

# Removal of Rhodamine B from Aqueous Solution by ZnO Nanoparticles

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**ABSTRACT:** ZnO nanoparticles are utilized as adsorbent for the removal of different harmful organic and inorganic impurities from water. In this work, the cationic dye Rhodamine B was removed from aqueous solution by adsorption process. The portrayal of prepared ZnO nanoparticles was finished by XRD and PSA. The adsorption of Rhodamine B on the surface of ZnO nanoparticles is subject to pH and contact time. At acidic pH (2) the most extreme evacuation of Rhodamine B was analyzed. The capacity of ZnO nanoparticles to remove Rhodamine B was about 100% at acidic pH. Langmuir and Temkin were utilized as adsorption isotherms to portray the balance adsorption of dye. Pseudo first and second order kinetics were applied to analyze experimental adsorption.

**KEYWORDS:** Rhodamine B, PSA, XRD, ZnO, Langmuir and Temkin isotherm.

## I. INTRODUCTION

The population of the world will become 9 billion till 2050 and demand of fresh water will become more in the future. According to World Health Organization report, 80% of sicknesses are water related to the emerging countries. The diseases generate from wastewater are because of the shortage of water cleaning arrangements. The bacteria (*E. coli*, *salmonella* and *cholera*), parasites and viral pathogens are responsible for approximately 3.3 million deaths [1]. The anthropogenic activities discharge much wastewater with a number of impurities. These impurities include pesticides, fertilizers, heavy metals, dyes, microbes etc. has been identified. These impurities can generate harsh side effects and few of them may be carcinogenic. These contaminants remain either in suspended, colloidal or soluble form, in water and spoil the water. The dyes are used by industries of textile, leather, food, pharmaceuticals, paints, cosmetics and photography. These industries yield extremely colored effluents which cause water pollution. More than 10,000 dyes exist commercially today. The complex structure of dyes creates problems in degradation. Utmost maximum dyes, having synthetic origin and exhibiting multifaceted aromatic molecular structure. Maximum dyes are toxic or carcinogenic for mammals [2, 3]. Numerous cases in many countries are reported about the role of dyes in connection with a variety of skin, lung, and respiratory disorders. Most dyes and chemical compounds cause critical undesirable changes in the water like pH, shading other than chemical oxygen demand (COD). Even a small quantity of dyes can be effortlessly detected and can cause inhibition of photosynthesis. These synthetic dyes are highly stable so the conventional methods become ineffective for the whole color elimination and degradation of dyes. Various methods and technologies include coagulation–flocculation, reverse osmosis, membrane filtration, biological degradation, solvent extraction and electrochemical processes are utilized for the evacuation of dyeing effluent. The high cost of these given methods required alternative methods, which are reliable along with green chemical in nature. These methods for water treatment are nondestructive. By these methods only contamination transfer from one stage to another. Hence a different kind of pollution is faced which calls for further treatment. The chromophoric configuration of dye is

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obliterated by effective oxidizing treatment. But, the whole mineralization of complex dye is not always accomplished by the traditional homogeneous oxidizing managements. So the adsorption has been accepted as a popular method for dye water treatment. Adsorption technique is simple, highly efficient and reusable so it is more applicable [4-7]. Nanomaterials makes revolutionary changes in nanotechnology. Due to attractive physicochemical aspects of nanomaterials they are used for water treatment. These can be profoundly specific and recyclable legends for toxic ions of metals, radionuclides, organic and inorganic solutes/ anions in aqueous solutions. A large number of opportunities or technologies can generate by the application of nanomaterials for water-purification, because they are having enormous surface areas. The different properties of ZnO including optical, electronic and catalytic, are size and shape-dependent. Various methodologies can use for ZnO nanoparticles preparation, including thermal evaporation, spray pyrolysis, homogeneous precipitation, mechanical milling, sol-gel processing, hydrothermal, reflux method, microwave method and mechanochemical synthesis. ZnO is an ecofriendly material which is used as an effective photo-catalyst in practical application which is sensitive to UV light. The chemical reactions are also induced by photo generated electron/hole pairs. The formations of relatively harmless end products represent an additional attractive feature of this procedure [8] [9]. Rhodamine B ( $C_{29}H_{30}ClN_3O_3S$ ) is a synthetic compound of xanthene group containing amino and imino groups which is utilized as a tracer dye inside water to calculate the rate and direction of flow and transport. It is found as a ruddy violet powder and goes under the trade name of D&C Red No. 19. It is hurtful if swallowed by people and creatures, and causes soreness of the skin, eyes and respiratory tract and is widely used in many industrial processes [10]. The Rhodamine b show maximum adsorption at 550-555 nm wavelength [11]. The chemical structure of the dye (Rhodamine B) is shown in figure 2. The shade of colors results from conjugated chains or rings which retain light at a noticeable wavelength [12]. Rhodamine B is extremely soluble in water (50 g/L). However, the solubility in acetic acid solution (30 vol.%) is ~400 g/L. Rhodamine B solutions adsorb to plastics so it is important to keep in glass. So Rhodamine B (dye) was selected for this research work because under 150 gram might be deadly or may deliver genuine harm to the strength of the person. In this work metal ZnO nanoparticles are synthesized by reflux method and used for the removal of Rhodamine B (dye) from aqueous solution.

## II. EXPERIMENTAL WORK

**Materials:** Dye Rhodamine B was purchased from HI media. HCl and NaOH purchased from SD Fine-chem limited. Zinc Acetate (AR) and Hexamethylenetetramine ( $C_6H_{12}N_4$ ) purchased from SRL Pvt Ltd. The chemicals used for this study were of analytical grade without further purification.

**Synthesis of ZnO nanoparticles:** The reflux method with continuous evaporation and condensation process, is used for the preparation of ZnO nanoparticles. In this process, aqueous solutions of 2.19 gm zinc acetate and 0.7 gm HMTA were mixed in 100.0 ml solution, after that solution was placed for continuous stirring and then NaOH was slowly added in this solution until the solution pH became 10. The obtained solution was then refluxed at 90.0°C for 5 h. White precipitates were found which were filtered off. Two times washing with distilled water and one time with ethanol given to the filtrate. The filtered powder dried in electric oven at 50°C.



Figure 1. Powder Zinc Oxide

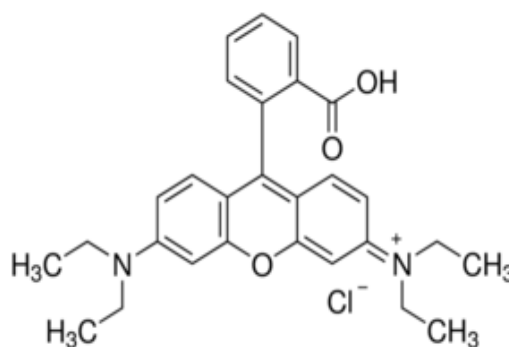


Figure 2. Chemical structure of Rhodamine b

### III. RESULT AND DISCUSSION

**XRD Analysis of ZnO:** The figure 3 exhibiting an x-ray diffraction pattern of zinc oxide prepared by reflux method. The Scherrer formula applied to compute the crystal particle size of the powder. The average particle crystal size of zinc oxide was 205.2456 nm. The peaks at scattering angles (2θ) of 31.88°, 34.52°, 35.84°, 47.72°, 56.96°, 62.24° and 67.52°.

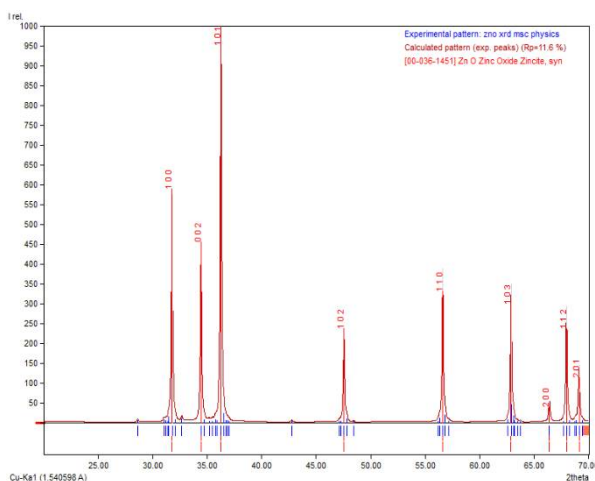


Figure 0 3. XRD analysis of ZnO

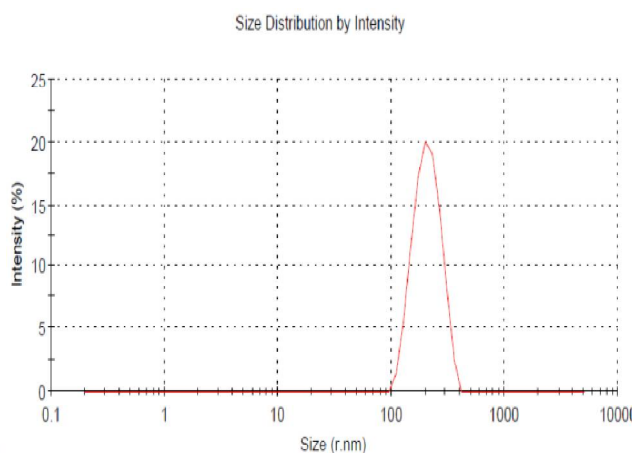


Figure 4. PSA analysis of ZnO

**Particle Size Analysis:** The analyzed particle size of ZnO nanoparticles was 244.5 nm as shown in figure 4 by Malvern Zetasizer Nano ZS90 (Malvern Instrument, India) based on quasi-elastic light scattering. Size measurements of ZnO nanoparticles were achieved in triplicate following a 1/100 (v/v) dilution of the nanoparticles suspension in water Milli-Q at 25°C. Before measurement, the properly sonicated sample was used for characterization. This characterization helped in the rough estimation of particle size of the nanoparticles using dynamic light scattering.

**Adsorption studies:** 0.01 gm of synthesized nanoparticles (ZnO) was added to 10 ml of 0.01 mM Rhodamine B (dye) solution followed by magnetic stirring. Different pH (acidic (2), neutral (7), and basic (12)) were used for adsorption studies. The pH was adjusted with the help of HCl (1N) and NaOH (1N). After equal intervals of time, equivalent sample amount was taken from stirred solution, centrifuged at 6000 rpm for 10 minutes. UV-Visible spectrophotometer was utilized to see the absorbance. Different pH was used for adsorption studies. The fraction degradation was computed from the experiments as follows:

$$\text{Dye removal efficiency (\%)} = \frac{(C_0 - C)}{C_0} \times 100$$

Where, C<sub>0</sub> is initial and C is adsorbance at any time (t) of the dye solution. The relative rate expulsion of dye from aqueous solution is given in table 1.

**Table 1.**

Dye concentration	Nanoparticles Quantity (gm)	pH	Max. Adsorption (%)
1 mM	0.01 gm	2	100
		7	80.95
		12	52.38

As nanoparticles have large surface area, so they have good adsorbing power. This property of nanoparticles was applied to adsorb dye from aqueous solution; it was done by zinc oxide nanoparticles. The uv-visible spectrophotometer gave the confirmation of dye removal from aqueous solution.

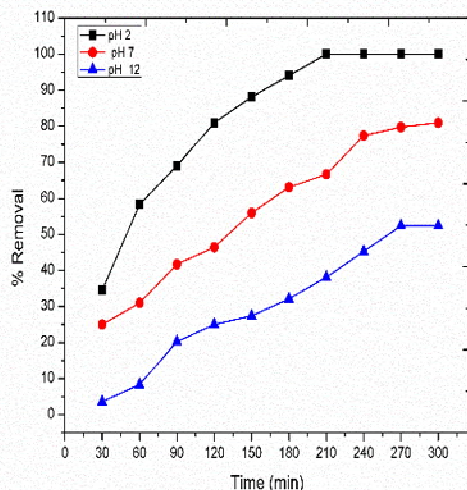


Figure 5. Time vs % removal of Rhodamine B

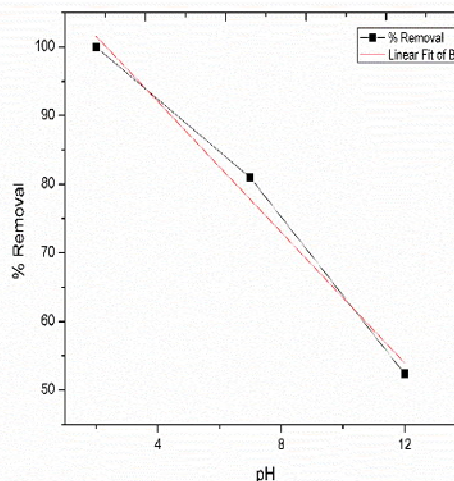


Figure 4. pH vs % removal of Rhodamine B

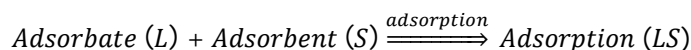
The figure 5 show the comparative % removal of Rhodamine B at acidic, basic and neutral pH with respect to 0.01gm nanoparticles. At acidic pH 100%, at neutral pH 80.95% and at basic pH 52.38% removal of Rhodamine B was done by ZnO nanoparticles. From figure 6, plainly the adsorption is pH subordinate. In this study, we found that the acidic pH produces more effect on adsorption than basic and neutral pH. The pH affects adsorbent (ZnO) by changing its surface charges, degree of ionization of dye, disintegration of functional group of active site and the chemical structure of dye. Stirring also having a direct effect on the dye removal process because without stirring the whole surface of nanoparticles cannot come in contact with dye which reduce the dye removal process.

**Adsorption Isotherms:** The adsorbate (dye) molecules adhere to the surface of adsorbent (nanoparticles) surface. This adsorbate-adsorbent interaction or adsorption phenomenon expressed by adsorption isotherm. Thus, it gives qualitative information about solute surface interaction. In the given work, the experimental data for adsorption isotherm depending upon the measurement of dye removed from the water, were explained by Langmuir and Temkin isotherms. A basic statement is that the active sites of the surface of adsorbate and adsorbent undergoes adsorption. When a dye molecule resides on a site of surface, it does not allow further adsorption because an equilibrium established between dye and nanoparticles. The equation given below, used to calculate adsorption on nanoparticles.

$$q_e = \frac{V(C_0 - C_e)}{M}$$

Where the adsorption capacity is  $q_e$  (mg dye adsorbed onto the mass unit of catalyst, mg/g),  $V$  is the volume of the dye solution (l),  $C_0$  and  $C_e$  (mg/l) are the initial and equilibrium dye concentrations, and  $m$  (g) is the mass of catalyst [13].

**Langmuir Isotherm:** A thin layer of adsorbate (dye) created on the adsorbent (nanoparticles), which is explained by Langmuir isotherm.



The following Langmuir equation was used in this study [14]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}} \times b$$

$C_e$  is final conc. (mg/l),  $q_e$  represents equilibrium conc. (mg/g),  $b$  is the Langmuir constant (L/mg), which is linked to the binding site; and  $q_{max}$  indicate monolayer's theoretical saturation capacity (mg/g). The values of  $q_{max}$  and  $b$  derived from the intercept and slope of the linear plot (Fig. 8) of  $C_e/q_e$  versus  $C_e$ .

**Temkin Isotherm:** The performance of adsorption systems on a heterogeneous surface was explained by Temkin isotherm (Fig. 7) [15] [16]. The fall in heat of sorption get to be direct generally than logarithmic in light of its reliance

on speculation. The atoms existing in the layer go through to adsorbate/adsorbent interactions, which downturn the heat of sorption. A plot of  $q_e$  versus  $\ln(C_e)$  is used to calculate isotherm constants.

$$q_e = \frac{RT}{b(aC_e)}$$

Where  $C_e$  is final conc. (mg/l),  $q_e$  represents equilibrium conc. (mg/g),  $b$  is the Temkin heat sorption constant (KJ/mol), gas constant is  $R$  [0.0083 KJ/(mol K)], Temkin isotherm constant is  $a$  (L/g) and  $T$  the absolute temperature (K). The curve was plotted between  $q_e$  and  $\ln C_e$  and values of both constants 'a' and 'b' were calculated.

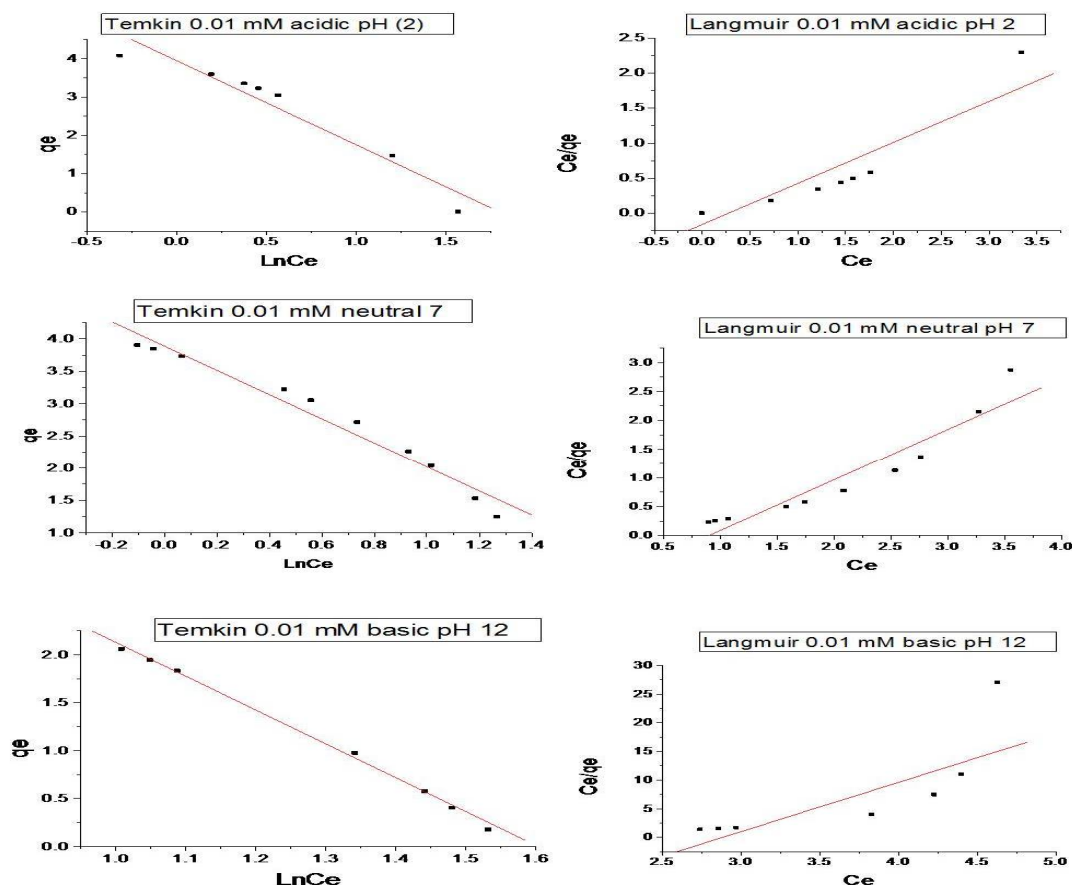


Figure 7. Temkin isotherm analysis of Rhodamine b

Figure 8. Langmuir isotherm analysis of Rhodamine b

**Adsorption Kinetics:** Adsorption of dye on metal oxide surface is impacted by three mass exchange processes which are outside dissemination of dye atoms from the fluid stage to the solid surface, adsorption on solid surface and intra-particle diffusion of dye molecules in the interior of the pores. The adsorption procedure is normally quick instead of inner and outside dissemination. It is surely understood that the adsorption balance is coming to in a few minutes. In any case, the long adsorption balance time proposes that the interior dispersion controls the response rate. Kinetics examination for adsorption procedure can anticipate the rate at which a toxin is expelled from watery arrangements and gives valuable information to comprehend the component of adsorption procedure. A few models are accessible to research the adsorption instrument and portrayal in view of trial information, for example, pseudo-first and second order. The high estimations of  $R^2$  and closeness of trial and hypothetical adsorption limit ( $q_e$ ) esteem demonstrate the appropriateness of the kinetic model in examination of the test information. To understand the exhaustive

characteristics of adsorption, pseudo first and second order kinetics was applied. The pseudo-first-order adsorption rate [17] and pseudo-second-order adsorption rate developed by Ho and McKay [18] have the following linear forms:

Pseudo first order equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Pseudo second order equation:

$$\frac{t}{q_t} = \frac{1}{2K^2 q_e^2} + \frac{t}{q_e}$$

Where  $K^1$  and  $K^2$  are rate constant for adsorption ( $\text{mg g}^{-1} \text{min}^{-1}$ );  $q_e$  is the amount of dye adsorption at equilibrium ( $\text{mg g}^{-1}$ );  $q_t$  is the amount of dye adsorption in time  $t$  ( $\text{min}^{-1}$ ). The pseudo first order curve was plotted between  $\log(q_e - q_t)$  and  $t$  (Figure 9) besides pseudo second order curve was plotted between  $t$  and  $t/q_e$  (Figure 10) and. The computed values of second order kinetics ( $q_e$ ,  $K^1$ ) have been represented.

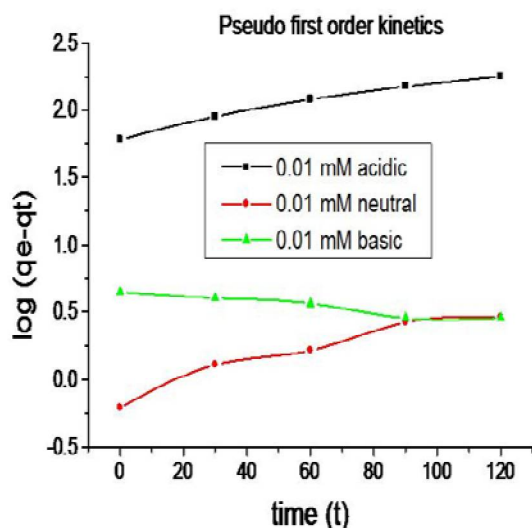


Figure 9. Pseudo first order kinetic model

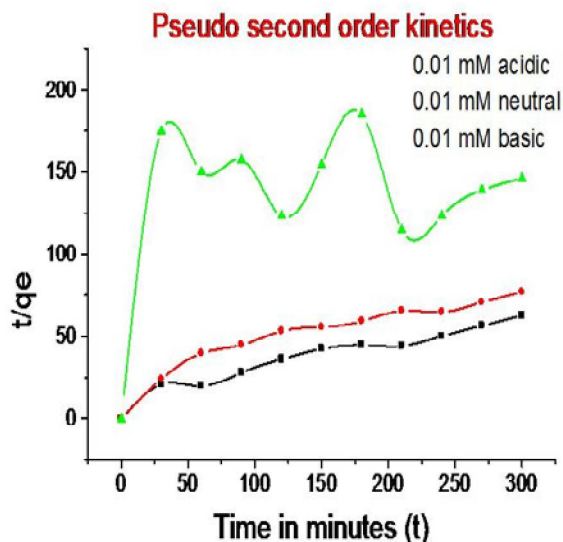


Figure 8. Pseudo second order kinetic model

#### IV. CONCLUSION

The ZnO nanoparticles are promising material for the removal of Rhodamine B (dye). It works efficiently as an adsorbent for the cationic dye Rhodamine B. The current work describes removal efficiency of zinc oxide at different pH (acidic, neutral and basic) of dye. The zinc oxide nanoparticles were synthesized by reflux method. The maximum adsorption capacity of adsorbent (ZnO) was 100% observed at pH 2. The adsorption percentage was also found to be decrease with increase in pH. The parameter such as contact time and pH were examined. The equilibrium adsorption of experimental data gave good fitting in Langmuir and Temkin isotherms. The dynamics of adsorption process was recognize by pseudo first and second order kinetics. Nano ZnO emerged as effective adsorbent for the treatment of dye effluent.

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