Preparation of Nano Zeolite and its Application in Water Treatment

Maryam Yousif Gadhban¹, Yossor Riadh Abdulmajeed², Fatima Dheif Ali² and Zainab T. Al-Sharify ³,4*

¹ Chem. Eng. Dep. College of Engineering, University of Technology. Baghdad – Iraq
² Chem. Eng. Dep. College of Engineering, Al-Nahrain University, Baghdad. Baghdad – Iraq
³ Env. Eng. Dep. College of Engineering, Mustansiriyah University. Baghdad – Iraq
⁴ School of Chemical Engineering, University of Birmingham, Birmingham, United Kingdom.

*z.t.alsharify@uomustansiriyah.edu.iq

Abstract: Nano-Zeolite was prepared for removing methylene blue from wastewater by the use of packed bed column. The prepared adsorbent was characterized by XRD and AFM. The characterization result shows that the size of diameter was 95 nm. It was observed that the nano-zeolite was active for the removal of methylene blue as adsorbent. Methylene blue are common wastewater contaminants at industrial installation. The adsorption of methylene blue by nano-zeolite was studied by a pilot plant packed bed column. Continuous flow tests were performed to find the breakthrough times. The breakthrough curve was examined for different parameters such as flow rate (0.5-1-1.5 ml/min), initial concentration (15-25-35 mg/lit) and bed height (4-6-8 cm). Based on these investigations, it appears that the time of the breakthrough increases with an increase in the bed height and decreases with increases in the initial concentrations and flow rates.

Keywords: Nano-Zeolite; Packed bed column; Methylene blue; Water Treatment, Continuous flow.

1. Introduction

Today, industries are massively utilizing artificial dyes for dyeing fabrics and thus the dyes have become an industry solid. Around the world, nearly 700,000 tons of dyes are found. Around 20% is available in the outlets of the industrial wastes without prior treatment. Artificial dyes are strongly toxic due to negative influence on all forms of life because they consist of sulfur, nitrates, enzymes chromium compounds, acetic acid, naphthol, vat dyes, surfactants, and metals such as cobalt, mercury, lead, copper, nickel, arsenic and cadmium [1-5]
Dyes exist in various concentrations in wastewaters produced from industries. Examples include plastic, dyestuffs, textile dye, etc [6, 7]. The flow of such chromatic effluents subjects colour to the accepting water bodies along with overlapping with their valuable usage. Dye removal from effluents of dye-bearing is the main problem because of the difficulty in the treatment of such wastewaters by methods of traditional treatments. Moreover, such methods are expensive and are usually inefficient in treating the vast ranges of colors found in wastewater [8-13].

Zeolites are immeasurably utilized for a few applications, for example, particle trade, partitions, adsorption and catalysis [14]. Furthermore, it is generally acknowledged that zeolites have a pore structure making them an active color adsorbent [15-17].

Tosheva, et al. [18] reported that the extent of a molecule of nano-zeolite is in the scope of 10 to 1000nm. It was delivered by aqueous circumstances. For example, Holmberg, et al. [19] mentioned that nano-zeolite Y blends (Si/Al proportion of starting arrangement of 4.3) with a size of 32 to 120nm at a temperature of 100°C. In addition, Mintova et al. [15] detailed that the extent of a molecule of 60 to 70nm of zeolite Y could be picked up at 90°C and 45 hr with SiO2/Al2O3 proportion of 4.35.

Zeolites are generally micro-pore minerals of silicate, ranging from colourless to white or light red possibly with colorations because of the existence of impurities and minerals traces. There are 106 various naturally occurring kinds of Zeolites [17]. For the tribo-mechanical treating in the patented machine, the crystalline Zeolite Clinoptilolite, has been chosen, mostly because of its characteristics of ion exchange capacity, selectivity, and absorbability. This material is wholly harmless, which has been pretended through chemical analyses and toxicological studies performed by scientists [20].

In water treatment, the natural zeolite (Alumina Silicate) material is economical and has no effects on the environment. Natural zeolite is in the cationic exchanger group. The wastewater is treated with natural zeolite and it removes metal cations [21]. Natural zeolite is an organic resin and economical as it releases potassium, sodium, calcium and magnesium ions to the environment and these ions are non-toxic [22, 23].

The addition of contaminated water into an open stream is a big setback as the use of such waters is very poisonous. Nowadays, the discharge of water from different industries like dying, food, textile, paper, cosmetics, and leather is the main problem of the 3rd world. According to research done earlier, about 10,000 dyes and pigments are in industrial use. These dyes are acidic, basic, reactive azo and diazo. The removal of these dyes is not an easy task [2, 24]. Researchers and experts are working hard to develop low-cost absorbents to remove dyes from wastewater. In this connection, they have worked on substances such as spent tea leaves, coffee ground, wheat straw, pinecone, ginger waste, and rice husk but the main problem after the use of these materials is the major environmental hazards they pose. It is a noticeable point that the use of fly ash obtained from the power plant for the treatment of wastewater is economical and financially affordable [25, 26].

The methylene blue, which is present in wastewaters, is a hazardous material and it's important that it is removed before water discharges in open streams, in order to save the environment. Thus, the use of natural zeolite is beneficial as its ion exchange and absorption properties remove impurities easily while ensuring that the chemistry of water is not affected [27, 28]. The main advantage of natural zeolite is in its ability to reduce the concentration of anion and cation in wastewaters. The natural zeolite is made of SiO4 and AlO4, which connect via oxygen ions. Also, these are highly porous in nature thus making them useful as they consist of cavities and channels in their structures [27, 29].

The natural zeolite is used for the treatment of wastewaters, surface waters, underground waters, drinking waters and grey waters as well. In fact, the oldest technique for treating wastewaters involved the use of natural zeolite. The metals (Cd, Cu, Mn, Zn, Cr, Pb and Fe) can be removed by natural zeolite [30-32]. In addition, the natural zeolite is used with other technologies like ion exchange, membrane filtration, flotation and coagulation. The natural zeolite has good ion
exchange capacities for cations [33]. For the treatment of surface waters, the use of zeolite shows the best results for the removal of acid as well as ammonia while maintaining the pH near to that of the natural water. The Fe as well as Mn is also removed by the use of natural zeolite [34]. Furthermore, in the treatment of drinking and grey water, natural zeolite appears as a metal absorbent. Arsenic is very harmful in drinking water and it is removed by using the absorptive properties of natural zeolite. It also removes Cu from drinking water. Ground water contains high content of fluoride ion with reaching up to levels of 30mg/l in Asia, Africa and United States. In terms of grey water, this is obtained from laundry and bathroom drains. It must be noted that a significant quantity of ammonium is present in grey water. The usage of natural zeolite allows for the elimination of ammonium from grey water[35, 36]

The most common procedures used for the removal of contaminants are the: batch process and column process.

In the batch process, a sample of water is made to contact with natural zeolite. The temperature is maintained at constant and zeolite removes the metal ions from the water. The efficiency of natural zeolite is improved by pretreatment of natural zeolite. Moreover, in sewage, agricultural waste and fertilizer waste, one of the main pollutants present is ammonium. Removal of ammonium is very important as it is responsible of eutrophication.

In the column process, main factors taken in consideration are temperature, flow rate and initial cation concentration along with particle size impurities and surface dust. Initially, the ground water is treated by air and sand filtration. In this way, ammonium, iron and manganese removal takes place. Natural zeolite with a layer of manganese oxide is used and results obtained show that iron is removed in a much higher quantity by allowing modifications in zeolite [37, 38]

This work aims to remove dye from wastewater; therefore, methylene blue was selected in the present work as pattern compounds. This was done for assessing the possibility and potential of nano zeolite in removing dyes from wastewaters.

2. Material and Experimental Work

2.1 Nano-Zeolite Synthesis

In the production stage, the suitable amount of 150 mL of 3 M NaOH solution was added to 20 g from fly coal ash and the solution was warmed for 24 h to 90°C. Next, the produced zeolitiform ash ZF was frequently washed, till the mixture reached a pH of about 10-11. This was followed by drying at 100°C for 24 h. Next, 1.8 mmol L⁻¹ HDTMA-Br of 400 mL was positioned on a mixer with 20 g of zeolite. The mixture was allowed to mix for 7 h at 160 rpm. The produced output was filtered and put for 12 h at 60°C in an oven.

2.2 Adsorption Experiments in Packed Bed Column (Continues Flow)

In this experiment, continuous processes were held in a 1.5 cm internal diameter and 25 cm height of glass column. A number of experiments were proceeded with various flow rates (0.5ml/min-1.5ml/min), different initial concentrations (15-25-35mg/lit) and heights of bed (4-6-8 cm). All these processes were carried at a fixed room temperature (25 ±2°C), as shown in Figure1. Nano zeolite was packed into a column and the solution of methylene blue was pumped into the column by gravity. At different interval times, the samples were accumulated in all of the processes. An UV spectrophotometer was used for examining the methylene blue concentration in the effluent.
3. Results and Discussion

3.1 Characteristic of Nano-Zeolite

From the X-ray diffraction (XRD) examination, it was observed that the prepared process had gained zeolite ZF. Figure 2 indicates the XRD patterns of the sample, where these patterns show peaks in the (2θ) range of (26°-28°). Next, it is seen that the samples appear to be highly crystalline. The average particle diameter of the prepared sample is 95 nm, based on the atomic force microscope examination (AFM).
3.2 Methylene Blue Structure and Hydrolysis Process

The chemical structure of methylene blue is shown in Fig. 3. Methylene blue is heterocyclic fragrant concoction and it intensifies (a phenothiazine subordinate) with the compound recipe \((\text{C16H18N3ScI})\). At room temperature, it shows up as a dim green, strong, powder and scentless that presents a blue arrangement. The hydrated type has 3 particles of water for each one atom of methylene blue. Methylene blue has a PH of 3 in water (10 g/l) at 25°C. Methylene blue have a wavelength of around 670 nm. The assimilation specifics rely upon many variables, including retention to different materials, protonation. The dimmers development and higher totals depends on focus and different connections. Methylene blue is utilized for testing of water; a shading response in a fermented type. Such a test is known as a MBAS (Methylene blue dynamic substances examine). The MABS test cannot recognize particular surfactants, however a few cases of anionic surfactants are sulfonates, phosphates, carboxylates and sulfates.

![Figure 2. XRD of nano zeolite from fly ash](image)

![Figure 3. Methylene blue structure](image)
3.3 Flow Rate Effect on the Breakthrough Curve

At different volumetric flow rates, the curves of breakthrough are shown in Fig.4, based on results obtained from the experimental data, presented in Table 1.

| No | Flow rate (ml/min) | Initial concentration (mg/l) | Bed height (cm) |
|----|--------------------|------------------------------|-----------------|
| 1  | 0.5                | 30                           | 6               |
| 2  | 1                  | 30                           | 6               |
| 3  | 1.5                | 30                           | 6               |

The curve of breakthrough happened rapidly with a greater flow rate. The breakthrough curve indicates that initially all flow rates have same effects but with the passage of time, the value of C/Ci rises with higher flow rate. The curve became smooth after 60 minutes. The time of the breakthrough reaching saturation rose symbolically with the drop in flow rate. The influence of lower flow rate of methylene blue resulted in additional time to impinged with adsorbent, that presented a higher elimination rate of Methylene blue molecules in packed bed column[39]

![Figure 4](image-url)

**Figure 4:** Flow rate effect on the breakthrough curve [initial concentration = 30 mg/l and bed height = 6 cm]

3.4 Effect of Initial Concentration

The influence of initial concentration of methylene blue on the curve of the breakthrough is shown in Fig.5, based on results obtained from the experimental data, presented in Table 2.

| No | Flowrate (ml/min) | Initial concentration (mg/l) | Bed height (cm) |
|----|-------------------|------------------------------|-----------------|
|    | 0.5               |                              |                 |
|    | 1                 |                              |                 |
|    | 1.5               |                              |                 |

![Figure 5](image-url)
It is shown that the time of breakthrough decreased with an increase in the initial concentration of methylene blue. Initially the breakthrough curve appears to be same at all concentrations but with the passage of time the curve of higher concentration rises. The breakthrough curve has similar effects at 25 and 35 mg/l of concentration, with showing slight differences in the results. Since the surface of nano zeolite will be saturated by the methylene blue faster, the time required to reach the status of the steady state increased significantly.

![Figure 5](image)

**Figure 5.** Initial concentration effect on the breakthrough curve \[flow rate =1 \text{ ml/min} \text{ and bed height }=6 \text{ cm}\]

### 3.5 Bed Height Effect on the Breakthrough Curve

The curves of breakthrough at various bed heights are illustrated in Figure 6, based on results achieved from the experimental data, presented in Table 3.

| No | Flowrate (ml/min) | Initial concentration (mg/l) | Bed height (cm) |
|----|------------------|-------------------------------|----------------|
| 1  | 1                | 30                            | 4              |
| 2  | 1                | 30                            | 6              |
| 3  | 1                | 30                            | 8              |

Initially, the curve of breakthrough appears similar at all bed heights. However, after 30 minutes, the curve for the lower bed height tends to rise rapidly. With increases in bed height, the curve rises slowly and the resulting breakthrough curve become steeper. This is due to the provision of an extra area of surface when the height of the bed increases as well as the service life of bed increases[40].
4. Conclusion

The current work demonstrates that preparation of nano-zeolite using coal fly ash and its potential application as an adsorbent to eliminate methylene blue from simulated wastewater. The structure and morphology of the nano-zeolite adsorbent were studied by atomic force microscope (AFM) and X-ray diffraction (XRD). XRD patterns showed that the adsorbent was in zeolite range and AFM examination showed that the adsorbent was in the nano scale range while the size of nano-zeolite diameter was 95nm. From the packed bed experiment, it is shown that the preparation of nano-zeolite leads to a high-quality adsorbent for the elimination of methylene blue. Moreover, it is observed that when the flow rate and initial concentration increased, the methylene blue time decreased. However, the removal of methylene blue increased, when the bed height increased.

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5. References

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