Synthesis and Characterization of C/ZnO Nanocomposite: Adsorption Isotherm of a Reactive Green from Aqueous Solutions

Masar Ali Awad[1*], Afaf Murtadha Kadhum[2], Shaimaa Hassan Mallah[3]

Abstract

The study demonstrates that Nanocomposite activated Carbone decorated zinc oxide is indeed viable, cost effective adsorbent materials for the adsorptive removal of Reactive Green (RG) dye from polluted wastewater with over 90% removal dye. The adsorption of RG dye onto decorated carbon ZnO nanoparticle was found to be highly dependent on equilibrium time, initial RG dye concentration, adsorbent mass and. The quantity of RG dye uptake (mgg^{-1}) was found to rise through increase in primary dye concentration. Percent removal of RG dye was found to increase with increase in contact time, adsorbent amount. The data indicated that the model Freundlich gave a better fit to the experimental result than the model Langmuir with high correlation coefficients (R^2 = 0.964). This suggests that multi-layer adsorption occurs which is in agreement with the best applicability of the isotherm Freundlich.

Key Words: Dye, Reactive Green, Isotherm, Removal, Adsorption, Pollution, Kinetic.

DOI Number: 10.14704/nq.2021.19.7.NQ21089 **NeuroQuantology 2021; 19(7):96-102**

Introduction

Water pollution is one of the most important and most dangerous problems facing the environment as a result of the increasing use of pollutants in many industries, especially dyes. It is considered one of the most dangerous pollutants due to its high concentrations in water and the difficulty of removing it. Therefore activated carbon has been used a lot in removing dyes due to its high surface area and cheapness (Pasamontes and Callao 2004; Layth S. Jasim 2018; Aljeboree 2019). Activated carbon is prepared from Available and very cheap materials such as coconut shells, walnut shells, pine shells, date kernels, apricot shells, and others. (Liu, Wang et al.). Various techniques have been used to remove organic dyes from water as ions exchange method, photo degradation, filtration and adsorption. The most important techniques used to remove pollutants from wastewater is the adsorption technique, which is an easy, cheap and inexpensive method. Adsorption is the phenomenon of atoms, molecules or ions sticking to the surface. Adsorption can be an advantageous method over other approaches (filtration, coagulation, ion-exchange, precipitation, osmosis reverse, and oxidative methods), mostly as it is design simple and minimum cost system, in addition to effective towards a wide series of contaminants (Homayoonfal and Mehrnia; Aljeboree 2019; Aljeboree 2019). For this purpose, activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of inorganic and (Y. Peng 2017; Arif Chowdhury 2020).

Corresponding author: Masar Ali Awad
Address: [1*,2,3]Department of Chemistry, College of Science, University of Al-Muthanna, Iraq.
[1*]E-mail: masarawad@gmail.com
Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Received: 15 May 2021 **Accepted:** 19 June 2021

In this study, zinc oxide was loaded on activated carbon and many techniques were measured to determine the identity of the prepared surface, and many influencing factors were applied such as the effect of concentration, weight, ionic strength and acidity function.

Method and Materials

Preparation of Activated Carbon

AC utilized in this study was prepared from waste Palm leaf. The impurities in the waste Palm leaf were removed via washing by D.W and subsequently dry at 75 °C for 3 h. The obtained Palm leaf was then crushed using electric pulverize and sieved with mesh sieve. The sieved Palm leaf precursor was carbonized in a muffle furnace at a temperature of 300 °C for 2 h and allowed to cool. The carbonized Palm leaf (150g) was soaked in a 150 ml of HNO3 solution for 2h at activation weight ratio of 1:1 g activator to precursor. The impregnated samples, Palm leaf activated carbon (AC) was then washed with D.W several times to obtain activated carbon of almost neutral pH (6.2-7.0) and subsequently dried in an electric oven, at 85 °C for 3 hours. Finally, the sample was stored in a tightly closed container.

Preparation of C Decorated (Zinc Oxide /Nanocomposite)

Nanocomposite (C decorated/ Zinc Oxide) were prepared by using hydrothermal process 5 g of Zinc Acetate, 5 g of Oxalic Acid and 0.5 g of AC, were maxed. then complete to 100mL with distilled water then mixed for one hour to get slurry solution. The resultant mixtures were kept at 160°C for 24 hr in an autoclave. The obtained dark brown precipitate was filtered, washed with distilled water then sonicated in10 min. intervals then dried at 90°C for 24 hr to get a fine powder.

Materials and Methods

A stock solution (1000 mgL^{-1}) of the preparing of Reactive Green dye by mixing (0.1 g) as an appropriate amount of RG in (1000ml) D.W, The law Beer's find to hold over the 1–10 mg/L of concentration RG was studied. Fig. 1. presents a linear analysis regression of information attained from calibration curve of the RG utilized from the relation A=a +bc, where A is the absorbance at the related peak in a quartz cell (b)1.0 cm and a are the slope and the intercept of the calibration curve and C is the conc. of RG (mg/L).

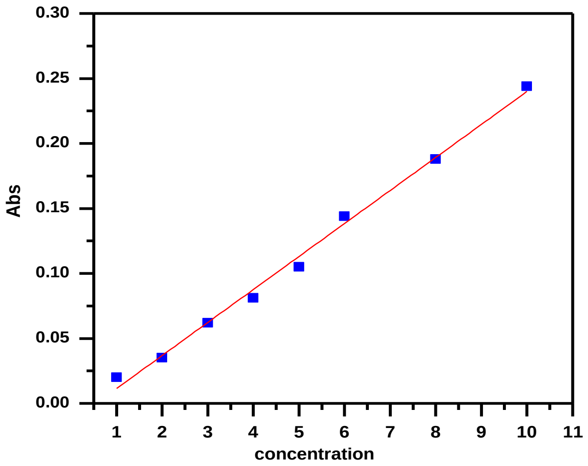

Figure 1. Calibration curve for the Reactive Green dye

Adsorption Studies

Introductory information gets it by batch adsorption studies to beneficial in pick out the optimum concentration, equilibrium time, Weight of nanocomposite, ionic strength, and solution pH.to get it best removal efficiency, all tests are carried out in many sets. Each set contains 0.05 gm of composite in different stoppered conical flasks, to each flasks 100ml from freshly prepared GR dye solution of primary concentration (100) mg/L. The shaking Incubator used the shaking samples at 160 RMP at 1h min. then separated by centrifugation at 6000 rpm for 10 min. and the solutions you obtained reading by, UV-Visible spectrophotometer PC 1800 at λ_{max} = 630 nm and used the following equation to determined adsorption capacity at equilibrium:

$$E\% = \frac{Co - Ce}{Co} * 100 \qquad (1)$$

$$Qe = \frac{Co - Ce}{W} * V \qquad (2)$$

Co (mg L^{-1}) the primary conc. of RG dye and Ce (mg L^{-1}) is equilibrium conc. the RG dye at time t (minute), W (gm) is the mass of adsorbent V (L) is volume of RG dye solution.

Results and Discussion

Characterization of Decorated Carbon ZnO Nanoparticle

Figure 2 appear the infrared spectra of decorated C/ ZnO nanoparticle within a series about 400-4000 cm-1, The FTIR spectra of the decorated C/ ZnO nanoparticle as appear in figure 2 for nanocomposite, the series (3500-3200) cm^{-1}, wide absorption that indicate overlapping among the O-Hand N-H peaks, The C = O, found in nanocomposite, has appear peaks of absorption within the series (1620-1740) cm-1and the choice (480-800) cm-1, the absorption peaks appear that the bonds C-N,C-C and C-O. but the FT-IR for nanocomposite showed the shift of the groups bands reveals the interactions among the C=O groups on AC/ZnO nanoparticles(Ahmad 2017; Fabryanty, Valencia et al. 2017).

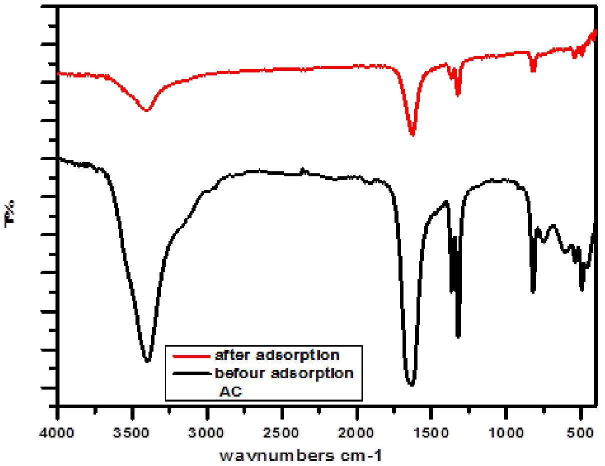

Figure 2. FTIR spectrum of- decorated C/ ZnO nanoparticle before and after adsorption dye

Using FE-SEM analysis shown that decorated C/ ZnO nanoparticle has a smooth surface. The surface contains several layers those are compacted on top of each other via Vander Walls force and the cross-linking agent. After the adsorption the surface is shown to be bumpy. The bumps on the surface, mostly from RG dye (Layth S. Jasim 2021) (Figure 3).

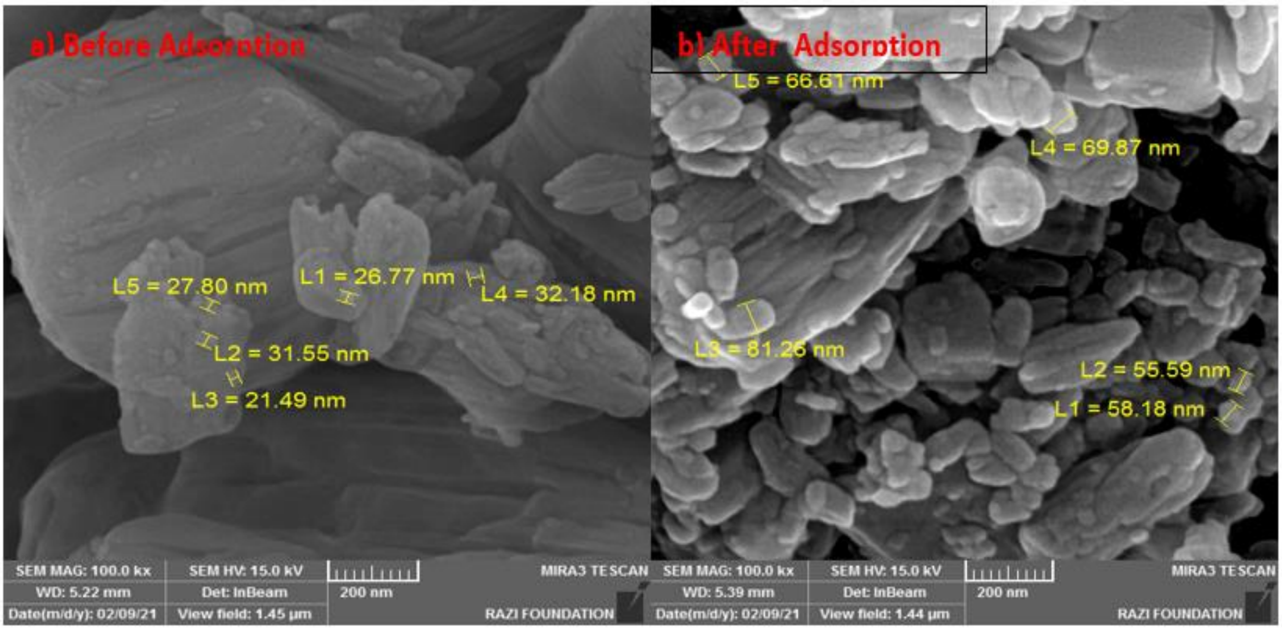

Figure 3. FESEM image of decorated C/ ZnO nanoparticle (a) before and (b) Reactive Green after adsorption

As appear in Figure 4. From the curve TGA (weight W vs temperature T plots) study stability of the thermal was prepared composite, the sample were heated under atmosphere with a rate of 100C min-1 about 41-600 0C, that heating the nanocomposite a mass loss of up to 46.272 % in the series of 374.10-436.23 0C due to the presence of moisture, next the loses composite 49.80% of its mass within the thermal series 441-5870C that due to the thermal breaking of the interlocking polymeric chains of the nanocomposite as appear in Figure (4) (Abbas N. Karim 2019).

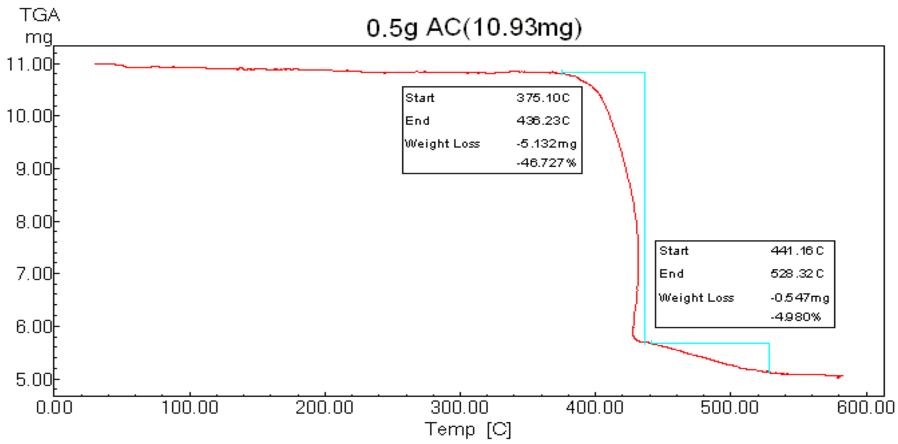

Figure 4. Analysis TGA of decorated C/ ZnO nanoparticle

The surface of morphology of decorated C/ZnO nanoparticle were investigated via utilizing TEM morphology surface analysis before and after adsorption; was clear from Figure (5) it is obviously seen that the Architecture-like nano structure is collected of numerous single-crystal Nano plates and the disordered wormhole-like pores is observed in the midst of particles, indicating the formation of structure mesoporous.

Fig. 5(a) shows images TEM of ZnO/AC before adsorption. nanocomposite s were spherical in shape with average size of 30 nm (Fig. 4b). images TEM of ZnO/AC after adsorption appear fine dispersion of black particles TEM studies were in best agreement with analysis FE-SEM (H.M. Xiong 2008; X. Zhou 2009; Y. Guo 2009).

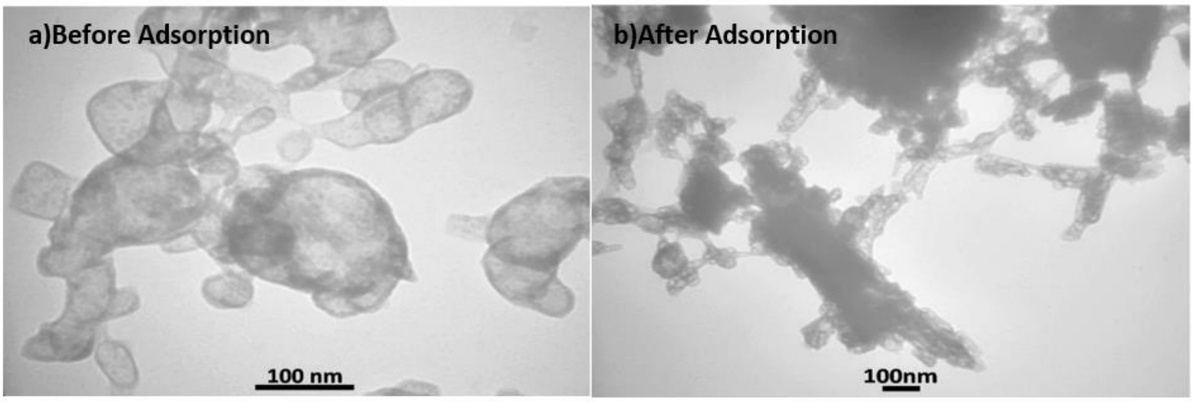

Figure 5. TEM image of AC/ZnO (a) before and (b) ZnO/AC after absorption

BET

Isothermal of nitrogen adsorption system was used to assess the surface area and pore structure of AC/ZnO Figure (3) depicts the isotherms adsorption-desorption as well as the pore size distributions of decorated C/ ZnO nanoparticle. The surface area, average pore diameter, and total pore volume were increased (Table 1). well-developed pores can be seen clearly in the surface morphology of decorated C/ ZnO nanoparticle**,** indicating that surface area and pore volume (Ghorai 2013).

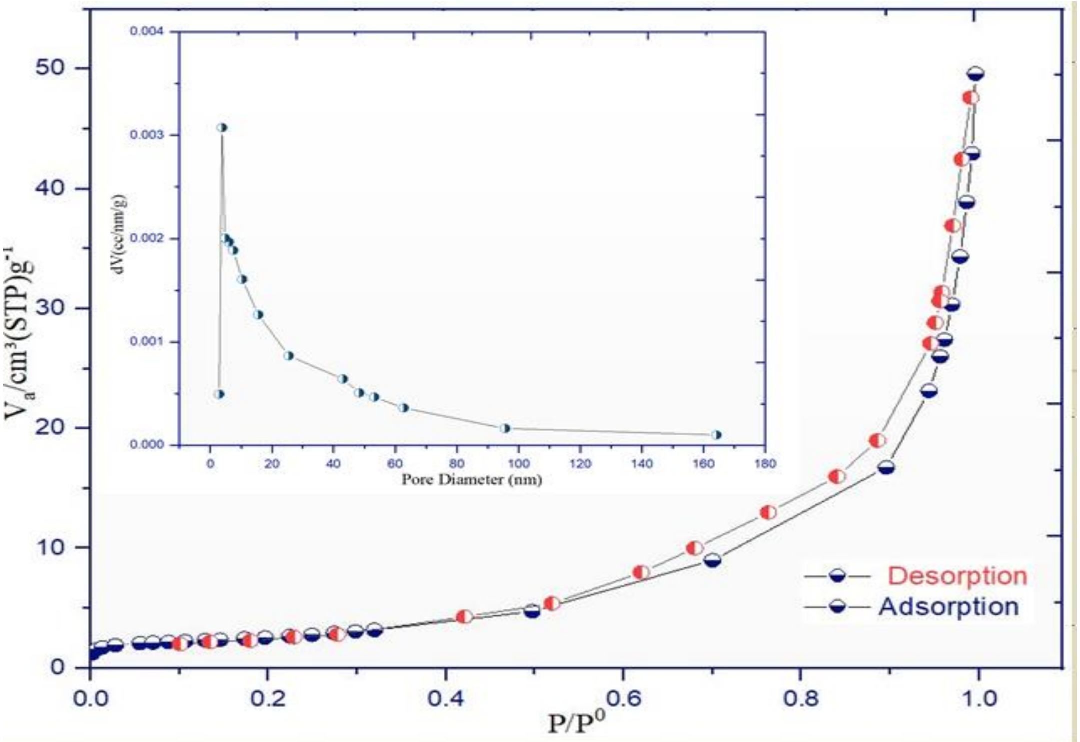

Figure 6. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curve of CNT/ZnO nanocomposite

Effect of Weight Adsorbent

Initial adsorbent quantity requires proper choice because it controls adsorption by obtainable surface area and binding sites. The influence of decorated C/ ZnO nanoparticle weight on Reactive Green RG dye adsorption at equilibrium time of 1 h was studied via varying the adsorbent mass from 0.003 to 0.15 gm in a 50 mg. L^{-1} RG solution. The effect of adsorbent mass is appear in Fig 6. (Aljeboree 2019; Aljeboree 2020)The data exhibit that removal and adsorption efficiency appear inverse relationship by adsorbent mass. Increase the surface area related with adsorbent amount enhancement the removal percentage of the RG and rise the number of adsorption sites obtainable from adsorption as reported previously. The increase of RG dye with decorated C/ ZnO nanoparticle amount due to the more binding active sites for adsorption and decrease adsorption capacity cases the adsorption active places stay unsaturated through reaction of the adsorption active site increases via means of increasing the amount decorated C/ ZnO nanoparticle (Basam W. Mahde 2018).

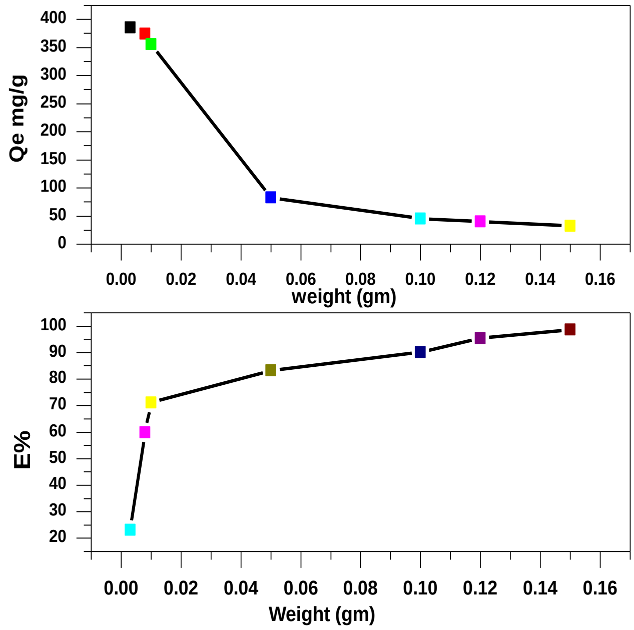

Figure 7. Effect of decorated C/ ZnO nanoparticle weight for Reactive Green dye Adsorption

Effect of Solution pH

An significant role in the adsorption method played via solution of pH particularly on the adsorption capacity. The charge surface of the adsorbent and the degree of the ionization of several contaminants can be affected via of solution pH. The influence of solution pH on the dye adsorption capacities of the decorated C/ ZnO nanoparticle was studied at varying pH (3-10) with 50mg/L fixed primary concentration of RG and mass 0.1g for 1hr Fig. 8 appear that the adsorption efficiency of RG rises through increasing the acidic from 3 to 6 and decrease when pH solution reach to above 6. The best adsorption efficiency of decorated C/ ZnO nanoparticle at pH 6was 48.2 mg/g. It is well-known the decorated C/ ZnO nanoparticle have carboxylic and hydroxyl groups after purification way via acid handling. The change in pH solution will influence on the status ionization of these functional groups(Febelyn Reguyal 2018; Ghaedi 2012).

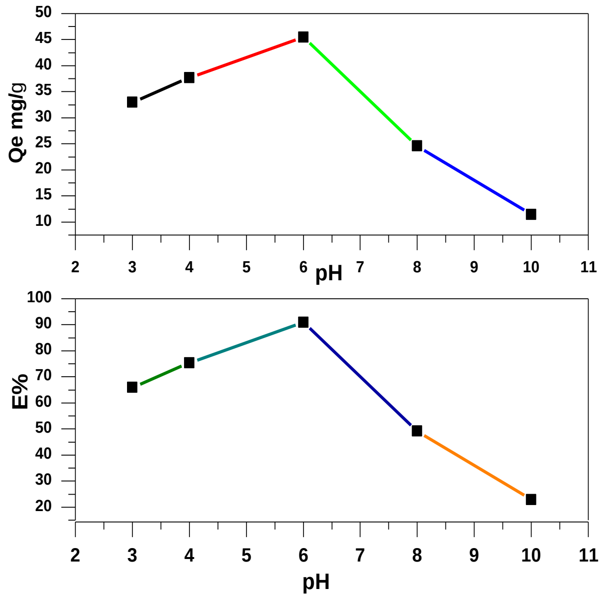

Figure 8. Effect of solution pH on Adsorption on Reactive Green on decorated C/ ZnO nanoparticle at 20°C, 1hr and 0.1g in (50 mg/L) 100 mL water.

Adsorption Models

To study the parameter dependence of the removal capacity, two model were analyzed, including model Langmuer and model Freundlech. The models imitation using an iterative procedure founded on a linear least squares algorithm. The model Langmuer isotherm equation,: (I. Langmuir 1916; I. Langmuir 1918)

$$q_e = \frac{q_0 K_L C_e}{1+K_L C_e} \qquad (3)$$

where qe, application at equilibrium (mg /g), K_L Langimuir constant (L mg^{-1}), q_o the mono-layer adsorption capacity (mg /g) and Ce the concentration equilibrium solution (mg L^{-1}). equation of the Freundleich is related for multi component adsorption. The Freundleich model is expressed through (Y.S. Ho 2002; M. Özacar 2003):

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where) K_f : Empirical constant Freundlich (L.g^{-1}) and n is the Freundlech exponent. The data of this isotherm are look in Fig. (9), and Langmueir constants are shown in Table (1).

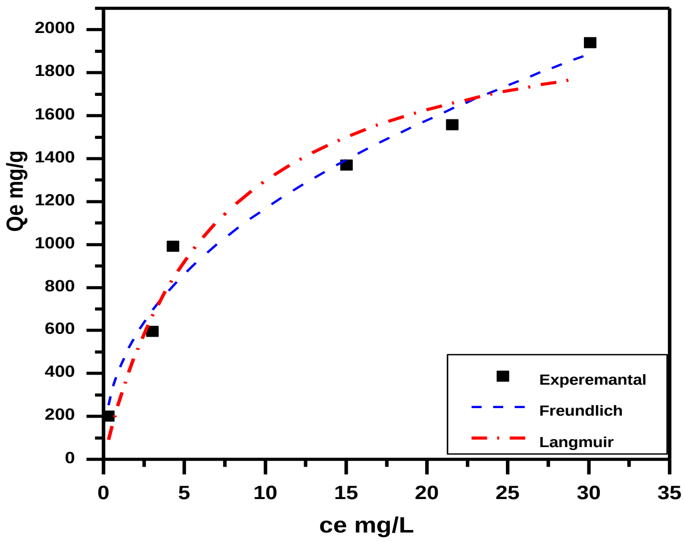

Figure 9. Several adsorption models nonlinear fit of adsorption RG dye on (decorated C/ ZnO nanoparticle

Table 1. The correlation coefficients and constants of model of Langmuir and Friendlich of adsorption Reactive Green dye adsorbed on decorated C/ ZnO nanoparticle at 20 oC

Langmuir equation			Freundlich equation		
K_L	qm	R^2	K_F	n	R^2
0.145	218.633	0.9435	927.63	0.436	0.9663

Conclusion

Most of adsorption factors as dye concentration, solution pH, equilibrium time and adsorbent amount have the effect of dye removal utilizing decorated C/ZnO nanoparticle The optimum conditions to achieved great adsorption efficiency at room temperature were contact time 1h, agitation speed 250 rpm and amount of (0.05 gm) decorated C/ZnO nanoparticle**.** The better removal capacity of RG dye was achieved on neutral medium which is useful on applied scale. It was concluded from these data that decorated C/ZnO nanoparticle can be considered as greatly effective adsorbent of RG dye percentage removal from waste water and can be reused which has economic viability.

References

Karim AN, Jasim LS. Synthesis and Characterization of Poly (CH/AA-co-AM) Composite: Adsorption and Thermodynamic Studies of Benzocaine on from Aqueous Solutions. *International Journal of Drug Delivery Technology* 2019; 9(4): 558-562.

Ahmad A, Razali MH, Mamat M, Mehamod FSB, Amin KAM. Adsorption of methyl orange by synthesized and functionalized-CNTs with 3-aminopropyltriethoxysilane loaded TiO2 nanocomposites. *Chemosphere* 2017; 168: 474-482.

Aljeboree AM. Adsorption and removal of pharmaceutical riboflavin (RF) by rice husks activated carbon. *International Journal of Pharmaceutical Research* 2019; 11(2): 255-261.

Aljeboree AM. Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals from Aqueous Systems by ZnO. *International Journal of Drug Delivery Technology* 2019; 9(2): 125-129.

Aljeboree AM. Spectrophotometric and Colorimetric Determination of Pharmaceutical by Oxidative Coupling Reaction: A Review. *Systematic Reviews in Pharmacy* 2020; 11(4): 609-615.

Aljeboree AM, Abbas AS. Removal of Pharmaceutical (Paracetamol) by using CNT/ TiO2 Nanoparticles. *Journal of Global Pharma Technology* 2019; 11(1): 199-205.

Chowdhury A, Kumari S, Khan AA, Chandra MR, Hussain S. Activated carbon loaded with Ni-Co-S nanoparticle for superior adsorption capacity of antibiotics and dye from wastewater: kinetics and isotherms. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2021; 611: 125868. https://doi.org/10.1016/j.colsurfa.2020.125868.

Mahde BW, Radia ND, Jasim LS, Jamel HO. Synthesis and characterization of polyacrylamide hydrogel for the controlled release of aspirin. *Journal of Pharmaceutical Sciences and Research* 2018; 10(11): 2850-2854.

Fabryanty R, Valencia C, Soetaredjo FE, Putro JN, Santoso SP, Kurniawan A, Ismadji S. Removal of crystal violet dye by adsorption using bentonite–alginate composite. *Journal of Environmental Chemical Engineering* 2017; 5(6): 5677-5687.

Reguyal F, Sarmah AK. Adsorption of sulfamethoxazole by magnetic biochar: effects of pH, ionic strength, natural organic matter and 17α-ethinylestradiol. *Science of the Total Environment* 2018; 628: 722-730.

Ghaedi M, Sadeghian B, Pebdani AA, Sahraei R, Daneshfar A, Duran CELAL. Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. *Chemical Engineering Journal* 2012; 187; 133-141.

Ghorai S, Sarkar AK, Panda AB, Pal S. Effective removal of Congo red dye from aqueous solution using modified xanthan gum/silica hybrid nanocomposite as adsorbent. *Bioresource technology* 2013; 144: 485-491.

Xiong HM, Xu Y, Ren QG, Xia YY. Stable aqueous ZnO@ polymer core−shell nanoparticles with tunable photoluminescence and their application in cell imaging. *Journal of the American Chemical Society* 2008; 130(24): 7522-7523.

Homayoonfal M, Mehrnia MR. Amoxicillin separation from pharmaceutical solution by pH sensitive nanofiltration membranes. *Separation and Purification Technology* 2014; 130: 74-83.

Langmuir I. The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American chemical society* 1916; 38(11): 2221-2295.

Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society* 1918; 40(9): 1361-1403.

Layth S, Jasim AMA. Removal of Heavy Metals by Using Chitosan/Poly (Acryl Amide-Acrylic Acid) Hydrogels: Characterization and Kinetic Study. *NeuroQuantology* 2021; 19(2): 31-37.

Jasim LS, Radhy ND, Jamel HO. Synthesis and Characterization of Poly (Acryl Amide-Maleic Acid) Hydrogel: Adsorption Kinetics of a Malachite Green from Aqueous Solutions. *Eurasian Journal of Analytical Chemistry* 2018; 13(1b): em74.

Liu Y, Wang F, Chen X, Zhang J, Gao B. Cellular responses and biodegradation of amoxicillin in Microcystis aeruginosa at different nitrogen levels. *Ecotoxicology and environmental safety* 2015; 111: 138-145.

Özacar M, Şengil İA. Adsorption of reactive dyes on calcined alunite from aqueous solutions. *Journal of hazardous materials* 2003; 98(1-3): 211-224.

Pasamontes A, Callao MP. Determination of amoxicillin in pharmaceuticals using sequential injection analysis and multivariate curve resolution. *Analytica chimica acta* 2004; 515(1): 159-165.

Zhou X, Li Y, Peng T, Xie W, Zhao X. Synthesis, characterization and its visible-light-induced photocatalytic property of carbon doped ZnO. *Materials Letters* 2009; 63(20): 1747-1749.

Guo Y, Wang H, He C, Qiu L, Cao X. Uniform carbon-coated ZnO nanorods: microwave-assisted preparation, cytotoxicity, and photocatalytic activity. *Langmuir* 2009; 25(8): 4678-4684.

Peng Y, Liu M, Chen X, Yuan H, Zhao J. Surface-enhanced Raman spectroscopy coupled with gold nanoparticles for rapid detection of amoxicillin residues in duck meat. *Spectroscopy Letters* 2017; 50(10): 579-584.

Ho YJ, Eichendorff J, Schwarting RK. Individual response profiles of male Wistar rats in animal models for anxiety and depression. *Behavioural Brain Research* 2002; 136(1): 1-12.

Cai X, Lin W, Liang C, Fan Y. The role and immune mechanism of brain-derived neurotrophic factor in the development of rat bone tumor pain. *NeuroQuantology* 2018; 16(6): 49-53.