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Research Article

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Photocatalytic Self-Cleaning of Cotton Fabrics Treated with ZnO and Gd Doped ZnO

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ABSTRACT

To enable photocatalytic self-cleaning cotton fabrics working under UV irradiation, ZnO and 2wt%Gd doped ZnO nanopartecle are synthesized using precipitation method. The morphology, optical and microstructure were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), attached with EDX Unit. Moreover, the morphology of ZnO and 2wt% Gd doped ZnO were studied by transmission electron microscope (TEM) and the functional groups for each ZnO and 2wt% Gd doped ZnO were studied using FTIR spectroscopy. According to the characterizations all nanoparticles are spherical in shape with hexagonal wurtzite structure. However, the cotton fabrics functionalized with 2wt% Gd doped ZnO are significantly enhanced photocatalytic activity for C.I Reactive red 195 (RR195) degradation.

Keywords: Self-cleaning; Cotton fiber; ZnO; Gd doped ZnO

INTRODUCTION

Chemical degradation and self-cleaning by hydrophilic semiconductor photocatalysts, such as zinc oxide (ZnO), have a wide range of applications including toxic chemical decomposition [1], protective/self-cleaning clothing [2], self-cleaning glass [3], and self-cleaning membranes [4]. Of particular note, chemically protective and self-cleaning clothing have obvious health, environmental, and military applications. Zinc oxide (ZnO), is an n-type wide band non-toxic compound semiconductor, with a direct band gap of 3.37 eV. ZnO can be applied as photocatalysts and self- cleaning hydrophilic semiconductor photocatalysts [5]. At ambient temperature, ZnO has a wurtzite crystal structure with polar surfaces [6]. For the degradation of toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents, semiconductors are being used as catalysts [7]. In this process, conduction-band electrons and valence-band holes would be generated on its surface. ZnO is a semiconductor and electron hole pair that is created upon irradiation with UV light having energy greater than its band gap energy, moves to the surface of ZnO where they cause oxidation-reduction reaction with water and oxygen. It was reported that the surface conditions of ZnO were modified with the incorporation of dopant ions and its photocatalytic properties were greatly enhanced [8]. The present study describes the removal of RR195 from the simulated industrial waste water using the concept of the photocatalytic reactions using a suspension of both zinc oxide and 2w% Gd doped zinc oxide onto cotton fiber. These two photocatalysts were used with treated cotton fiber.

EXPERIMENTAL SECTION

Reagents

All reagents were used as received without further purification. C.I. Reactive Red 195 (RR195, Figure 1) used is provided from high purity grade of Aldrich Company and used without further purification (Molecular Formula $C_{31}H_{19}ClN_7Na_5O_{19}S_6$, Molecular Weight 1136.31 g/mol and λ_{max} 542 nm).

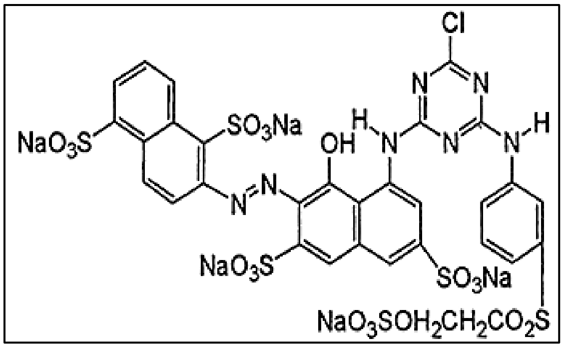

Figure 1: Chemical structure of CI reactive red 195

Photoreactor

The home-made photoreactor (Figure 2) consist of 18 low pressure mercury lamps (180 watt).

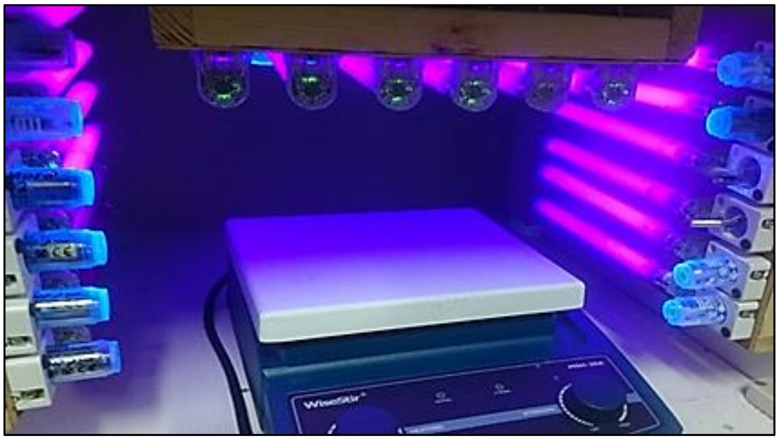

Figure 2: Schematic description of the homemade photoreactor that used in photocatalytic degradation

Preparation of ZnO and 2wt% Gd Doped ZnO Nanoparticles

For typical synthesis of Gd ions doped ZnO Nanoparticles using precipitation method [9], 2 gm of Zn (acetate)2 obtained from loba Chemie 99.5% pure grade was added to 100 ml of distilled water and stirred for 30 min. Then 2 wt% of gadolinium nitrate dopant (Aldrich (99.9% pure grade) was added with further stirring for 10 min. In the prepared solution, 15 ml of 4 M NaOH solution were introduced to adjust pH range (pH 10-11) as a white precipitate was produced and stirred for 1 h at room temperature. The resulting products were taken out and removed along with some existing impurities and ions by washing with deionized water till being neutral. The final products were dried at 80°C and calcined at 400°C for 30 min. Pure ZnO was also prepared in the same way without doping for comparison. All chemicals employed were of analytical grade and were used as received.

Preparation of Cotton Coated with ZnO and 2w% of Gd Doped ZnO Nanoparticles

Washing of the cotton:

The cotton fabric was cut into pieces of dimension 5 cm × 5 cm. The cotton was washed first with water and detergent at 80°C for 30 min to remove the impurities such as wax and fat. Then it was washed several times with a large amount of deionized water. They were further cleaned in acetone then in ethanol for 30 min at 60°C and dried at room temperature for 24 h.

Fabric coated with ZnO and 2wt% Gd doped ZnO nanoparticles:

The fabric samples were soaked for 30 min in 2-propanol (98%) dispersion of ZnO and 2wt% Gd doped Zinc Oxide nanoparticles separately (under gentle magnetic stirring). The fabrics were squeezed to remove the excess dispersion and dried in an oven at 130°C for 15 min under atmospheric pressure (dry heat).

Photocatalysis Experiment

Self-cleaning photocatalytic studying:

In this study cotton was used after loading with ZnO and 2wt% Gd doped ZnO separately in a set of experiments for each case. The dimensions of this piece of cotton were 5 × 5 cm in a solution of 10 ppm in 250 ml of the RR195 dye solution. The photocatalytic ability of ZnO and 2wt% Gd doped ZnO coated cotton was tested by photodegradation of RR195 dye. Reactions were carried out in a homemade reactor as shown in Figure 2. The resultant mixture was stirred for one hour in order to reach adsorption equilibrium at room temperature under dark conditions. Then reaction mixture was irradiated with UV light from low pressure mercury lamp (180 watt) with continuous stirring, a sample of 3 ml of reaction mixture was withdrawn and centrifuged and the absorbance was recorded at λ_{max} 542 nm [10].

Samples Characterization

XRD measurements (X-ray diffraction) were conducted using a A PANalytical X-Ray Diffraction equipment model X Pert PRO with Mono chromator, Cu-adiation (λ_{max}1.542Å) at 45 KV, 35 MA and scanning speed 0.030/sec. The surface morphology of the dried nanoparticles of ZnO and 2wt% Gd doped ZnO were studied using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses, EDX), with accelerating voltage 30 KV, magnification14x upto 1000000 and resolution for Gun.1n). FEI company, Netherlands. Moreover, the morphology of ZnO and 2wt% Gd doped ZnO were studied by A JEOL JEM-2010 transmission electron microscope (TEM) which operated at a 200 KV accelerating voltage. The wave number and intensities of the FTIR bands of the different types of the function groups were determined in a range of 4000-5000 cm^{-1} using FTIR Spectrometer Model Type Mattson- Infinity Series Bench top 961.The photocatalytic activities of RR195 was determined by measuring the degradation of RR195 under UV light irradiations. The photocatalytic activity was followed by measuring the absorbance of the dye at λ_{max} 542 nm by UV-visible spectrophotometer (JENWAY UV-spectrophotometer).

RESULTS AND DISCUSSION

Characterization of Zinc Oxide (ZnO) 2wt% Gd Zinc Oxide Nanoparticles (Gd/ZnO)

X-ray diffraction (XRD):

Figure 3 **s**hows the XRD patterns of ZnO and 2wt% Gd doped ZnO. For ZnO (Figure 3), the diffraction peaks in XRD indicated the nanocrystalline nature and pure ZnO with hexagonal wurtzite structure [11-13]. For 2wt% Gd doped ZnO, no diffraction peaks of Gd or other impurity phases were detected suggesting that Gd^{3+} ions would uniformly substitute into the Zn^{2+} sites in the lattices of ZnO. The higher intensities of calcined nanostructure peaks with narrower width reveal a highly crystallized wurtzite structure [14].

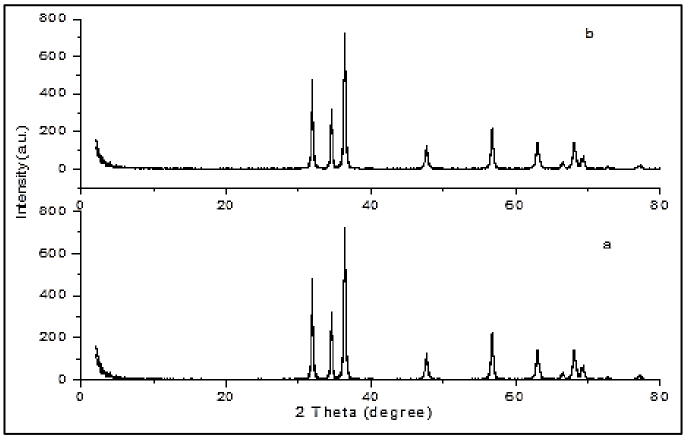

Figure 3: XRD patterns of ZnO and 2wt%Gd doped ZnO

Scanning electron microscope (SEM)-microstructural studies:

SEM is one of the techniques for the topography study of the samples and it gives important information regarding the growth mechanism, shape and size of the particles. The surface morphology of the ZnO and 2wt% Gd doped ZnO nanoparticles are given in Figure 4. The entire SEM picture clearly shows the average size of the nanoparticles is the order of nanometer size. The ZnO nanoparticles Figure 4 shows the synthesized nanoparticles are homogeneous, uniformly distributed over the surface and good connectivity between the particles containing the spherical and randomly oriented particles. In ZnO and 2wt% Gd doped ZnO nanoparticles the tendency of high agglomeration is noted.

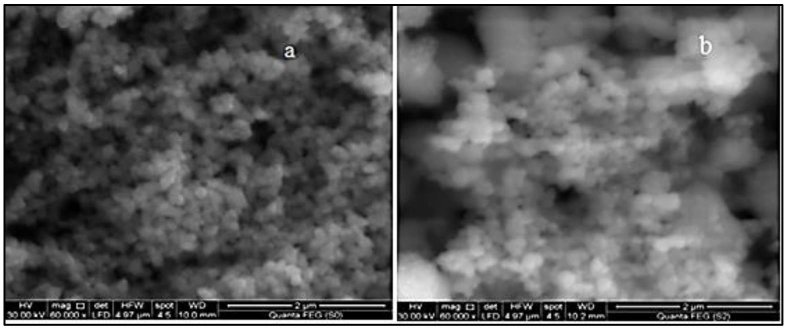

Figure 4: SEM image of ZnO (a) and 2wt% Gd doped ZnO NPs (b)

Energy-dispersive analysis X-ray spectra (EDX):

The energy dispersive analyses X-ray (EDX) is used to analysis the amount of elements in ZnO and 2wt% Gd doped ZnO. The chemical compositional analysis of 2wt% Gd doped ZnO have been carried out using EDX as shown (Figure 5). The EDS analysis confirms the presence of Gd in the ZnO system and wt% very nearly equal to their nominal stoichiometry within the experimental error. Therefore, the EDX spectra show well agreement with the experimental concentration used for 2wt% Gd-doped ZnO system.

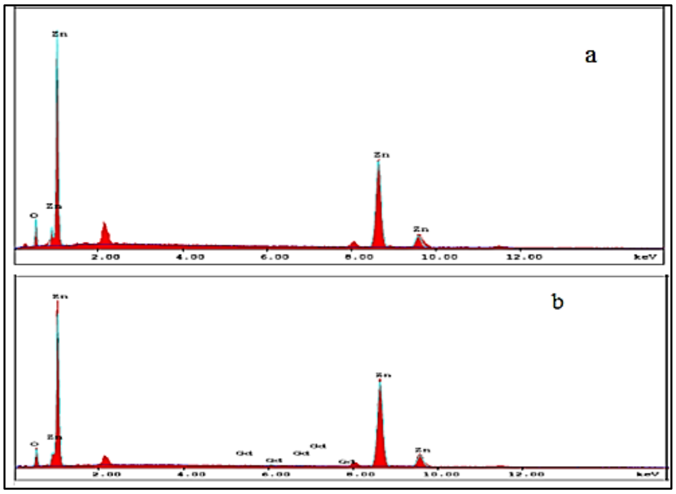

Figure 5: EDX spectra of ZnO NPs (a) and Gd doped ZnO (b)

Transmission electron microscope (TEM) microstructural studies:

To gain further insight into the surface morphology of the ZnO NPs and 2wt% Gd doped ZnO samples were monitored under TEM (Figure 6). In Figure 6 the TEM image of ZnO and 2wt% Gd doped ZnO is fully aggregated and spherical in shape. FTIR spectra of ZnO and 2wt% Gd doped ZnO (Figure 7).

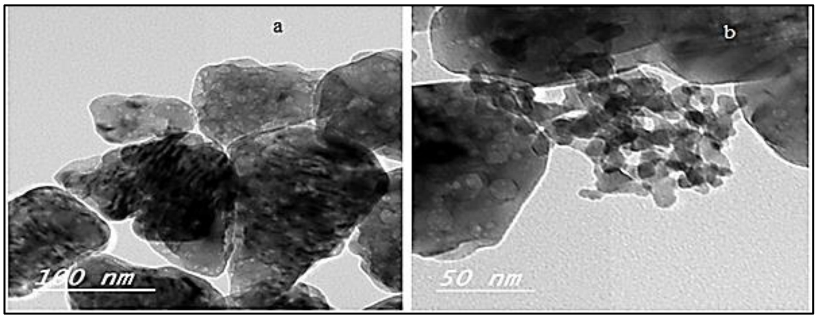

Figure 6: TEM image of ZnO (a) and 2wt%Gd doped ZnO (b)

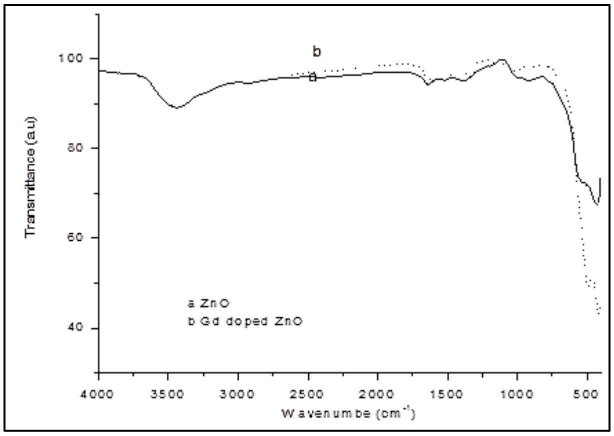

Figure 7: FTIR spectra of ZnO and 2wt% Gd doped ZnO

Self-cleaning Application of ZnO and 2%Gd Doped ZnO Treated Cotton Textile of RR195

Effect of different gadolinium doping:

Photocatalytic self-cleaning properties of treated cotton textile were evaluated by photocatalytic degradation of RR195 dye under UV illumination. Figure 8 shows the plot of absorbance at λ_{max} 542 nm vs. time for ZnO and 2w% Gd doped ZnO self-cleaning treated cotton textile of RR195 [RR195] = 10 ppm at pH = 9.0. The effect of self-cleaning materials (ZnO and 2w% Gd doped ZnO treated cotton fiber) on the photodegradation of RR195 dye have been examined. The evaluation of the absorbance at different time intervals for irradiation of RR195 describing the photodegradation of RR195. The absorption is assumed to be in linear proportion with the concentration of RR195 according to the equation (Equation 1) [15].

$$C/C_0 = A/A_0 \quad (1)$$

Where C_0 represents the initial concentration, C represents the changed concentration; A_0 represents the initial absorbance, and A represents the changed absorbance of the dyes at the characteristic absorption wavelength.

The photocatalytic oxidation kinetics of many organic compounds has often been modeled with the Langmuir–Hinshelwood (L-H) equation, which also covers the adsorption properties of the substrate on the photocatalyst surface [16-18]. Equation 2:

$$r = -dC/dt = (k_r KC)/(1-KC) \quad (2)$$

Where, r represents the rate of reaction that changes with time, C concentration at any time t during degradation (ppm), K equilibrium constant for adsorption of the substrate onto catalyst and k_r limiting rate constant of reaction at maximum coverage under the given experimental conditions. In Equation 2, the constants k_r and K can be calculated from the corresponding integrated expression. When the initial dye concentrations are relatively low, the rate equation is simplified to be a pseudo-first order rate equation with respect to the dye concentration, the term KC << 1 then Equation 2 is reduced to:

$$r = -dC/dt = =k_r KC \quad (3)$$

Integrating Equation 3 with respect to limits: C = C_0 at t = 0 and C = C at t = t, L-H expression reduces to pseudo-first order kinetics and is given by:

$$-\ln C/C_0 = k_{app}\, t \quad (4)$$

$$\text{where } k_{app} = k_r K \text{ and } r = k_{app} \,.\, C \quad (5)$$

Equation 4 shows a pseudo-first order reaction with respect to the dye concentration. The semi-logarithmic graphs in the presence of different catalyst (ZnO and 2w% Gd doped ZnO versus irradiation time loading yield straight lines indicating pseudo-first order reaction. The apparent reaction rate constants (k_{app}) for photocatalytic degradation of RR195 dye (Figure 8) are evaluated from experimental data using a linear regression. In all cases, r (correlation coefficient) values are higher than 0.98, which confirm the proposed kinetics for decolorization of dye in this process. The calculated apparent reaction rate constants (k_{app}) of the photocatalytic degradation of RR195 dye are given in Figure 8 and listed in Table 1. Data in Table 1 shows that the photocatalytic degradation rate of 2w% Gd doped ZnO is much higher when compared with of ZnO.

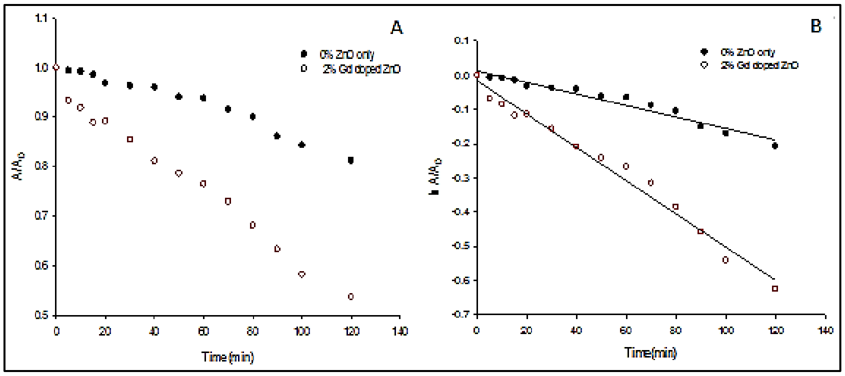

Figure 8: Plot of absorbance vs. time (a) and Kinetics of photodegradation (b) for the photodegradation of RR195 with ZnO and 2w% Gd doped ZnO, [RR195] =10 ppm at pH= 9.0

Table 1: Kinetics of photodegradation of RR195 with ZnO and 2% Gd doped ZnO, [RR195]= 10 ppm at pH= 9.0

Gd%	**RR195**	
	$k_{app}\times 10^3\,min^{-1}$	r
0%	1.1	0.989
2%	4.5	0.997

Effect of pH:

Surfaces of oxides normally having unsaturated oxygen atoms, this possessing bonding deficiency and consequently are affected by basic/acidic environment. This differs depending on the type of atoms and crystal structure of the catalyst. According to this observation the surface of oxide in the reaction mixture would be either positive or negative depending on the abundance of H^+ and/or OH^-. In acidic media the surface of oxide would have a positive charge while exhibits a negative charge under basic media. The surface of the catalyst exhibits a zero net charge of the surface at its point zero charge (PZC), for pH values lower than PZC surface has a positive charge while exhibit a net negative charge at pH values higher than its PZC. Generally PZC value for zinc oxide ranged from pH values (8-10) [10]. Figures 9 and 10 show the Plot of absorbance at λ_{max} (542 nm) vs. time for RR195 with ZnO and 2wt% Gd doped ZnO self-cleaning treated cotton textile, [RR195] = 10 ppm at different pH values. Figures 9 and 10 show that the photocatalytic degradation was increased with increasing the value of pH towards basic values and the best result was obtained around pH= 9 for RR195. The apparent reaction rate constants (k_{app}) for photocatalytic degradation of RR195 dye are evaluated from experimental data using a linear regression analysis. In all cases, r (correlation coefficient) values are higher than 0.98, which confirm the proposed kinetics for decolorization of dye in this process. The calculated apparent reaction rate constants (k_{app}) of the photocatalytic degradation of RR195 dye are listed in Table 2. The efficiency of dye removal was enhanced in basic pH values and reduced in acidic values [10].

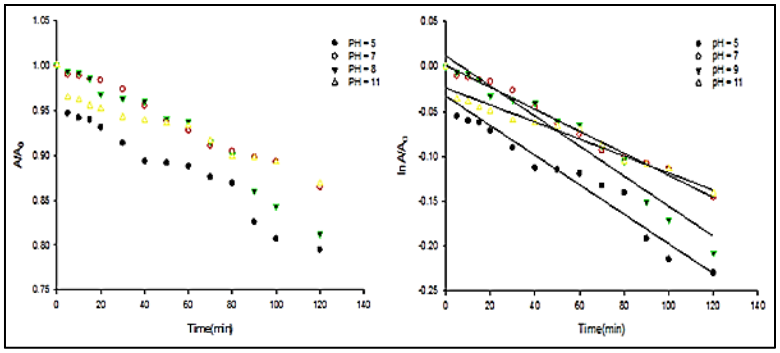

Figure 9: Plot of absorbance vs. time (a) and Kinetics of photodegradation (b) for RR195 with ZnO at different pH values, [RR195] 10 ppm

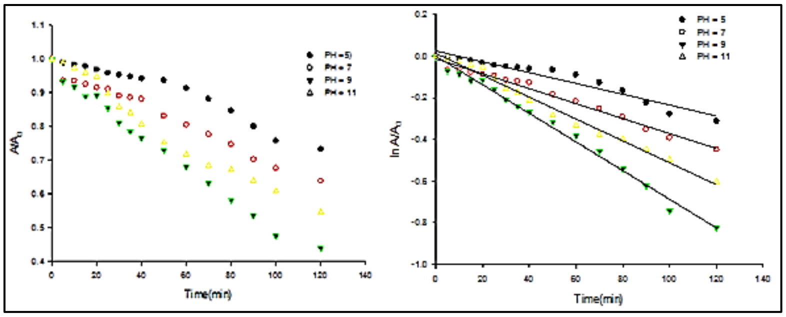

Figure 10: Plot of absorbance vs. time (a) and kinetics of photodegradation (b) for RR195 with 2w% Gd doped ZnO at different pH values. [RR195] 10 ppm

Table 2: Kinetics of photodegradation of RR195 for ZnO and 2wt% Gd doped ZnO at different pH values [RR195] = 10 ppm

pH	**ZnO**		**2w% Gd doped ZnO NPs**	
	k_{app}×10^3 cm^{-1}	**r**	**k_{app} × 10^3 cm^{-1}**	**r**
5	1.5	0.986	2.6	0.939
7	1.2	0.997	3.6	0.994
9	1.7	0.989	6.9	0.998
11	0.9	0.985	5.3	0.997

CONCLUSION

By considering the rate constant for each pH value, it was found that the rate of dye removal was affected considerably with the change in pH value of reaction mixture. The efficiency of dye removal was enhanced at pH values Table 2 that are close to the PZC value and this arises from the surface charge neutralization at these ranges of pH values. This effect can minimize the repulsion forces of molecules on the surface [10].

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