

## **Application of plasma-treated natural zeolite nanorods for heterogeneous Fenton-like degradation of an azo dye**

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### **ABSTRACT**

In the present study, modification, characterization and evaluation of a novel nanocatalyst for heterogeneous Fenton-like degradation of C.I. Acid Red 17 (AR17), were reported. In the first step, natural clinoptilolite zeolite was modified by the glow discharge plasma. The characterization of plasma-treated sample was investigated by field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), BET surface area analysis. The SEM images of untreated and plasma-treated samples confirmed that the morphology of natural clinoptilolite was changed to nanorod after plasma treatment. Also, the XRD analysis revealed that there was no significant destruction of zeolite structure during the modification process. The BET results showed that the plasma treatment was led to the enhancement of specific surface area of treated zeolite (45.16 m<sup>2</sup>/g) compared to untreated one (23.92 m<sup>2</sup>/g). The catalytic performance of plasma-treated zeolite was investigated in the heterogeneous Fenton process towards the decolorization of AR17 solution. Results indicated that the decolorization efficiency of the dye was significantly increased from 60.02 % (during 90 min of reaction), in the presence of untreated catalyst, to 100 % (during 30 min of reaction) by the using of plasma-treated natural zeolite nanorods.

### **1. INTRODUCTION**

In most of industrial factories including the textile, cosmetic, paper, leather, pharmaceutical, and food industries, large amounts of dyes are annually produced and applied in many different sections. Introduction of these huge amounts of pollutants including synthetic dyes from factories to the environmental wastewater streams lead to chronic pollution of water sources. Also, various problems related to their carcinogenicity, toxicity to aquatic life could be immersed. Moreover, dyeing effluents are difficult to treat, due to their resistance to biodegradability, stability to light, heat and oxidizing agents. So the development of new techniques for management of wastewater

resources is a crucial. The simplicity and high efficiency of advanced oxidation processes (AOPs) make them a proper choice for the removal toxic and recalcitrant chemicals from wastewaters in the recent years (Dukkancı 2010, Neamtu 2004).

Among various AOPs, the use of  $\text{H}_2\text{O}_2$  and Fenton reagent has been extensively reported as a homogeneous catalytic process for removal of various pollutants. However homogenous Fenton process has some well-known disadvantages, including a narrow pH range, the production of iron-contained sludge, the catalyst deactivation by the produced intermediate. These duntreatedbacks can be removed by using heterogeneous Fenton-type catalysts such as synthetic and natural zeolites, bentonites, pillared clays or resins (Dukkancı 2010, Neamtu 2004). Among them, zeolites have been efficiently used within heterogeneous Fenton-type processes due to their unique physical and chemical properties including crystallinity, stability in thermal and chemical processes, regular cage structure in molecular size and ability to ion-exchange (AkgulKarabakan 2010).

Zeolites are microporous crystalline hydrated aluminosilicates. Their structure is similar to the inorganic polymers manufactured from an infinitely expanded three-dimensional network of tetrahedral  $\text{AlO}_4^{5-}$  and  $\text{SiO}_4^{4-}$  tetrahedral units connected by sharing of oxygen atoms. Each aluminum ion in the zeolite framework gives a net negative charge, which is balanced by an extra framework cation, usually from group IA or IIA. Their structure consist of regular channels or cages of size ranging between 3–20Å° occupied by the charge balancing ions and water molecules(Doula 2007).

As it was mentioned earlier, both natural and synthetic zeolites have been used within heterogeneous Fenton process. However, clinoptilolite, the most famous natural zeolitic mineral, has been widely used in research studies owing to its abundance and considerable low cost (Chmielewska 2002, Armbruster 1993). In this context, clinoptilolite exhibited no toxicity and made no environmental pollution so these properties spark the author's interest to investigate the substitution of homogenous catalyst by clinoptilolite in this work.

Despite the mentioned novel properties for this natural zeolitic mineral, still some matters are remained. One of them is the relatively sole and low specific surface area and micropore area in clinoptilolite which considerably influence the mass transport in many catalytic reactions (Chauhan 2012). These subjects not only decrease its catalytic efficiency, but also limit its application(Wang 2012). So, in order to enhance the efficiency of clinoptilolite the thickness of its crystals should be decreased from the micrometer scale to nanometer scale which leads to fundamental changes in its performances. Also, nanosized zeolite provides a short diffusion path of organic molecules. Moreover, the large external surface area of nanosized clinoptilolite makes more active sites to be exposed on the external surface. All of these advantages make nanosized zeolite more efficient than traditional zeolite in catalytic reaction. They are significantly a proper choice for catalysis applications due to these features. The discussed novel applications and properties of nonoasized clinoptilolite depend on its structure and composition of its surface both of which can change in response to variations in the environment.

Recently various synthetic methods have been developed to produce the nanosized zeolites with various morphologies (Cheng 2013, Xue 2012). However, most of the used synthesis processes generally require highly sophisticated equipment and toxic metal–organic precursors.

More recently, non-thermal plasma techniques including glow discharge, silent discharge and RF discharge have been used for modification (Liu 2006), improvement of the stability and acidity and activity of catalysts (Van Durme 2008). Nevertheless, there have been no reports regarding the production of nanosized clinoptilolite particles under glow discharge plasma. So, in the present work we present a novel method to prepare clinoptilolite nanorods using glow discharge plasma technique. Then, the obtained nanorods were modified with iron to be used as a heterogeneous Fenton-type catalyst for decolorization of AR17 solution. The physical properties of the produced samples were characterized by XRD, SEM, and BET analysis. To the best of our knowledge, there is no previous literature report concerning the use of Fe impregnated clinoptilolite nanorods in heterogeneous Fenton process.

## 2. EXPERIMENTAL SECTION

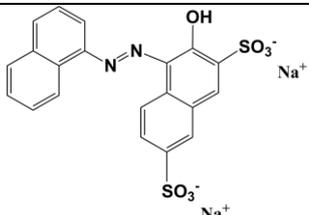
### 2.1 Materials

All chemicals used in this study were of analytical grade and were used without further purification.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  (30%) were obtained from Merck Co (Germany). Clinoptilolite was purchased from Kan Azar Tabriz Co. (Iran) and its main characteristics were presented in Table 1. AR17 was purchased from Alvan Saabet Co. (Tehran, Iran). Also, its characteristics were given in Table 2.

Table 1. Chemical composition of untreated clinoptilolite.

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$	$\text{TiO}_2$	$\text{MnO}$	$\text{P}_2\text{O}_5$
66.5%	11.81%	3.12%	3.11%	2.1%	1.3%	0.72%	0.21%	0.04%	0.01%

Table 2. Characteristics of C. I. Acid Red 17

Color index name	Chemical structure	Molecular formula	Color index number	$\lambda_{\text{max}}$ (nm)	$M_w$ (g/mol)
C.I. Acid Red 17		$\text{C}_{20}\text{H}_{11}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$	16180	510	502.435

### 2.2 Plasma treatment procedure

The experimental apparatus for plasma treatment is shown in Fig. 1. The glow discharge plasma reactor made of a pyrex tube reactor with a size of 40 cm × 5cm. The plasma is generated by the two electrodes connected to a DC high-voltage generator

(Tabriz, Iran). During the plasma treatment, the dried clinoptilolite samples were laid on the talc plate and located in a pyrex tube. Clinoptilolite powder was located at the region of “negative side” of glow discharge that characterizes itself with highly energetic electrons at low gas temperature. During the plasma treatment, feed gas is introduced into the reactor at normal pressure. Before the generation of discharge, the system was evacuated, and N<sub>2</sub> was applied as the plasma-forming gas in this work. The glow discharge was initiated at room temperature in this work. The treatment time was ranged from 45 to 60 min and the optimum operating time was selected.

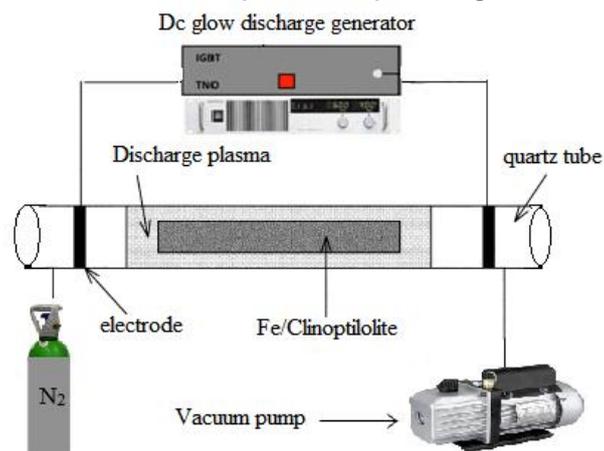


Fig.1 Schematic diagram of the plasma catalyst treatment using glow discharge

### 2.3 Preparation of Fe-Clinoptilolite catalyst

The Fe-Clinoptilolite catalyst was prepared by mixing 50.0 g of clinoptilolite, 200 mL of freshly prepared 0.125M FeCl<sub>3</sub>.6H<sub>2</sub>O solution, and 50 mL 2 M NaOH solution in a 500 mL pyrex flask. The addition of NaOH solution was rapid and with stirring. The flask was kept in a water bath at 60 °C for 6 h. then the sample was several times washed with distilled water and dried in an oven in air at 60 °C overnight. This procedure was repeated for three times (Dukkancı 2010, Neamtu 2004).

### 2.4 Heterogeneous Fenton procedure

All reactions were performed in a batch glass reactor equipped with a magnetic stirrer at atmospheric pressure and ambient temperature. In a typical run, the Fe-Clinoptilolite catalyst was placed into 500 mL of an aqueous dye solution (20 mg/L). In all the experiments, pH value was adjusted to 5 by addition of 0.1 M H<sub>2</sub>SO<sub>4</sub> to solution. Then a solution of 30% H<sub>2</sub>O<sub>2</sub> was added to achieve the selected H<sub>2</sub>O<sub>2</sub> concentration of 3 mmol/L. At different time intervals during 30 min, 3 mL of the sample was taken and the color removal of clean and transparent solution was evaluated by determining its absorbance at  $\lambda_{max}$ = 510 nm by using UV–Vis spectrophotometer, Lightwave S2000 (England). The color removal efficiency (CR (%)) was expressed as the percentage ratio of decolorized dye concentration to that of the initial one.

### 2.5 Characterization instruments

XRD (PANalytical X'Pert PRO) was used to identify the crystal structure, mean crystal size and phase purity of the clinoptilolite and plasma treated particles with CuK $\alpha$

radiation (40 kV, 30 mA) and a PIXcell solid state detector. The patterns were recorded at room temperature with step-sizes of  $0.02^\circ$ . The surface morphology and the structure of the prepared particles were obtained with the aid of a FESEM (S-4200, Hitachi, Japan). Nitrogen sorption analyses were obtained with a sorptometer (Micrometrics, Gimini series) using standard continuous procedures at 77.35 K on calcined samples that had been degassed at 363 K for one hour and then at 403 K under high vacuum for at least 10 hours. The surface area was calculated according to the Brunauer–Emmett–Teller (BET) model over a relative pressure range of 0.009–0.90.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization results of the synthesized samples

The XRD patterns of the untreated and plasma treated clinoptilolite are depicted in Fig. 2.

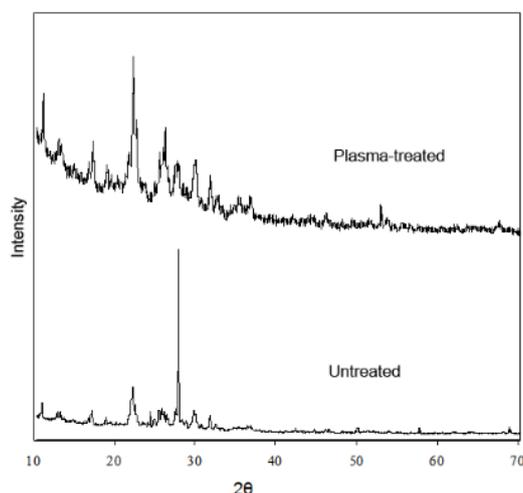


Fig. 2 The XRD patterns of untreated and plasma treated clinoptilolite

The achieved XRD diffraction pattern for the untreated clinoptilolite was typical one for the well crystallized clinoptilolite with trace of impurity such as feldspar, quartz and mica. It exhibits main peaks of the clinoptilolite ( $2\theta = 10.06, 22.66$  and  $30.38$ ) (Doula 2007). Also, the same typical peaks with reduced intensities were detected for plasma treated clinoptilolite sample, indicating that there is no significant change in the crystal structure upon plasma treatment. However, plasma treated clinoptilolite observed to have developed degradation resulting in the decreased intensity of the clinoptilolite peaks and a little increase of the background peaks. The decrease in the main peak intensities also, an slight increase of the background peak intensities with the slight shift of the peak positions indicates that there is a slight expansion of the lattice or in another words, there is a loss in crystallinity due to the removal of framework Al, resulting in a less ordered framework structure (AkgulKarabakan 2010). It should state that the expansion of the clinoptilolite lattice during plasma treatment will lead to the higher surface area of the treated samples wick was discussed and justified according to the achieved BET results as follows.

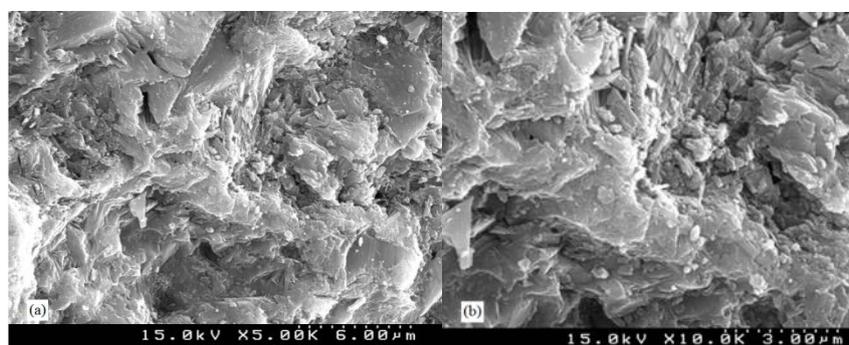
Table 3 shows the physical properties derived from  $N_2$  adsorption–desorption data. As it was shown the BET surface area was increased from  $23.92 \text{ (m}^2/\text{g)}$  for untreated

clinoptilolite sample to 45.16 (m<sup>2</sup>/g), suggesting the presence of surface cracks and defects resulted by the dissolution of framework Al atoms (dealumination) from the framework positions while introducing e<sup>-</sup> into the few remaining cation locations. In addition, the increase in mean pore diameter indicates that the plasam treatment affected the characteristics of the pore system significantly. The micropore area is larger for modified samples than for its natural clinoptilolite. Furthermore, mean pore diameter is decreased from 56.52 Å to 40.71 Å after plasma treatment. The increased surface area and decreased mean pore diameter of the plasma treated sample comparing to the untreated clinoptilolite propose the formation of micropores in the clinoptilolite. This increase can be ascribed to other reasons such as the opening of 10-membered rings or side pockets, removal of the amorphous material present in the channels and the formation of secondary micropores of the clinoptilolite.

Table 3. Surface area and porosity characteristics of untreated and plasma-treated clinoptilolite catalysts

Sample	untreated	plasma-treated
Specific surface area (m <sup>2</sup> /g)	23.92	45.16
External surface area (m <sup>2</sup> /g)	9.9756	10.8801
Micropore area (m <sup>2</sup> /g)	13.9501	34.2802
Micropore Volume (cm <sup>3</sup> /g)	0.006424	0.015953
Total Pore Volume (cm <sup>3</sup> /g)	0.033809	0.045971
Median Pore Diameter (Å)	56.52	40.71

The surface morphology of the untreated and treated zeolite was studied by a FeSEM microscope. Fig. 3 shows the SEM graphs for the untreated and treated clinoptilolite. It could be seen that morphology of natural clinoptilolite microparticles was changed to nanorod after plasma treatment.



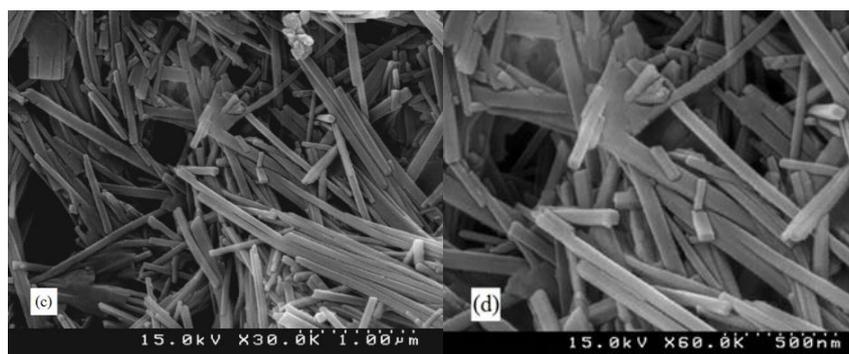


Fig. 3 SEM images of (a,b) untreated and (c,d) plasma treated clinoptilolite.

### 3.2. HETEROGENEOUS FENTON PROCESS

Fig. 5 shows the catalytic performance of Fe-modified-untreated-clinoptilolite and Fe-modified- plasma-treated catalysts in the decolorization of AR17, during 60 min. Fig. 5 exhibited that the Fe-modified-plasma-treated catalysts decolorized more than 95 % of the pollutant in 30 min which confirms its significance potential in Fenton process. The obtained results emphasized the excellent chemical activity of the prepared catalyst in oxidation process that is advantageous for practical applications.

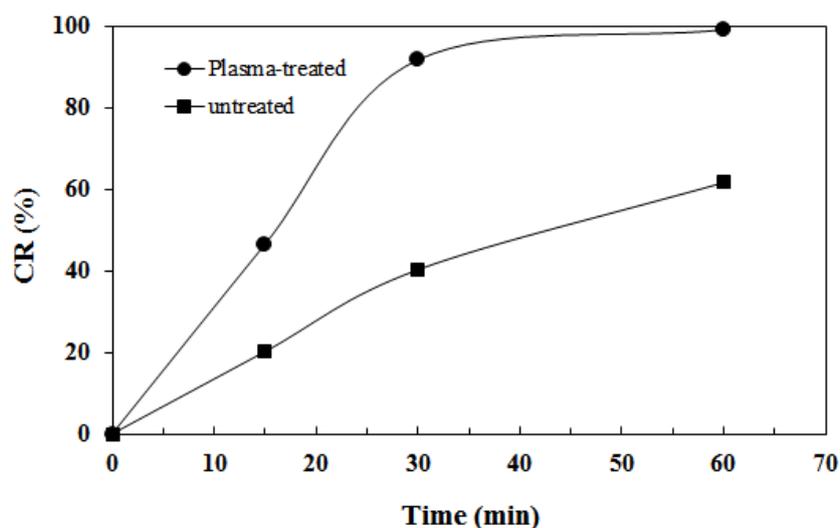


Fig. 4 The potential of untreated and plasma untreated catalysts on decolorization process (pH=5, 3 mmol/L H<sub>2</sub>O<sub>2</sub>, 20 mg/L dye concentration and 2 g/L catalyst).

### 4. CONCLUSIONS

In this study, for the first time, we have applied the glow discharge plasma technique to produce nanorods from microparticles of natural clinoptilolite. The SEM images of untreated and plasma-treated samples confirmed the production of nanorods. Also, the XRD analysis revealed that there was no significant destruction of zeolite structure during the modification process. The BET results showed that the plasma treatment was led to the enhancement of specific surface area of treated zeolite (45.16 m<sup>2</sup>/g) compared to untreated one (23.92 m<sup>2</sup>/g). The catalytic performance of plasma-treated clinoptilolite in Fenton process for the decolorization of AR17 solution indicated that the decolorization efficiency of the dye was considerably increased from by the using of

plasma-treated clinoptilolite nanorods. The present investigation will lead to a significant improvement in the preparation and modification of nanocatalysts for removal various pollutants.

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