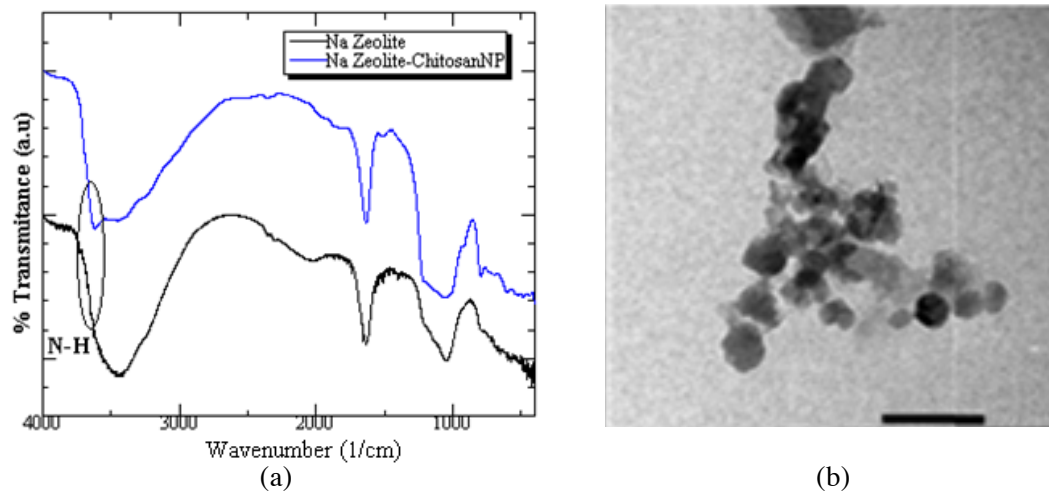


Figure 1. (a) FTIR spectra of Na-zeolite and Na-zeolite@chitosan nanoparticles, (b) TEM image of chitosan nanoparticles.

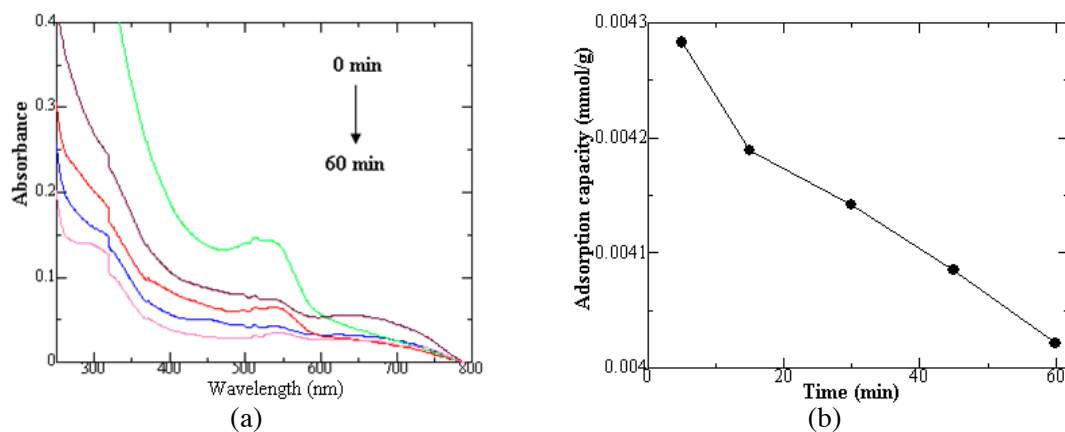


Figure 2. (a) UV-Vis absorption spectra as a function of time for the reduction of Congo red using Na-zeolite@chitosan nanoparticles, (b) Adsorption capacity of the Na-zeolite@chitosan nanoparticles measured during a period of 60 min.

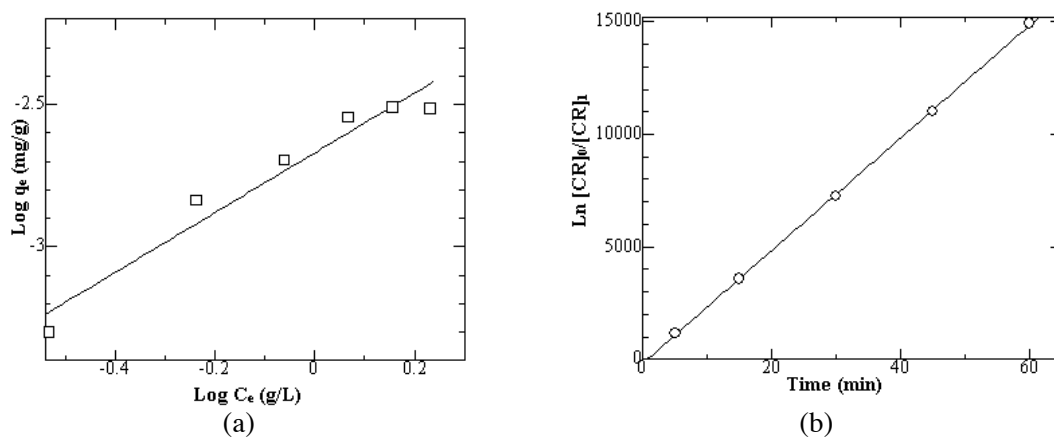


Figure 3. (a) Freundlich's adsorption isotherm, (b) Plot of $\ln [CR]_0/[CR]_t$ versus reaction time.

in figure 1b, which were carried out to determine the particle shape and size. Figure 1b shows the shapes and sizes of the Na-zeolite@chitosan nanoparticles. As can be seen, they have an irregular and almost spherical shape, and their size varies from 20 to 40 nm. These results show that the synthesized adsorbent is composed of chitosan nanoparticles. The presence of these nanosized structures leads to an increase in the number of active sites, thereby improving the adsorption properties of the material.

Congo red was adsorbed on the Na-zeolite@chitosan nanoparticle material, and the adsorption activity was monitored by following the decrease in absorbance of the peak observed at 499 nm. The relationship between UV–Vis absorption spectra and time is shown in figure 2a. As can be seen, absorbance decreases at longer times, indicating the adsorption of Congo red. The Na-zeolite@chitosan nanoparticles absorbed 98.019% of Congo red at pH 5 after 60 min. The adsorption capacity was 0.00428 mmol/g at the optimum time of 5 min, as shown in figure 2b, and the adsorption process occurred because of electrostatic interactions between the SO_3^- group of Congo red and the NH_2 group of nanochitosan.

Adsorption isotherms were calculated in order to determine the adsorption mechanism for the studied system. We found that Congo-red adsorption on Na-zeolite@chitosan followed Freundlich's adsorption isotherm with an R^2 value of 0.976. The corresponding graphic is shown in figure 3a. The kinetic model for Congo red adsorption on the Na-zeolite@chitosan material was determined by plotting $\ln [C]_0/[C]_t$ versus the reaction time, as shown in figure 3b. The results show that Congo-red adsorption follows a pseudo-second-order behavior with an R^2 value of 0.999.

4. Conclusions

A Na-zeolite@chitosan nanoparticle material with a particle size of 20–40 nm was successfully synthesized. The modified zeolite was applied as a Congo-red adsorbent, exhibiting an adsorption ability of 0.00428 mmol/g and achieving 98.019% Congo-red adsorption (for a concentration of 800 ppm) at pH 5 after 60 min. Congo-red adsorption can be described by Freundlich's isotherm and a pseudo-second-order kinetic model.

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