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Zinc oxide/natural –Zeolite composite nano-powders: Efficient catalyst for the amoxicillin removal from wastewater

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ABSTRACT
In this study, a nano- composite of zinc oxide/natural–Zeolite was synthesized by mechanical method. The obtained microstructure was studied by scanning electron microscopy (SEM). X-ray diffraction analysis (XRD) was used to identify the phases formed. The prepared nanocomposite is used for the removal of amoxicillin from aqueous solution. It was exhibits high removal performance in adsorption of amoxicillin antibiotic.
Keywords: *zinc oxide/natural–Zeolite nano-composite; ZnO; natural–Zeolite; amoxicillin.*

1. INTRODUCTION
The widespread entrance of antibiotics from the pharmaceuticals industry and human medication into aquatic environment increased concern over public health. The high percentage of antibiotics is un-degradable in the human or animal body. Moreover some of antibiotics are toxic for aqua organisms such as algae which can lead to a long term on ecological sustainability. Thus the removal of antibiotics from the wastewaters is an important and attractive case study to be considered [1-3]. In general, conventional methods for the removal of antibiotics are problematic as they are costly or produce toxic products which require additional purification. Adsorption is a simple and efficient process to be considered for the removal of contaminants from wastewaters. Historically, effective adsorbents including activated carbon, chitosan beads and almond shell ashes have been used for these investigations. However, some of efficient adsorbents such as activated carbon are high cost and other low cost adsorbents have low adsorption capacity when pH is varied. Therefore, a modified and low cost adsorbent is required to improve the adsorption capacity [1-6].

Zeolites are drilled crystalline solids which are often referred to as molecular sieves. They are mineral compounds which mainly consist of aluminosilicate and mainly have been used as adsorbents in the industry. Zeolites are high porous, inexpensive and naturally available materials with high capacity and high specific area which promote it as a good sorbent for the removal of antibiotics [7-9]. Zeolites properties can be improved by various methods such as ion exchange process, chemical improvements and mechanical mixing. In this study, in continue of our studies [10-22] a nano- composite of zinc oxide/ natural – Zeolite was synthesized by mechanical method. The as prepared nano- composite was used as a new sorbent in the removal of amoxicillin from aqueous solution.

2. EXPERIMENTAL SECTION
2.1. Material and instrumentation.
All reagents were purchased from Merck and Aldrich and used without further purification. XRD data were collected from the synthesized powders for phase identification and determination of crystallite size by Philips TW3710 X'Pert diffractometers using Cu-Kα radiation. FE-SEM was taken by a Hitachi S-4160 photograph to examine the shape of the samples. Dynamic light scattering (DLS) measurement was done using a Malvern Zetasizer Nano ZS (ZEN 3600) instrument.

2.1. Preparation of zinc oxide/ natural –Zeolite nano-composite.
The nano- composite was prepared via mixing of the molar ratio of 1/5 (ZnO/Zeolite) as starting materials. The mixing materials were grinded using a high-energy planetary ball mill at rotational speed of 600 rpm and a ball-to-powder weight ratio of 1:7. The mixture was grinded in air atmosphere for 2 h.

2.3. Adsorption procedure.
Different solutions of amoxicillin with concentration of 0.5, 1, 2, and 4 gL^{-1} were prepared by dissolving 0.5, 1, 2, 4 g of the amoxicillin in double distilled water. 10 mL of each solution was inserted to a test tube and combined with appropriate amount of catalyst. The mixture was stirred for 5h at room temperature. The changes on the concentration of amoxicillin were measured by a GC Agilent instrument (Model 7890A). The effect of amoxicillin concentration, catalyst dosages and pH on the removal percentages was investigated.

3. RESULTS AND DISCUSSION
Figure 1 shows the X-ray diffraction (XRD) patterns of zinc oxide/ natural –Zeolite nano- composite. The XRD pattern shows that this composite has a two-phase structure: ZnO and Zeolite. It was observed that ZnO exhibited the hexagonal phase

and the corresponding peaks are 31.7, 34.3, 36.2, 47.4, 56.5, 62.7, 67.8, 68.9 and 89.4 [2θ degrees]. Whereas the characteristic peaks of Zeolite which shows an orthorhombic symmetry of aluminum silicate are 19.3, 23.7, 26.0, 26.4, 30.8, 33.4, 35.2 and 40.9 (2θ degrees).

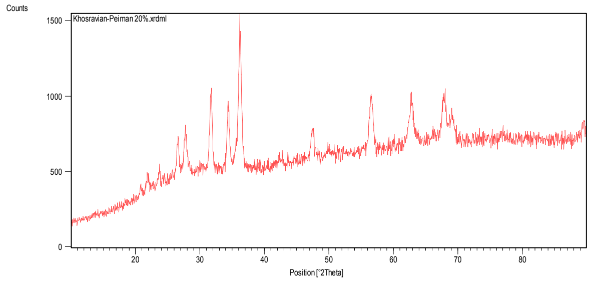

Figure 1. XRD pattern of ZnO/natural–Zeolite nano-composite.

The average crystal size of the nanoparticles was calculated by the Debye–Scherer formula (1), and found to be 86 and 141 nm for ZnO and Zeolite phases respectively.

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

Where, k is the shape factor, D is the crystallite size, θ is the diffraction angle, β is the full width half maximum of diffraction angles in radians.

The surface morphology and grain size of the as-prepared ZnO/ natural –Zeolite nano- composite were characterized by FE-SEM technique (Figure 2). The FE-SEM image shows that the composite consist of uniform particles and ZnO homogeneously distributed on the surface of the natural –Zeolite (Figure 2). The FE-SEM image also shows that the particles in the composite nano-powder have a diameter less than 100 nm.

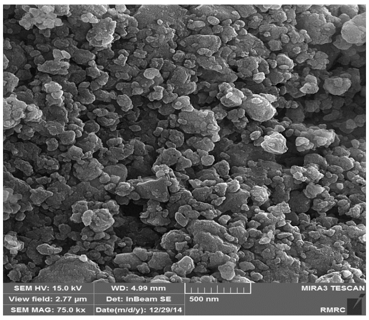

Figure 2. FE-SEM photographs of ZnO/natural–Zeolite nano-composite.

The dynamic light scattering (DLS) technique used to determine the particle size distribution of the nano-powders dispersed in ethanol (1gL^{-1} was sonicated in 20 ml of ethanol for 2h). According to DLS-measurement, the size distribution of the nanoparticles is almost in less than 100 nm with an average of 93 nm (Figure 3).

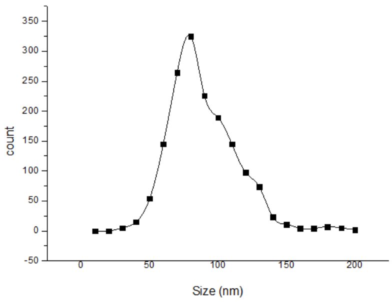

Figure 3. DLS analysis of ZnO/natural–Zeolite nano-composite.

3.1. Adsorption investigations of amoxicillin.

Four different solutions of the amoxicillin including 0.5, 1, 2, and 4 gL^{-1} were prepared by dissolving of the appropriate amount of amoxicillin in double distilled water. The Tracking for the removal of amoxicillin from the aqueous solution was investigated by gas chromatography (GC) technique.

The following equation was used for the calculation of the mass of the adsorbed amoxicillin:

$$R = \frac{C_0 - C_t}{C_0} * 100 \quad \textbf{(1)}$$

Where R is yield of the adsorption, C_0 and C_t are the concentrations of amoxicillin at time 0 and t, respectively.

3.2. Effect of catalyst amount and amoxicillin concentration.

Next, the effect of nano-composite dose on the removal percentage of amoxicillin was investigated and the results are shown in Figure 4. It is revealed that the removal of amoxicillin increased with increasing in the catalyst amount at a range of 0.01 -0.05 g. This may be due to increasing on the availability of adsorption sites and adsorbent surface area. The maximum of amoxicillin adsorption is achieved when 0.05 g of catalyst was used.An increase on the catalyst dose to 0.1 g shows a decrease on the removal percentage. This may be due to the more agglomeration of the particles on the reaction media and non-availability of active sites on the nano-composite.

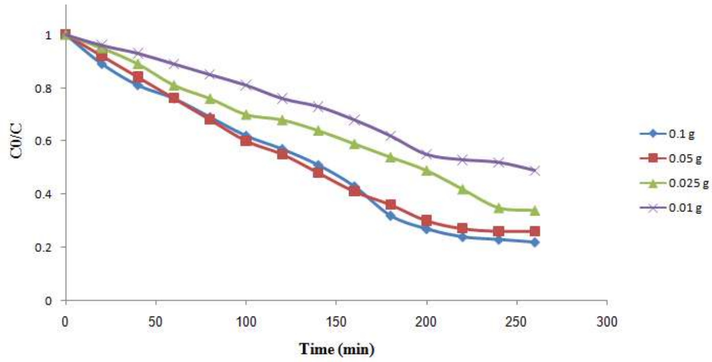

Figure 4. Amoxicillin removal: effect of catalyst dosage.

Next, in order to find the optimum of the amoxicillin concentration, various concentration of amoxicillin including 0.5, 1, 2, and 4 gL^{-1} was investigated (Figure 5). The adsorption yield of nano-composite adsorbent for amoxicillin increased with increasing initial concentrations from 0.5 to 4 g/L and afterwards decreased due to the saturation of the adsorption sites.

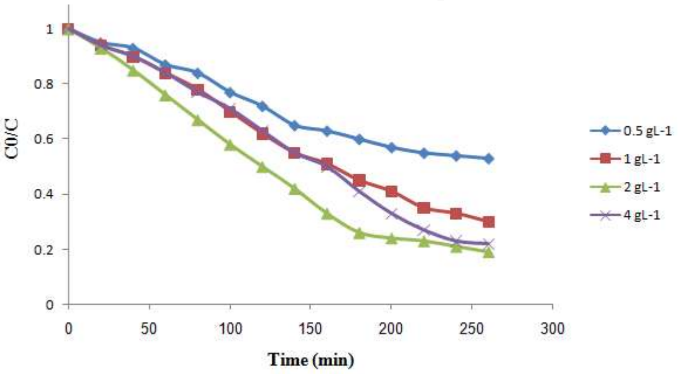

Figure 5. Amoxicillin removal: effect of amoxicillin solution concentration.

The higher yield of 2 gL^{-1} concentration rather than 4 gL^{-1} is due to the saturation of adsorbent surface when the concentration increased. Due to the higher yield of degradation, 2 gL^{-1} was chosen as optimum concentration.

3.3. Effect of pH levels

In order to study of pH effect on the removal efficiency of amoxicillin, the pH of solutions was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH). It is believed that the pH level can influence the adsorption capacity of nano-composite. In fact the pH level influences the surface charge properties of nano-composite and also amoxicillin. In basic condition both nano-composite and amoxicillin have negative charge and repel each other. Thus the adsorption capacity has lead to zero. In contrast, of basic condition, acidic media has a remarkable increase in the removal of amoxicillin (Figure 6). The pH level less than 3 disturb the catalyst and is not applicable to select for study.

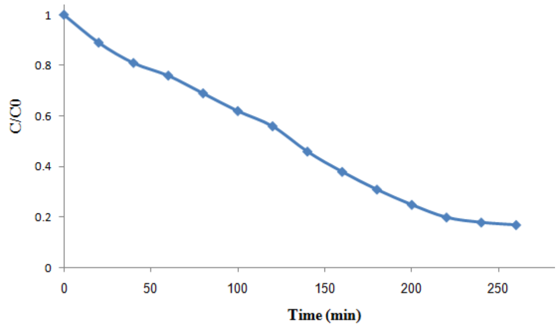

Figure 6. Amoxicillin removal: effect of initial pH solution.

Finally, the optimum condition for the removal of amoxicillin over ZnO/natural–Zeolite nano-composite is: solution concentration (2 gL^{-1}), catalyst dosage (0.05 g) and pH = 3.5.

4. CONCLUSIONS

A high efficient procedure for the removal of penicillin was developed using ZnO/natural–Zeolite nano-composite as efficient catalysts. ZnO/natural–Zeolite nano-composite is prepared by ball-milling technique and was characterized by XRD and FE-SEM techniques. The adsorption behavior of the as prepared sample was evaluated on the removal of Penicillin from wastewater. From the view of green chemistry, the use of ball-milling can improve the crystal quality, uniformity, aspect ratio and simplicity preparation of nanostructures which is fundamentally important for practical applications.

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