Recycling of wastewater contaminated with cationic dyes using nonporous silica extracted from rice husk

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Abstract
The world-wide production of dyes generates wastewaters contaminated with toxic materials which makes the environmental pollution. Textile, paper and pulp mills, tanneries, distilleries, and food industries discharge colored wastewaters. The carcinogenicity and toxicity of dyes necessitate the wastewater treatment. Silica based materials are one the most important adsorbents employed in industrial applications. This material is produced in nano scale with nano-porous structure. In the present study, the rice husk which is well-known as an agricultural waste was used to synthesize silica adsorbent and the effect of processing factors such as sodium hydroxide, gelation pH and ageing time on dye removal efficiency were investigated based on designed experiments. The optimal conditions for the effective synthesis of silica were determined as: sodium hydroxide concentration: 0.5 mol.l⁻¹, pH: 9 and ageing time: 12 h.

Keywords: Adsorption, Nano-porous silica, Rice husk, Cationic dye, wastewater treatment.

Introduction
The widespread use of nano-porous materials in various branches of industry has made the development of adsorbent from different resources[1]. One of the applications of nano-technology is to treat wastewaters contaminated by cationic dyes. The huge quantities of wastewater are produced in many industries, such as textiles, food carpet, rubber, plastic, cosmetics, paper production, clothing, printing, paint, etc. [2]. The textile industry is a major contributor in generation of wastewaters contaminated with dyes. Therefore, the toxicity of wastewaters is a major environmental challenge and concern [3]. Therefore, the treatment of wastewaters is needed before discharging to the environment. Various methods have been used for the treatment of effluents containing organic dyes, including biological treatment, adsorption, coagulation, reverse osmosis, chemical oxidation (ozonation and ultraviolet radiation), filtration and adsorption [4]. In fact, the most of these methods are costly [3]. The adsorption technique is preferred due to low cost and simple operating conditions, rapidity and adaptability to the environment [5]. Hydrothermal, sedimentation, sol-gel and combustion synthesis, are applied to produce nano-porous adsorbent, but the energy and cost required for the synthesis and purity of product are of great importance [1]. By consideration of environment problems, researchers are looking for use of agricultural wastes to synthesize nano-structured adsorbents. Rice husk is one of the agricultural wastes that is produced annually in the huge quantities. This waste is usually burned in atmospheric condition and
creates the environmental pollution and respiratory diseases [6]. Because of its high silica content, rice husk is a reliable resource of silicone materials such as silicon carbide, silicon nitride and zeolite [7]. Liu synthesized silica particles from rice husk, based on very inexpensive method [8]. A study was carried out on rice husk that simultaneously extracted nano-silica and lignin from the waste. The size of nano-silica particles produced by this method is about 17 nm and has different applications due to the fine particle size [9]. The silica nano particles also was produced by alkali extraction [10]. The nano-silica was extracted from two types of rice husk in Brazil. The results showed that there is a good relationship between commercial silica and that obtained from rice husk. Silica extracted from the ash show the particle size between 181.2 to 294.7 nm and is smaller than commercial one [11]. The produced nano-silica from rice husk used to remove crystal violet dye and the effect of ultrasound condition on the adsorption properties of nano-materials was investigated [12]. The aim of present work is to produced nano-porous silica from Iranian rice husk in Gilan province to prevent the environmental pollution and to remove methylene blue from wastewater. The role of process factors on the adsorption efficiency were evaluated by experimental design and the optimum conditions for the preparation of silica were determined to maximize the yield.

**Experimental**
The rice husk produced in Gilan province in Iran was employed as starting material for synthesis silica powder. Sodium hydroxide (99 %), chloride acid (37 %), sulfuric acid (98 %), methylene blue was used to produced dye solution stock. The rice husk was firstly washed with distilled water to remove the dust and then dried in the laboratory oven at 100 °C for 24 h. The dry rice husk was washed with hydrochloric acid 3 mol.l⁻¹ at 80 °C for 4 h. Then, the obtained material is heated at 700 °C in the furnace to decompose unwanted substances such as cellulose and to increase the purity of produced silica. After calcination, the rice husk ash was dissolved in alkaline sodium hydroxide solution. The solid silica was transformed into the soluble silica and finally precipitated by sulfuric acid 5 mol.l⁻¹. The obtained gel was aged for 6 and 12 h at room temperature. The above produced was repeated in sonication condition to understand the role of ultrasound atmosphere on gelation. The occurred reactions are summarized as follows:

\[
\text{SiO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \quad (2)
\]

A dye solution stock with the concentration of 40 mg.l⁻¹ was prepared using distilled water. The initial dye concentration was measured with a UV-Visible spectrophotometer at a maximum wavelength of 666 nm. 10 mg of synthesized adsorbent was added to 20 ml of dye solution to determine the adsorption yield. After reaching the equilibrium, the suspension was centrifuged to separate the adsorbent and the dye concentration was measured again. The adsorption efficiency was calculated based on the obtained data.

**Results and discussion**
Synthesis of nano-porous silica adsorbent from rice husk is dependent on processing factors such as sodium hydroxide concentration, pH of gelation and aging time. In order to find out the optimum conditions, the following experiment was conducted by Minitab software. Based on the highest adsorption efficiency, the optimum conditions were determined. The
concentration of sodium hydroxide was changed between 0.5 and 1.5 mol.l$^{-1}$. pH also was altered in the range of 7-9 and aged for zero, 6 and 12 h.

**Effect of sodium hydroxide concentration and gelation pH**

Figure 1 shows the effect of sodium hydroxide concentration and pH synthesis on dye adsorption efficiency in both normal and ultrasound conditions. It is observed that the increase in NaOH concentration reduces the adsorption efficiency onto the silica. It should be noted that pH plays an important role in increasing efficiency. To achieve the maximum uptake efficiency under normal conditions, it is necessary to adjust the NaOH concentration at the level of 0.5 mol.l$^{-1}$ and control the pH in the range of 7.5 to 9. However, the gelation in the sonication condition leads to extension of NaOH concentration up to 0.75 mol.l$^{-1}$, which is important from engineering point of view.

![Figure 1](image)

**Figure 1. Dye adsorption efficiency versus NaOH concentration and pH, (a) normal (b) sonication conditions.**

**Effect of pH and aging time**

Figure 2 shows the effect of gelation pH and aging time on the dye adsorption efficiency. It is noteworthy that the appropriate concentration of sodium hydroxide is 1 mol.l$^{-1}$ to achieve maximum adsorption yield. Also, the pH should be adjusted between 7 and 8.5 based on the data represented in Figure 2. It is absolutely impossible to achieve efficiency about 90 % if the silica synthesis is performed by sonication condition.
**Effect of sodium hydroxide concentration and aging time**

Figure 3 shows that the efficiency of silica is strongly dependent on the concentration of sodium hydroxide and ageing time. For both of silica produced in the normal and sonication conditions, the adsorption efficiency decreases with rise in NaOH concentrations. Normally, for silica extraction, the concentration of sodium hydroxide should be controlled between 0.75 and 1 mol.l\(^{-1}\) without ageing. Although the sodium hydroxide concentration should be considered in the minimum level, 0.50 mol.l\(^{-1}\), when synthesis is carried out in sonication condition, the gel should be aged between 4 and 6 h.

![Figure 3](image)

**Conclusions**

The extraction of silica from rice husk has been evaluated by changing sodium hydroxide concentration, gelation pH and ageing time based on the relationship between cationic dye adsorption efficiency and production factors in normal and sonication conditions. The silica obtained with minimum concentration of NaOH is responsible for uptake of dye. The sodium hydroxide concentration controls the formation of meso-porous structure to create active sites.
which facilitates the adsorption of dye. The higher concentration of NaOH leads to prevent the formation of active sites, which reduces the adsorption capacity. The porous structure formed via alkali treatment, pH: 9, is benefit for the dye adsorption. The progressive dissolution of ash and the formation of porous structure effectively depend on synthesis environment condition. This reactivity is independent of ageing time although the treatment between 4 and 6 h in sonication condition leads to achieve controllable condition with minimum content of NaOH.

References