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ZnO-embedded Hydrogel for phenol degradation from synthetic wastewater

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Abstract

A graft copolymerization were used to create ZnO nanoparticles with carboxymethyl cellulose-g-poly(acrylic acidco-acrylic amide) hydrogel coating (Zn(NO3)2]. Hydrogel material with an average size of 46.94 nm were successfully coated on the zinc nitrate surface, according to the results of several characterization tests.

Zinc oxide (ZnO) nanoparticles were synthesised using a wet chemical technique. scanning electron microscopy (SEM), X-ray diffraction (XRD), and the distribution of particle sizes was utilized to examine the structural and morphological aspects of the produced ZnO nanoparticles. The developed ZnO nanoparticles were used to remove phenol from industrial and synthetic wastewater. This study examined the effects of beginning pH, ZnO dosage, contact time, and phenol initial concentration on the percentage of phenol removed. For the sorption data, Freundlich and Langmuir isotherms were used. When compared to various isotherms, the findings indicate that the Langmuir isotherm fits the phenol removal data quite well.

Keywords: nano-zinc oxide; isotherms; wastewater; chemical technology; phenol uptake process

Introduction

Phenols and related chemicals are among the most prevalent organic chemical pollutants found in industrial effluent[1]. Because phenols cause harm to species at low quantities, they are categorized as priority pollutants. Phenol may be absorbed via the skin and is poisonous and mutagenic at high quantities[2]. The most well-known techniques for removing phenol from water-based solutions include adsorption, chemical oxidation, biological treatment, and precipitation. Distillation, ion exchange, solvent extraction, and membrane procedures, microbial fuel cells, reverse osmosis, and electrochemical techniques are some more well-known techniques for eliminating phenol from aqueous solutions[3–6].

Through chemical and physical interactions, adsorption, a physiochemical process, is necessary for the movement and destiny of pollutants in both natural and artificial aquatic systems[7–9]. Because of its simplicity, adsorption systems have low capital and operating expenses as well as fouling issues, protecting them from dangerous substances[8].

Phenol can be removed using a variety of physical, chemical, and biological treatment techniques, but each of these methods has limitations, such as secondary effluent, dangerous and hazardous final products, higher energy consumption, lengthy response times, **non-economic,** and low efficiency. Adsorption by nano particles is a straightforward solution to these issues compared to other approaches [10]. Because they are effective biocompatible adsorbents with more active locations, a high specific surface area, and low intra-particle resistances, nano adsorbents have a variety of uses in the engineering field. Nano-scale pores, high surface area, great selectivity, along with elevated permeability, good mechanical durability, and good thermal firmness are characteristics of nano adsorbents [11,12,13].

Since zinc oxide nano particles are safe, they can be employed as sorbents to remove pollutants from the environment. Because of its special qualities and numerous uses with chemical sensors, piezoelectric devices, UV light emitters, transparent electronics, and spin electronics, nanoparticles of zinc oxide have attracted a lot of scientific attention. Wet chemical methods, sol-gel methods, hydrothermal techniques for synthesis and chemical vapor deposition methods, precipitation methods, laser vaporization condensation methods, and spray-pyrolysis techniques have all been employed to create ZnO [14, 15].

The majority of these strategies weren't commonly applied on a broad scale; still, chemical synthesis has been frequently used because it is less complicated and costly. In wastewater engineering, nanoparticles of zinc oxide are repeatedly employed to remove dyes, metals, nitrogen, and phosphorus [16–18]. Therefore, ZnO nanoparticles are synthesized and utilized in this research to degrade phenol from aqueous and industrial effluent. In this work, coprecipitation and in situ graft copolymerization are used to create carboxymethyl cellulose hydrogel-coated Zn(NO3)2 nanoparticles.

Materials and methods

Materials: LobaChemie, India, supplied sodium hydroxide (NaOH), zinc nitrate ($Zn(NO_3)_2$), and other necessary chemicals. Double-distilled water was used to prepare all aqueous solutions.

N, N'-methylene bisacrylamide , acrylic acid , acrylamide , ammonium persulfate , carboxymethyl cellulose sodium , and H_2O_2 (30%, weight%) were obtained from Sigma-Aldrich.

Synthetic Effluent Preparation: 1.0 g of phenol dispersed into freshly heated and cooled distilled water to create the solution of stock phenol, which was then diluted to 1 liter (1 mL = 1 mg phenol). The stock solution was used to create the functioning solution. A spectrophotometric technique was used to analytically quantify the phenol levels in the synthetic effluent [19].

ZnO Nanoparticle Development: An Experimental Method

14.85 g of zinc nitrate [$Zn(NO_3)_2$)] were dissolved in 100 ml of double-distilled water to create a aqueous solution at 0.5 M. The zinc nitrate solution was continuously agitated for one hour at 70 °C to achieve complete dissolution, while 100 mL of 1 M NaOH solution was prepared separately in another beaker.

Under continuous vigorous stirring, the zinc nitrate solution was gradually introduced into the sodium hydroxide solution using a burette. The reaction led to the immediate formation of a whitish suspension, which was further maintained under constant agitation for nearly two hours to ensure proper reaction completion. Following overnight settling, the supernatant was separated by filtration, after which the obtained precipitate underwent two successive washes with double-distilled water and was subsequently treated with ethanol.

Preparation of ZnO-embedded hydrogel:

ZnO nano composites coated with hydrogel were produced using a one-pot process. In short, 100 ml of an aqueous solution containing 2700 mg/l of carboxymethyl cellulose sodium was combined with the generated zinc oxide suspension.

Following 30 minutes of mechanical stirring at 50^0 C, the reaction solution was quickly and successively supplemented with 0.5 ml of acrylic acid, 0.5 g of acrylamide, 25 mg of N, N'-methylene bisacrylamide, and 25 mg of ammonium persulfate. For three hours, the resultant mixture was stirred at 70^0C. The resulting black products, known as ZnO hydrogel nano composites, were gathered, cleaned with deionized water, and subsequently dried in a hot air oven for further usage.

Degradation of phenols using zinc oxide nano particles

The degradation efficiency of phenol was evaluated by varying key operational parameters, including initial pH (3–7), phenol concentration (100–400 ppm), contact duration (0–40 min), and ZnO dosage (1–4 g/L).

Experiments were conducted at 30^oC in a 1 L batch reactor to examine the impact of contact time. To start the sorption process, 3g/L of ZnO nano particles were introduced to 0.5 L of diluted phenol solution with a concentration of 100 ppm and a pH of 6. The sample was taken every ten minutes and filtered to get rid of nanoparticles after the solution was thoroughly mixed using a magnetic stirrer. The phenol content of the filtered sample was estimated analytically using the spectrophotometric technique. The process described above was repeated with a modified pH and ZnO dose.

Characterization techniques

Zinc Oxide Nanoparticle X-Ray Diffraction Analysis (XRD)

A Bruker AXS D4 Endeavor diffractometer with a Cu K radiation source filtered by a graphitic monochromator was used for the analysis, producing X-rays with a wavelength of 1.54060 Å.

Scanning Electron Microscopy (SEM)

A method for creating a picture of a surface is scanning electron microscopy (SEM). The JSM-5610 instrument was used to perform the SEM study.

Results and discussion

ZnO nano particles characteirization

Figure 1 examines the ZnO nano particles' XRD patterns. The hexagonal ZnO structure's most distinctive peaks are located at 2ϴ = 31.740, 36.830, and 47.620, which match the (100), (101), and (102) planes. High material crystallinity is implied by the peaks' high intensity degree. Figure 1 makes it clear that there are no distinctive peaks for contaminants. As a result, the materials that were manufactured were pure and free of PVA stabilizing agent contamination.

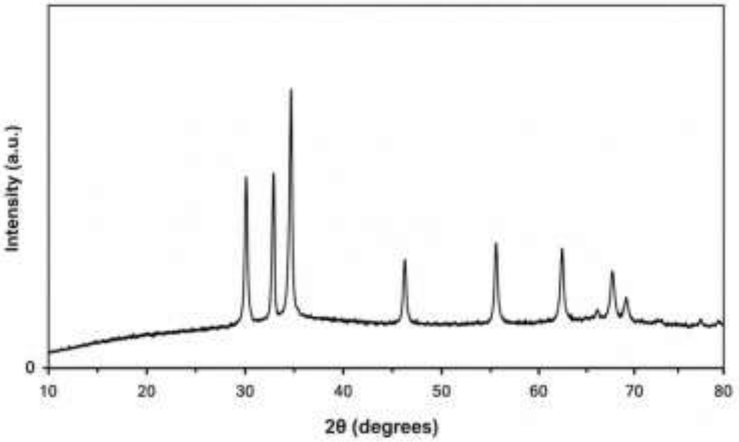

Figure 1. X-ray diffraction (XRD) patterns for ZnO nanoparticles

Using X-ray diffraction (XRD) data, the Scherrer equation calculates the average crystallite size of ZnO nanoparticles. In particular, it is stated as:

$$D = K\lambda / \beta\cos(\theta) \qquad (1)$$

$$D = \frac{0{,}9x0.15406}{0.003x0.98454}$$

D≈46.94nm

Where

D: Size of crystallites (usually in nm).s Particle shape is represented by the Scherrer constant,
K: It is commonly assumed to be 0.9 or 0.94 for spherical ZnO nanoparticles with cubic symmetry.
λ: X-ray source wavelength. For $Cu\text{-}K\alpha$ radiation, this is typically 0.15406 nm.
β: Full Width at Half Maximum (FWHM) of the diffraction peak in radians
θ: Bragg angle

Figure 2 displays the SEM images of zinc oxide nanoparticles made from a solution of sodium hydroxide and zinc nitrate. It can be seen from the figure that the particles have a homogeneous size distribution and are nanoscale. The particles are uniformly shaped, spherical granules. The surface area that was available for reaction was expanded by these structures.

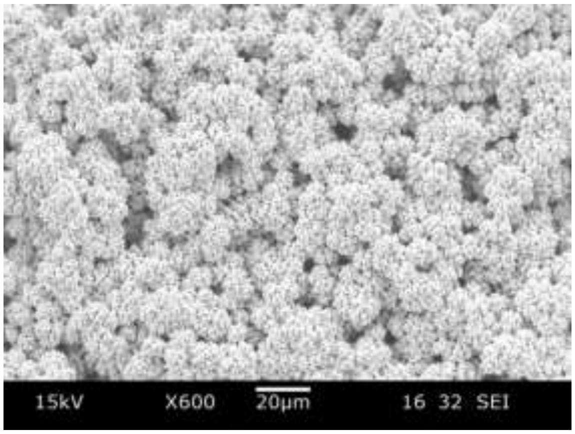

Figure 2: Zinc Oxide Nanoparticle SEM scans at 20µm/600 X

Influence of initial phenol concentration and contact time

Figure 3 illustrates the impact of contact time on phenol removal from aqueous solutions at concentrations of 100, 200, 300, and 400 ppm at pH 6. It was established from the figure that phenol elimination rises as contact time increases. Phenol was shown to sorb onto ZnO quickly over the first 20 minutes, reaching equilibrium after 30 minutes for various initial phenol concentrations. The elimination of phenol by the nanoparticles is barely affected by an additional increase in contact duration. Because the zno nanoparticles had a greater surface area at first, the removal effectiveness of phenol was higher. Figure 3 also displayed the influence of the initial phenol concentration on the phenol removal. As the initial phenol concentration rises, the elimination rate of phenol falls.

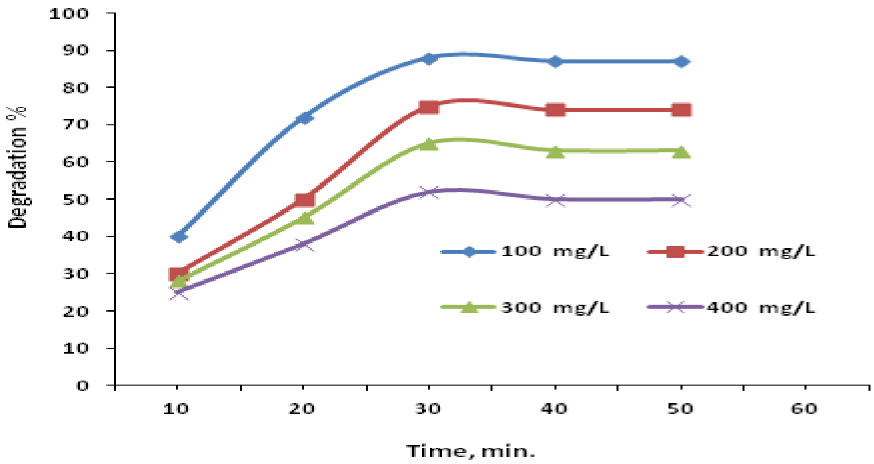

Figure 3: Influence of initial phenol concentration and contact time (experimental conditions: phenol concentration = 100–400 ppm; pH = 6; ZnO dosage = 6 g/L;

Nano-ZnO Dosage's influence on the Phenol Adsorption Process

Figure 4 illustrates how the dosage of ZnO nanoparticles affects the degradation of phenol. The pH was kept at 6 and the original phenol concentration was kept at 100 ppm. The degradation of phenol is increased when the dosage of ZnO nanoparticles is increased from 2 to 8 g/L. When the ZnO dosage was raised to 6 g/L, phenol degradation increased; however, subsequent increases in the dosage of nanoparticles did not accelerate the degradation. At ZnO of 6 g/L, the maximal phenol degradation efficiency was discovered to be 90.5%.

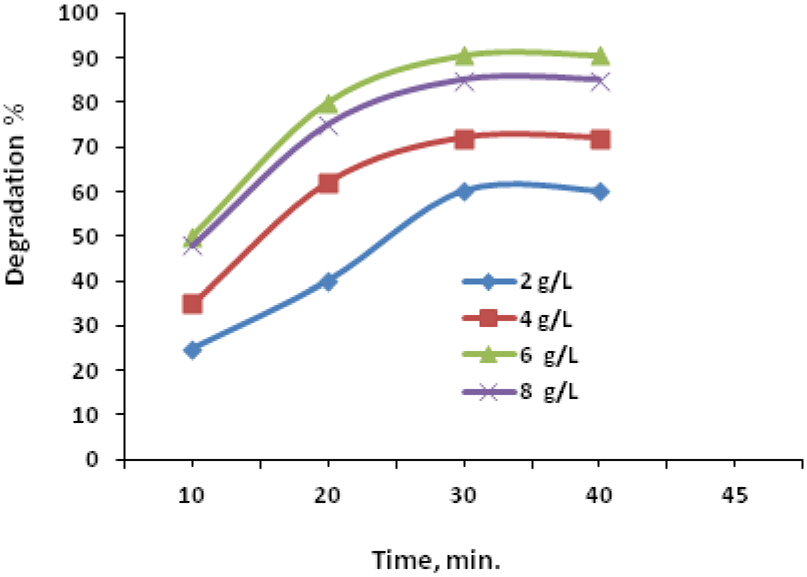

Figure 4: ZnO dose influence (experimental conditions: pH = 6; phenol concentration = 100 ppm)

Influence of pH

The ability of hydrogen ions to compete with phenol for active sites on ZnO is closely correlated with pH. The pH of the solution significantly affects both the degree of phenol ionization and the surface charge of the adsorbent material, which in turn controls the phenol adsorption process on to magnetic ZnO nanotubes[20]. In the pH range of 3.0 to 6.0, the impact of solution pH on phenol degradation onto ZnO nanoparticles was assessed; the outcome is displayed in Fig. 5.

Figure 5 shows that adsorption is high at pH< 7, indicating that magnetic ZnO has a higher capacity for adsorption in an acidic media. For ZnO, phenol elimination reached its lowest values at pH 3.The proportion of phenol degradation increased as the pH rose from 3 to 6. The elimination of phenol was impacted by the first pH increase, and the ideal pH was determined to be 6. At a pH of 6, a maximum phenol removal of 90.1% was attained in 30 minutes.

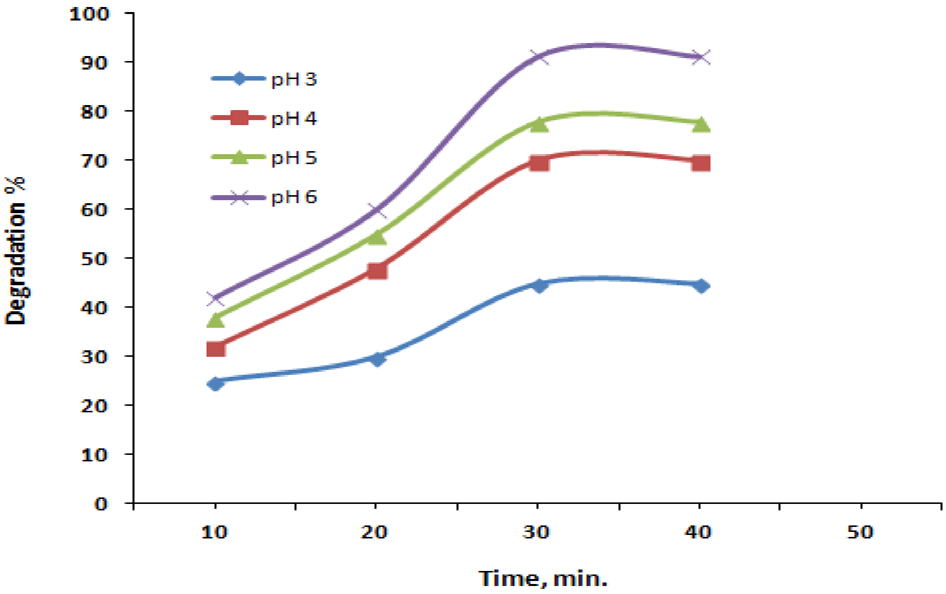

Figure 5. Influence of solution pH on the degradation of phenol (Experimental Conditions: Phenol Concentration = 100 mg/L , ZnO dosage = 6 g/L)

Equilibrium isotherms

When designing an adsorption system, the equilibrium adsorption isotherm is fundamentally important. Adsorption equilibrium studies provide the adsorbent's capability. The sorption data in this article were analyzed using the Freundlich and Langmuir isotherms.

Langmuir isotherm

The Langmuir (1916) isotherm's linear form [21] is provided by

$$\frac{1}{qe} = \frac{1}{q_m b_{ce}} + \frac{1}{q_m} \qquad \textbf{(2)}$$

where q_m is the sorbent's monolayer sorption capacity (mg/g), q_e is the sorbent's equilibrium metal uptake (mg/g), Ce is the solution's equilibrium phenol concentration (mg/L), and b is the Langmuir sorption constant (L/mg) associated with the sorption's free energy.

The Langmuir isotherm is used to estimate the equilibrium uptake (e q) from the experimental data. Figure 6 displayed the Langmuir plot for the sorption of phenol.

Figure 6 displayed the Langmuir plot for the sorption of phenol. Table 1 displays the results of the evaluation of the constants. According to the findings, the fitting of the Langmuir isotherm indicates that the process of phenol adsorption onto nanoparticles involves both homogeneous and heterogeneous sites.

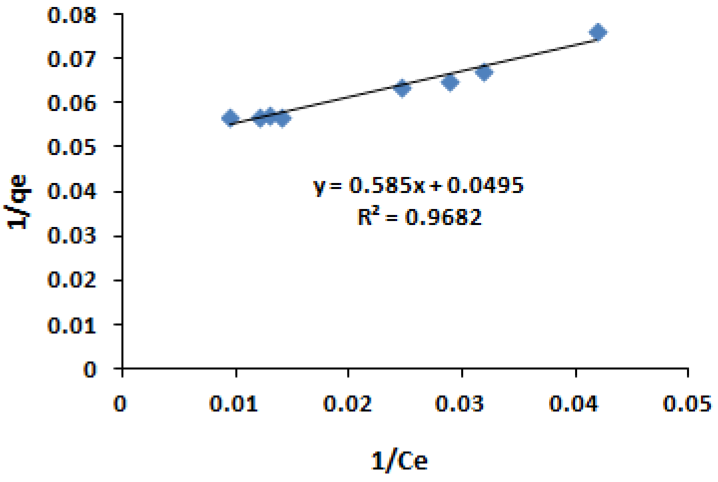

Figure 6: Langmuir isotherm graphical representations showing ZnO nanoparticle sorption

Freundlich isotherm

Heterogeneous systems are described by the Freundlich [22] isotherm. The heterogeneity factor 1/n is what defines it. The isotherm's linear form is:

$$log\ qe = logK_f \ + \frac{1}{n}\ logC_e \qquad \textbf{(3)}$$

Ce is the equilibrium concentration (mg/L), qe is the quantity of phenol adsorbed at equilibrium (mg/g), 1/n is an empirical value related to the sorption intensity, and Kf is a constant related to the sorption capacity that changes depending on the material's heterogeneity. The phenol sorption isotherm at various starting phenol concentrations is displayed in Figure 7. The slope value of the log qe against log Ce plot indicates Kf, and the intercept value indicates 1/n. Table 1 provides the constants Kf and 1/n.

Nevertheless, the Langmuir isotherm model has a higher R^2 value than the Freundlich isotherm. As a result, the Freundlich isotherm does not suit the experimental data as well as the Langmuir isotherm.

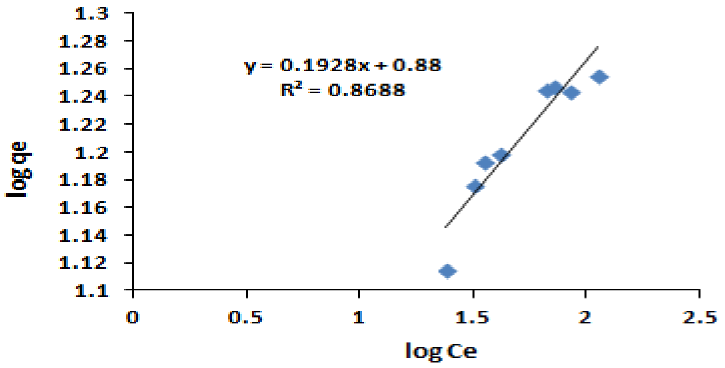

Figure.7. Freundlich isotherm plots for the sorption of ZnO nano particles

Table 1: ZnO nanoparticle sorption isotherm constants

Isotherm	Parameter	Values
Langmuir	qmax	19.6 mg/g
	b	0.10
	R^2	0.9682
Freundlich	Kf	8.47
	1/n	0.163
	R^2	0.8688

Conclusions

To effectively break down phenol in aqueous solution, hydrogel-coated Zno nano particles with diameters of 46.94 nm were created and used as an adsorbent.

The present study demonstrated that ZnO nanoparticles are an effective adsorbent for the removal of phenol from aqueous solutions under optimized conditions. The adsorption efficiency of phenol was strongly influenced by contact time, initial phenol concentration, ZnO dosage, and pH. Phenol removal increased rapidly during the initial adsorption period and equilibrium was achieved within 30 minutes, indicating the fast adsorption capability of ZnO nanoparticles. However, the adsorption efficiency decreased with increasing initial phenol concentration, suggesting saturation of available active sites at higher pollutant concentrations. Furthermore, an increase in ZnO nanoparticle dosage enhanced phenol degradation efficiency due to the greater availability of adsorption sites, with an optimum dosage of 6 g/L yielding a maximum phenol removal of 90.5%. The pH of the solution also played a significant role in adsorption performance, with acidic conditions favoring phenol removal and the optimum pH determined to be 6, where a maximum removal efficiency of 90.1% was achieved. Overall, the findings confirm that ZnO nanoparticles possess excellent adsorption potential for phenol remediation and can be considered a promising material for wastewater treatment applications.

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