

SYNTHESIS OF NANOSILICA FROM RICE HUSK AND OPTIMIZATION OF THE REMOVAL OF CRYSTAL VIOLET DYE FROM AQUEOUS SOLUTION

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ABSTRACT

Nanosilica was synthesized via the hydrothermal technique, followed by the vacuum frying system at low temperature and pressure. Then, the achieved nanoparticles were used for removing of Crystal Violet dye (CV) from wastewater. The adsorbent and absorption process were studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM), X-ray Fluorescence (XRF). Batch adsorption experiments were conducted under different conditions including contact time, initial concentration of dye and adsorbent dose. The kinetic study of CV dye on the nanoparticles can be well depicted theoretically by using pseudo-second-order kinetic model.

Keywords: nanosilica, adsorbent, crystal violet dye.

1. INTRODUCTION

Water pollution in various industries such as printing, food, rubber, leather, plastic and cosmetic releases more than 100 tons dyes per year into the environment, so that such toxic cationic dyes cause the known harmful effects to humans and animals via the skin, eyes and respiratory tract [1-4]. Due to the dyes having complex aromatic structures and a matter of great concern, they are usually biologically non-degradable and present high stability and toxicity and it is therefore necessary to treat effluents containing these and related dyes [5-6]. Different methods have been used to remove dye molecules from wastewater, which can be classified in many categories such as physical, chemical, biological, radiation, and electrochemical processes.

Adsorption is an effective and eco-friendly process for the treatment of wastewater due to its low-cost and simplicity [6]. The low-cost adsorbents such as activated clay, activated charcoal, activated carbon, zeolites, coal fly ash, were used to remove different dyes [7-8]. Rice husk (RH), an agricultural waste, is abundantly available in rice producing countries like Vietnam, Thailand and India. Recently, burning of RH produces the rice husk ash (RHA) that might cause a serious environmental and human health related problems due to the low bulk density of RHA. On the other side, the amorphous silica as the main component (83-90%) of RHA can be used in wide range of applications and exhibits commercial value [9]. The synthesis of silica is mainly influenced by pH, temperature, time and drying process. And these factors influence the size of SiO₂ particles, their morphology, aggregation and specific surface area [10].

In this paper, we report the study of using precipitated silica of amorphous SiO₂ prepared from RH ash for the adsorption capacity of Crystal Violet dye from wastewater. The main effects of initial dye concentration, pH, temperature and adsorbent dose were investigated. The kinetic data obtained at different concentrations have been analyzed using a pseudo-first-order, pseudo-second-order equation. Langmuir and Freundlich models were adjusted to experimental data. Kinetic models were evaluated in order to identify potential adsorption process mechanism and to understand the possible physical-chemical interactions involved in the adsorption of silica surface and dye molecules.

2. MATERIALS AND METHODS

2.1. Materials

Crystal Violet (CV) (CAS 548-62-9, $\lambda_{\max} = 592$ nm, molecular formula C₂₅H₃₀N₃Cl) was purchased from Sigma-Aldrich. A stock solution of CV dye (1000 mg/l) was prepared by dissolving 1 g of CV dye powder in 1 L distilled water. To prepare various solutions at desired concentrations (20-100 mg/l) from the stock solution, distilled water was used for dilution.

The rice husk was collected from a rice mill in Can Tho province.

2.2. Synthesis of nanosilica

RH was washed several times with distilled water to remove soil and dust. RH was dried at 100 °C for 12 hours and was burned at 700 °C for 3 hours. After cooling to room temperature, silica was extracted by refluxing with HCl 6 M for 4 hours and washed repeatedly using distilled water. It was then dissolved by stirring in NaOH 3M and was boiled in a covered 500 ml flask for 3 hours to sodium silicate solution. The solution was filtered, and residue was washed with 50 ml of boiling water. The colorless solution was cooled down to room temperature and added HCl 1M until pH = 7. The pure silica was dried at 50 °C for 24 hours [11-15].

2.3. Characterization and analysis

An IS 50 Nicolet Thermo FT-IR instruments was used to identify the chemical functional groups present in the adsorbent. FTIR analysis was conducted using KBr pellets in the spectral range varying from 4000 to 400 cm⁻¹. The adsorbent surface was analyzed by using Field Emission Scanning Electron Microscopy (FESEM, Hitachi, Japan). The structure chemical composition of the adsorbent was investigated by X-ray diffractometer (PANanalytical, Netherlands) with 2 θ range of 10-100° using Cu-K α X-ray source ($\lambda = 1.542$ Å), and X-ray fluorescence (Bruker S8 Tiger, Germany); respectively.

2.4. Adsorption experiments

50 ml of dye solution of various initial concentrations were shaken with different weights of pure nanosilica. The solution was shaken at speed of 150 rpm and room temperature (25 ± 2 °C). Then, the samples were centrifuged at 4500 rpm for 10 min to eliminate the adsorbent. The residual CV dye concentration was analyzed by UV-vis spectrophotometer (Cary 50 Conc, Varian, USA) at the maximum absorbance wavelength of 592 nm. To determine the effect of adsorption parameters, the experiments for the removal dye were conducted by different adsorbent dosage of 4 to 24 g/L, initial dyes concentration of 20 to 100 mg/L and initial pH of 4 to 10. Each experiment was repeated in duplicate, and the averaged values are given as the results. The amount of CV adsorbed per unit mass of the adsorbent was evaluated by using the mass balance equation (Eq.1) and the percentage of the CV removal was determined (Eq.2).

$$q_e = \frac{C_o - C_e \times V}{m} \quad (1)$$

$$\text{Removal \%} = \frac{C_o - C_e \times V}{C_o} \quad (2)$$

where q_e (mg/g) is the dye uptake at equilibrium, C_o and C_e (mg/L) are the initial concentration and equilibrium concentration, respectively; V (L) is the volume of dye solution and m (g) is the mass of adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of nanosilica

The FT-IR spectra of extracted nanosilica shows Fig.1a. The peaks of 1103 and 825 cm^{-1} are the Si-O-Si asymmetric and symmetric stretching modes, respectively [12-15]. The band centered at 464 cm^{-1} is due to the bending frequency of Si-O-Si [12-15]. A large broad band around 3432 cm^{-1} is attributed to the presence of the O-H stretching frequency for the silanol group and the remaining adsorbed water. A band around 1627 cm^{-1} is the bending vibration of water molecules bound to the silica matrix. No peaks were found between 2800 and 3000 cm^{-1} . It means that there were no original organic compounds in the silica after controlled combustion and extraction. The obtained XRF spectrum of silica on matrix with the content of more than 99 % (Table 1).

Table 1. Chemical composition of pure silica produced from RH.

Composition	Value (wt.%)	Composition	Value (wt.%)
Si	99.15	Al	0.1
Na	0.2	S	0.09
Ca	0.19	K	0.04
Fe	0.15	Ti	0.05

The XRD result (Fig. 2b) shows that there is a broad peak at $2\theta = 22^\circ$ associated with amorphous silica and the size of the particles was estimated by half width of peak (β) using Scherer's formula:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

where, $K = 0.9$ nm is a constant, $\lambda = 1.542 \text{ \AA}$ is the wavelength of Cu- K_{α} and β is the full width at half the maximum in radians of the X-ray diffraction peak. Using the above formula (Eq. 3) of the XRD diffractogram, the diameter of particles was found to be about 50 nm. The FE-SEM image showed the shape of silica particles is spherical with an average particle size of 40 nm (Fig. 1c).

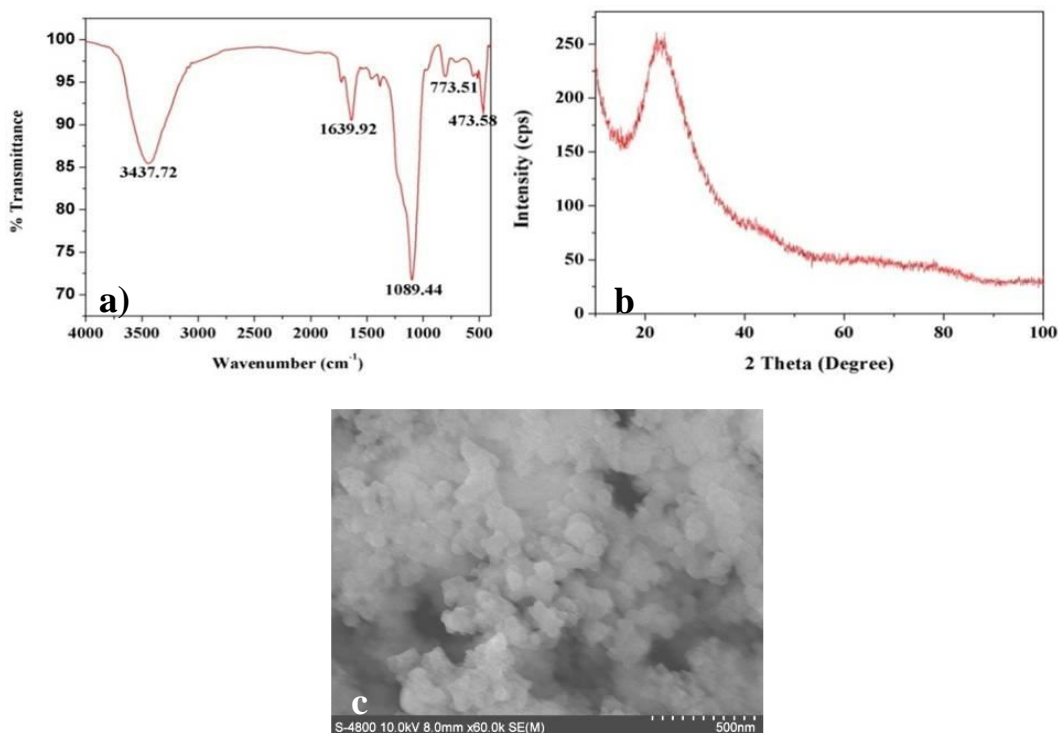


Figure 1. Material characterizations: (a) FT-IR spectra, (b) XRD pattern; (c) FE-SEM image of nanosilica

3.2. Effect of pH

pH is one the most important factors controlling the dye adsorption process of the adsorbent. The removal of CV dye by nanosilica is indicated in Fig. 2a for $C_0 = 10$ mg/l, $t = 1$ h and $m = 2$ g/l in a pH_0 range of 4-10. The color of change reduced significantly above $pH_0 = 8$ and the color intensity is stable at pH_0 range of 4-8. The pH of 7 is commonly accepted to be an optimization value for all the experiments and was used in various studies for the removal of CV dye [16-17].

3.3. Effect of contact time and initial dye concentration

The effect of contact time was investigated by the variation of time from 1 to 120 min (Fig. 2b) for various initial dye concentrations of 20, 40, 60, 80, 100 mg/L at pH of 7. The dye uptake of nanosilica increased sharply in the first 1 min and the removal was more than the maximum (95 %) and then it gradually slowed to get equilibrium at about 60 min.

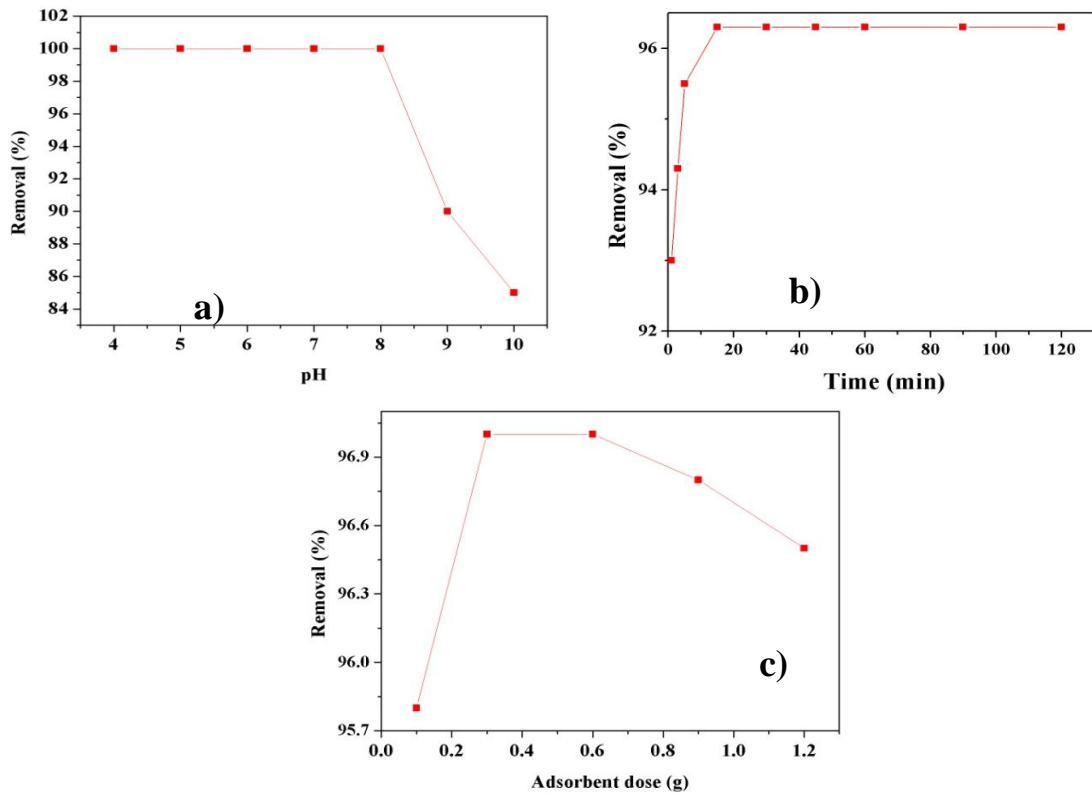


Figure 2. Effects of pH (a) and contact time (b); adsorbent dose (c).

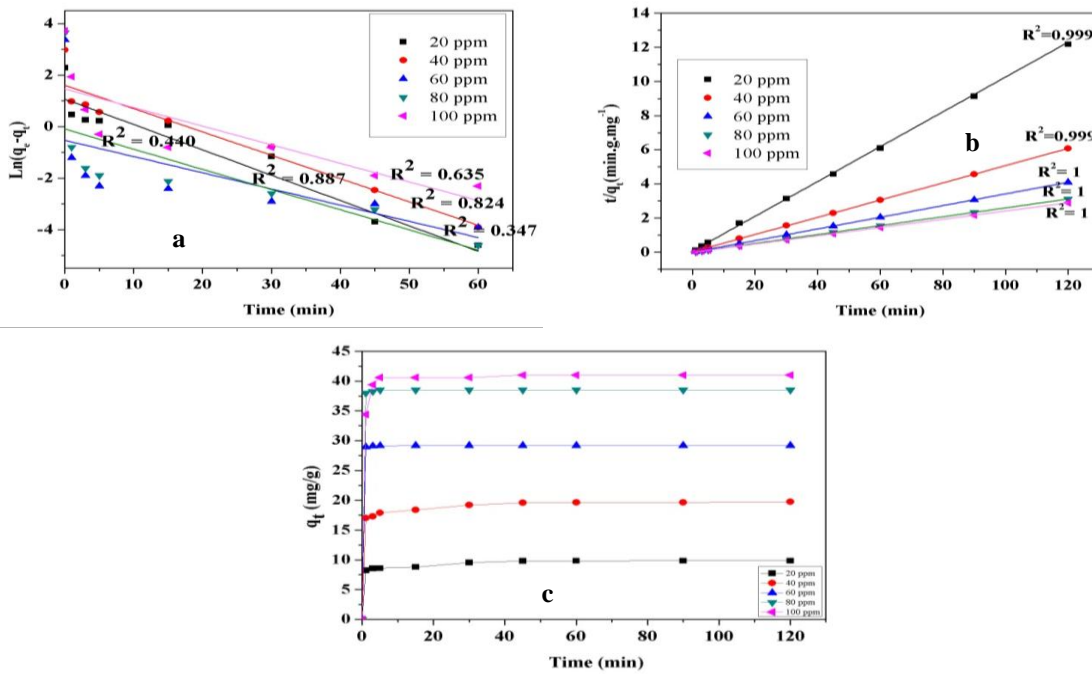


Figure 3. The pseudo-first order (a) and pseudo-second order (b) models; Effects of initial concentration (c)

The adsorption capacity of the silica is attributed to the abundance of silanol sites on the nanosilica surface and the efficiency of dye removal for low concentration was greater than high concentration at the same reaction time. The amount of CV adsorbed, in equilibrium, increased rapidly from 8.25 to 41.35 mg/g (Fig. 3c) when the initial dye concentration was increased from 20 to 100 mg/L, respectively. The pseudo-first order (Fig. 3a) and pseudo-second order (Fig. 3b) models were applied for the interpretation of experimental data. The calculated q_e values agree with the experimental q_e values, and the correlation coefficients for the pseudo-second-order kinetics plots were found to be very high [5].

3.4. Effect of adsorbent dosage

Figure 2c shows the effect of nanosilica dosage on the uptake of CV from aqueous solution. The maximum color removal was found to be 96 % at 0.3 g adsorbent dosage for CV. The adsorption process can be explained on the higher surface area as well as increased availability of the silanol sites on the surface. On the other hand, with higher adsorbent dosage, lower rate of adsorption has been presented due to the aggregation of adsorption and enhanced diffusion path length, which reduces the adsorption of dye molecules [3].

3.5. Adsorption isotherms

Adsorption isotherms play a very important role for understanding adsorption mechanism. The variation of the dye concentration with the same mass of the adsorbent is used to determine an adsorption mechanism. The Langmuir and Freundlich isotherm models were applied to describe the nanosilica adsorption process on the CV dye (initial concentrations of 20 to 100 mg/L). It is evident from Fig.4 that the Langmuir isotherm model shows a better fit with experiment data in comparison to the Freundlich model studied here. This indicates that the dye adsorption on the surface of nanosilica takes place by homogeneous sites with an established mechanism [5].

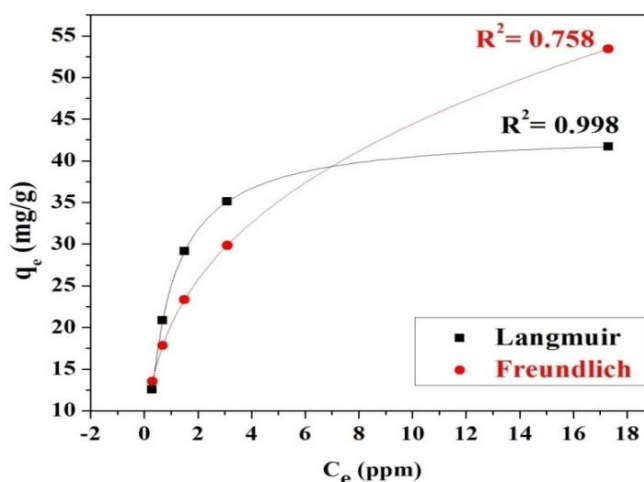


Figure 4. Adsorption isotherms of nanosilica adsorption process on the CV dye

4. CONCLUSIONS

This paper reports our first results on the synthesis of nanosilica from rice husk. The nanosilica is an effective adsorbent for the removal of CV dye from aqueous solutions and the

best removal yields were investigated with contact time of 60 min, in agreement with the pH 7 value for all the experiments. Moreover, the correlation was obtained using the pseudo-second-order kinetic model and the equilibrium data were fitted to the Langmuir isotherm model. Thus, nanosilica from rice husk might be promising adsorbent for the removal of CV dye.

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