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# Preparation and particle size effect of clinoptilolite on the removal of color, suspended solids, and chemical oxygen demand from real textile wastewater

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ABSTRACT

As textile wastewater is a major source of surface water pollutants when not sufficiently treated prior to discharge, strict disposal regulations were set and monitored by environmental authorities. As such, continuous research is necessary in textile wastewater remediation. In this study, real textile wastewater samples were directly collected from the wastewater discharge point of a manufacturer in Prai, Malaysia. Various particle sizes of clinoptilolite were applied to treat the wastewater in a series of batch experiments at a predetermined dosage, pH, and contact time. Removal of three main parameters [i.e. color, suspended solids (SS), and chemical oxygen demand (COD)] was monitored. The removal rates of color, SS, and COD were 47.9, 48, and 37.4%, respectively, at particle sizes larger than 2 mm and then increased to 91, 96, and 62%, respectively, at particle sizes of 75–250 μm. The highest COD removal of 70% was also achieved at particle sizes smaller than 75 μm. These findings indicate that 75–250 μm is the optimal size range of clinoptilolite for simultaneous removal of the three parameters under the same experimental conditions. After wastewater treatment, the residual concentration of SS was 10 mg/L, which is within the standard limit of 50 mg/L effluent discharge.

*Keywords:* Clinoptilolite; Color; Suspended solids; COD; Textile wastewater

## 1. Introduction

The textile industry is of great importance for manufacturing clothes and clothing materials. Nevertheless, wastewater discharge from the textile industry has been identified as a major source of surface water pollutants, when insufficiently treated prior to discharge. Hence, environmental departments and institutions ensure continuous wastewater disposal monitoring, and establish strict regulations and penalties to offenders. In comparison with other industries, the textile industry is one of the major consumers of water and, consequently, generates large amount of wastewater from different production stages [1–3]. Textile wastewater is mainly characterized by intense color, as well as high chemical oxygen demand (COD) concentration, pH, temperature, total suspended solids, total dissolved solids, turbidity, toxic chemicals, and biochemical oxygen demand (BOD) [4].

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A combination of methods has been used to treat textile wastewater because no single method is self-economical and technically viable for complete removal of all pollutants at a given time. As primary treatment methods—involving physical, biological [5], and chemical technologies [6]—are often insufficient for textile wastewater treatment, the combination of two or more methods is usually employed [7–13].

Adsorption is a physical or chemical process in nature but often presents as a combination of both; this process is a simple and efficient technique for textile wastewater treatment when used alone [14] or in combination with other methods [13,15]. Activated carbon is the most commonly used adsorbent to effectively treat textile wastewater because it features large surface area and porosity which greatly enhances adsorption, [16,17]. Although simple and efficient, commercially available activated carbon is relatively expensive [18]; hence, cost-effective adsorbent must be developed [19–22].

Zeolite, which occurs naturally and in abundance, has been investigated and used in various applications, particularly in water and wastewater remediation. Zeolites are aluminosilicates produced by a corner sharing of oxygen atoms within its tetrahedral framework of molecules [23,24]. Zeolites exhibit properties related to ion exchange, catalysis, and adsorption. Previous studies on the applications of zeolites in water and wastewater treatment have focused on removal of heavy metal ions [25–28] and ammonium ions [29–31]. Recently, clinoptilolite, which is the most abundant of the zeolite family, has received continuous research interest [32] because of its potential for treatment of textile dye effluents and other wastewater [33–36]. Natural and modified clinoptilolites are applied similarly to textile wastewater treatments, but the modified forms are preferred because of their improved properties.

Zorpas et al. [37] investigated the influence of the particle size of clinoptilolite on removal of heavy metals from sewage sludge compost. Other studies have also determined the effect of particle sizes on the adsorptive capabilities of selected adsorbents [38,39]. In a study on removal of selected heavy metals, the effectiveness of titanium dioxide ($TiO_2$) nanoparticles was compared with that of bulk particles [40]. Although the particle sizes of medium employed generally influence the uptake of pollutants, no specific report is available regarding the effect of clinoptilolite particle size on the treatment of the important but recalcitrant textile wastewater.

This study investigates the influence of particle size on removal of color, suspended solids (SS), and COD on treatment of textile wastewater. The chemical composition of the clinoptilolite sample used is presented in Table 1. The corresponding percentage by weight is listed against each chemical component, as provided by Bio Organic LLC, the producer, and the supplier.

## 2. Materials and methods

### 2.1. Materials

Commercially available clinoptilolite and raw samples of textile wastewater were primarily used in this study. Clinoptilolite was produced and supplied in granular form by Bio Organic LLC and processed prior to use. Textile wastewater samples were collected from a factory in Prai, Malaysia. Double-distilled water was used for washing and rinsing.

### 2.2. Wastewater sampling and characterization

Textile wastewater samples were directly collected from the effluent discharge point of a textile factory that manufactures polyester staple fiber and films. This factory is located in the north of Peninsular Malaysia. Samples were collected in 20 L plastic bottles, which were tightly covered with lids. The samples were then analyzed to determine their characteristics. Collection and storage of samples were performed in accordance to the standard methods for the examination of water and wastewater.

### 2.3. Preparation of clinoptilolite medium

Clinoptilolite (1 kg) was washed thoroughly for several times with double-distilled water to remove turbidity and other impurities [41,42]. The medium was then oven dried at 105˚C for 24 h [43]. The dried medium was cooled in a desiccator for 24 h, ground in a stainless steel ball mill, and passed through sieves

Table 1
Chemical composition of clinoptilolite

| Chemical composition | Weight (%) |
|---|---|
| $SiO_2$ | 65.44 |
| $Al_2O_3$ | 9.36 |
| $Na_2O$ | 1.70 |
| $K_2O$ | 1.61 |
| CaO | 1.58 |
| $Fe_2O_3$ | 1.14 |
| $Ti_2O$ | 0.81 |
| MgO | 0.39 |
| $MnO_2$ | 0.05 |

with different mesh sizes to separate based on particle size [44]. Seven different particle sizes were used for subsequent experiment.

### 2.4. Experimental procedure

Each set of experiment was conducted in a 250 mL Erlenmeyer flask reactor, with 200 mL of the wastewater sample and 15 g of clinoptilolite medium. All experiments were conducted at room temperature.

Preliminary experiments were conducted to determine the range of basic operational variables, including medium dosage, initial pH, contact time, and agitation speed. Values obtained in the preliminary experiments were applied to the main experiments, in which 15 g of clinoptilolite medium was added to the wastewater sample in the reactor. Based on the results of the preliminary experiment, the pH was also adjusted to 2 by adding 5 M hydrochloric acid or 5 M sodium hydroxide (5 M was used to reduce the dilution effect). The reactor was then agitated using a laboratory orbital shaker at 150 rpm for 60 min. Experiments were conducted three times to obtain a "technical replicate."

## 3. Results and discussion

### 3.1. Textile wastewater characterization

All characteristics of the textile wastewater samples presented in Table 2 were higher than the standard limit, except for temperature, which fell at the boundary of the specified limit.

### 3.2. Effect of particle size on the removal of color

The results of color removal by clinoptilolite of different particle sizes are shown in Fig. 1. At an initial color concentration of 2,560 mg/L, the color removal rate was 47.9% for particle size larger than 2 mm and then increased to 91% for particle size between 75 and 250 μm. The removal rate did not significantly increase for particles size less than 75 μm. This finding could be attributed to possible structural damage, pore clogging, or both, as reported by Zorpas et al. [37]. Thus, the optimal size of clinoptilolite for color removal was 75–250 μm, at which the residual color concentration was 240 mg/L.

Increase in color removal with decreasing particle sizes could be due to increase in surface area, resulting in increased number of available sites for adsorption [38]. Similarly, Engates and Shipley [40] reported that $TiO_2$ nanoparticles exhibited faster adsorption rate and were able to remove multiple metals (Zn, Cd, Pt, Ni, and Cu) than bulk particles.

Table 2
Characteristics of textile wastewater

| S/no. | Parameters | Range of values[a] | Standard[b] |
|---|---|---|---|
| 1 | Temperature (℃) | 37–40 | 40 |
| 2 | pH | 11.3–12.4 | 5.5–9.0 |
| 3 | $BOD_5$ (mg/L) | 550–561 | 20 |
| 4 | COD (mg/L) | 1,780–2,369 | 400 |
| 5 | SS (mg/L) | 190–284 | 50 |
| 6 | Color (Pt. Co.) | 2,320–4,200 | 100 |

[a]Average of monthly sampling; February, 2013–May, 2014.
[b]Standard by Malaysian Environmental Quality Act, 1974.

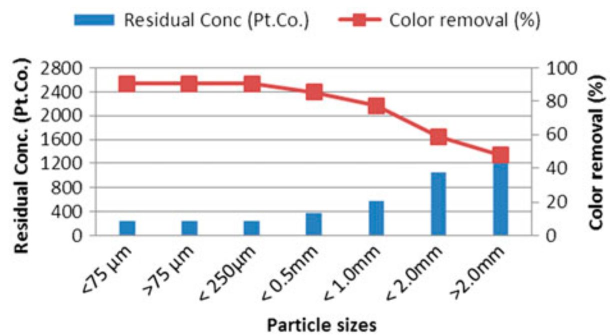


Fig. 1. Color removal at different particle sizes (dosage: 15 g, contact time: 60 min, agitation speed: 150 rpm, and pH 2).

### 3.3. Effect of particle size on the removal of SS

Similar to the results of color removal, SS removal rate increases with decreasing particle sizes of clinoptilolite (Fig. 2). The SS removal rate was 48% for

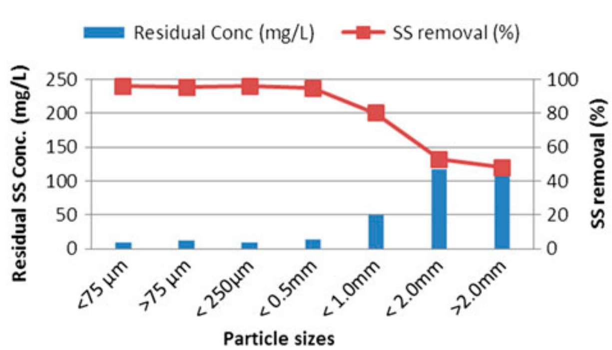


Fig. 2. Suspended solid removal at different particle sizes (dosage: 15 g, contact time: 60 min, agitation speed: 150 rpm, and pH 2).

particle sizes larger than 2 mm and increased to 80% for particle sizes ranging from 0.5–1.0 mm. The rate further increased to 96% for particle sizes ranging from 75 to 250 μm. The SS concentration decreased from the initial amount of 250 to 10 mg/L, which is within the standard limit of 50 mg/L effluent discharge and thus, considered acceptable. This finding is in agreement with the theory of Helfferich [45], as reported by Zorpas et al. [37]; in this theory, adsorbents with small particle sizes can achieve a high rate of ion exchange. Similar to the observation in color removal, changes in SS removal rate were insignificant for particle sizes smaller than 75 μm. Thus, the optimal clinoptilolite particle size for SS removal was within the range of 75–250 μm.

### 3.4. Effect of particle size on the removal of chemical oxygen demand

Although COD removal reached 70%, this rate was the lowest compared with the removal rate of color and SS, as shown in Fig. 3. In previous studies on treatment of textile wastewater, COD removal was also lower than color removal under the same experimental conditions [46,47]. This findings maybe attributed to the difficulty in oxidizing organic pollutants in wastewater.

In the present study, the COD removal rate was 37.4% for clinoptilolite particle sizes larger than 2 mm and then increased to 62% for particle sizes of 75–250 μm. The rate further increased to 70% at particle sizes smaller than 75 μm, which is regarded as the optimum for the sole removal of COD. A corresponding residual COD concentration of 545 mg/L was recorded against the initial concentration of 1,800 mg/L.

In general, the results of the present study, as shown by the pattern of removal of all the three

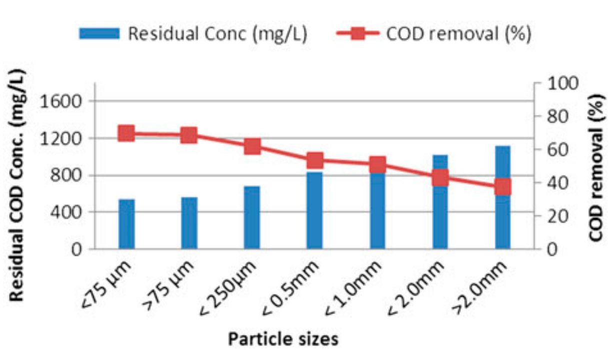


Fig. 3. COD removal at different particle sizes (dosage: 15 g, contact time: 60 min, agitation speed: 150 rpm, and pH 2).

pollutants (color, SS, and COD) investigated, are in agreement with the findings of Bond [48]. Also, the reactions involving all the pollutants may be considered as "structure sensitive" [49].

## 4. Conclusions

The removal of the three parameters investigated continuously increased with decreasing clinoptilolite particle size. In contrast to color and SS removal, COD removal significantly increased (i.e. 62–70%) when clinoptilolite particle size was reduced to 75 μm and below. Nevertheless, the size range of 75–250 μm is considered the optimal range when all the three parameters were simultaneously removed under the same experimental conditions. Who reported that, in atomic models, the average coordination number of surface atoms decreases with increasing particle size. Furthermore, the reactions in the current study may be considered as "structure sensitive".

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