Removal of Congo Red Dye From Aqueous Solution Using Eco-Friendly Adsorbent of Nanosilica

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Abstract:

The development of a new, cheap, efficient, and ecofriendly adsorbents has become an important demand for the treatment of waste water, so nano silica is considered a good choice. A sample of nanosilica (NS) was prepared from sodium silicate as precursor and the nonionic surfactant Tween 20 as a template. The prepared sample was characterized using various characterization techniques such as FT-IR, AFM, SEM and EDX analysis. The spectrum of FTIR confirms the presence of silica in the sample, while SEM analysis of sample shows nanostructures with pore ranging (2-100nm).

The adsorptive properties of this sample were studied by removing Congo red dye (CR) from aqueous solution. Batch experimental methods were carried out at room temperature (25^0C) to study the different variables which affect the adsorption process like: NS amount, initial concentration of CR, and contact time. The results were 0.2 g of NS/50 ml of dye solution and 60 min contact time to reach equilibrium. The experimental results at equilibrium were analyzed using Langmuir and Freundlich adsorption isotherms and showed the best fitted with Freundlich model which reveal heterogeneity of the surface of NS adsorbent. Kinetics aspects were also investigated by evaluating parameters from pseudo- first and pseudo-second order reaction equations on adsorption rate which show good fitting with both kinetics equations, but pseudo-second order equation was the best to describe the kinetics parameters.

Key words: Congo red, Freundlich model, Langmuir model, Nanosilica, Sodium silicate, Tween 20.

Introduction:

Nanotechnology refers to materials which have dimensions less than 100 nm. This technology has rapidly improved with the development of industrial, commercial and agricultural fields as well as with the improvement in the pharmaceutical and medicine science.

Nanosilica, a new product of nanotechnology, is one of the pozzolanic materials which have high surface area and low density. Recently, researchers have paid a great attention to this type of materials because it is easy to prepare, has low toxicity, and can be used in a wide range of applications such as: an additive for plastic and rubber, in modified magnetic materials, removal of pollutants, oil recovery, cement enforcement and many other applications (1-5).

Nanotechnology is preferred in the area of water purification because it offers the possibility of an efficient method for water treatment and removal of pollutants and germs from wastewater.

Contamination of water resources to dye pollutants is considered as an environmental important problem. Thousands of types of dyes have been used in various fields such as the textiles, paper, printing, paints, plastics, cosmetics and leather industries, and food technology industries (6). These dyes are carcinogenic in nature and contaminate the surface and ground water, thereby, making it unfit for irrigation and drinking.

Many treatment techniques have been used for removing dyes from aqueous solution like photodegradation (7) membrane filtration (8), ion exchange (9), electrochemical and adsorption processes (10). Due to its high efficiency, low cost and simple to operate, adsorption is considered an attractive treatment to remove dyes from water.

An acidic dye Congo red (CR) is an azo dye, high soluble in water and organic solvents forming aggregations like micelles. High stability of its chemical structure, Fig. 1, makes it difficult to

biodegrade and photodegrade and hence many organisms were affected by carcinogenic properties and chemical toxicity of this dye. CR dye is used in textile and paper industry due to its ability to change color and high affinity toward cellulose fibers (11).
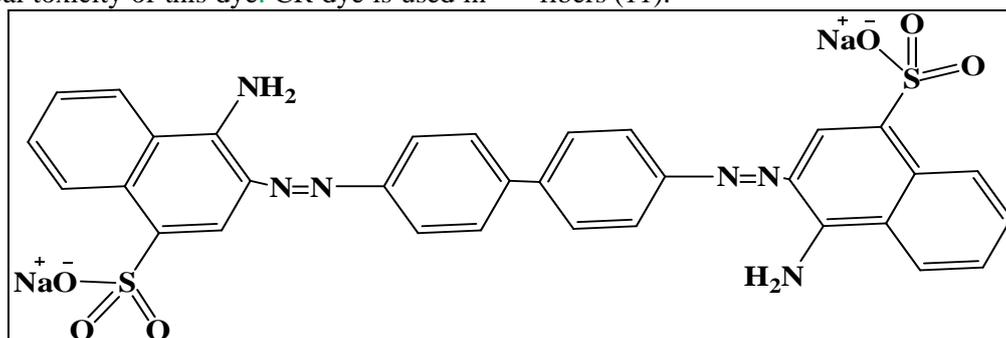

Figure1. Chemical formula of CR Dye

Although many treatment processes were adopted to remove Congo red from solutions, few studies have used cheap, clean, and ecofriendly adsorbents such nanosilica . Farias et al. (12) investigated the recovering of Congo red dye from aqueous solution using amino-functionalized silica gel as an adsorbent. Their data of equilibrium adsorption were analyzed using many adsorption isotherms, but Langmuir isotherms show the best fitting, while Kinetic data will give good fitting with pseudo-second order. The effect of temperature on adsorption process also strongly influences the adsorption of CR dye onto amino-functionalized silica. Jiajin and coworkers (13) synthesized the composite of ZnO/SiO_2 nanosphere to study its ability for removing Congo red dye from wastewater solution. The adsorption kinetic data fitted well with the Pseudo-second-order rate equation and equilibrium data was described by Langmuir adsorption isotherm which gives the best correlation coefficients.

In this work, a new sample of nanosilica was prepared, characterized and utilized to study the effective behavior of adsorption of Congo red dye from aqueous solution. Different variables such as nanosilica dosage, contact time and effect of initial concentration of CR dye were examined to achieve the best conditions of the adsorption process.

Materials and Methods:
Materials
Sodium silicate (14% NaOH, 27% SiO_2) was purchased from local market, Tween 20 was supplied by Sigma Chemical Co. Congo red dye ($C_{32}H_{22}N_6Na_2O_6S_2$) MW = 696.67 g mol^{-1} and HCl (36%) were supplied by BDH Chemicals LTD.

Instrumentals
Fourier Transform Infrared Spectrophotometer (FT-IR) : SHIMADZU (IR-PRESTIGE 21).

Scanning electron microscope (SEM) : Bruker Nano GmbH, Germany.
Atomic Force Microscopy (AFM) SPM-AA 3000, Advanced Angestrum Inc., USA.

Synthesis Procedure of nanosilica
The preparation of nanosilica has been performed using the following procedure: 1g of Tween 20 surfactant was dissolved in 25 mL of deionized water mix with the solution of 1g of sodium silicate also dissolved in 25 mL of deionized water. To the resulting mixture, 15 mL of (36%) HCl was added drop by drop until reaching pH 5. The white precipitate was formed spontaneously and then it was recovered by filtration, washed, aging for three days, dried at 100°C and finally the sample was calcined at 600^{0}C to remove the remaining surfactant.

Adsorption Procedure
Series of Cong red dye concentrations (5-50 mg/L) were prepared from stock solution (1000 ppm) and the calibration curve was established at λ_{max} = 497 nm. Adsorption experiments were duplicated and carried out by taking 50 mL from each concentration of Congo red (5-40 mg/L) in 250 mL conical flask with 0.2 g of nanosilica and placed in a thermostatic shaker water bath (Julabo SW23) at 25^{0}C. Every 10 min interval, 5mL from each flask was withdrawn and filtered to measure the absorbance of dye at the maximum wavelength 497nm. The average of the results was taken to calculate the concentration of Congo red in all experiments. The amount of dye adsorbed at equilibrium q_e (mg/g) was determined according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad \ldots\ldots\ldots(1)$$

Where C_0 and C_e are the concentration of Congo red (mg/L) at initial and at equilibrium stage respectively, V is the volume of solution (L), w is the weight of nanosilica (g).

Results and Discussion:
Characterization of Nanosilica Sample

The sample of prepared nanosilica which shows band at 3425 cm^{-1} represents stretching vibrations of adsorbed water and potentially surface hydroxyl groups. The band at 1631 cm^{-1} is assigned to O-H bending vibrations of the adsorbed water molecules as shown in Fig.2. Typical strong absorption bands for anti symmetric and symmetric Si-O-Si stretching vibrations are centered at 1080 and 806 cm^{-1} respectively. The presence of band at 455 cm^{-1} is assigned to symmetric Si-O-Si vibrations. The band at 952 cm^{-1} corresponds to Si-OH stretching vibrations of the surface silanols, which are the characteristics of silica [14].

Elemental analysis of the surface of the nanosilica was adopted using dispersive X-ray spectroscopy EDX associated with electron microscopy to study the microscopic morphological characteristics and elemental composition of the sample. The result of EDX analysis Fig.3 confirms the presence of oxygen, silicon and small amount of carbon and shows that the precipitated silica contains 66.3wt % of silicon. It can be confirmed from EDX analysis that the sample contains more than 99% purity of silica with free silicon.

The surface microstructure of nanosilica was studied with scanning electron microscope (SEM) which provides the information about the size and shape of the particle and pore. The SEM photographs of nanosilica are shown in Fig. 4 and reveal that the sample consists of small and big grain. However, the sample prepared with Tween 20 show nanostructures with deep pores ranging from (2-100nm).

Atomic force microscopy (AFM) was utilized to confirm the surface morphology and to determine the particle size of the prepared sample. The image of AFM analysis is shown in Fig. 5, so the diameter of the particles was in the range of (20-120 nm) and the average particle size was 88.41 nm. We can conclude that a high regularity of the surface of sample reflects real surface organization characteristic of this sample [15].
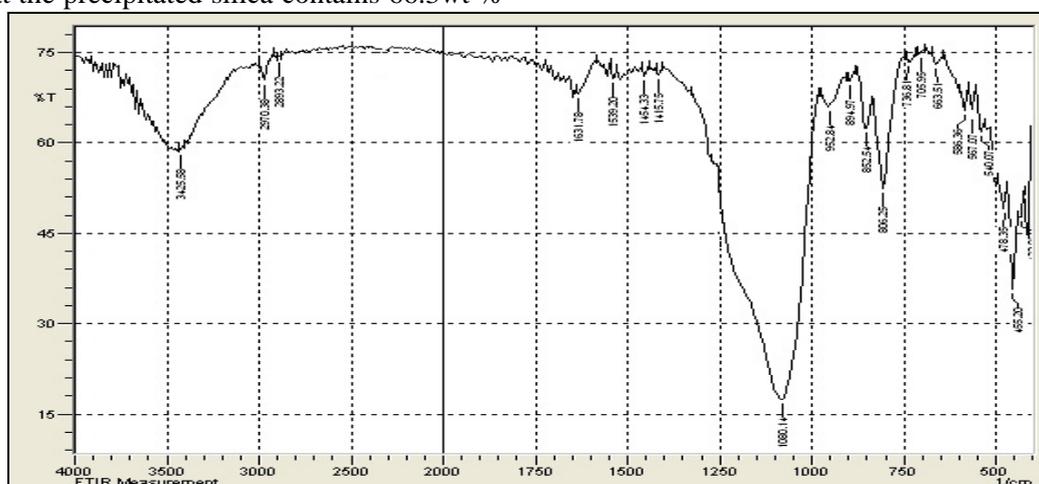

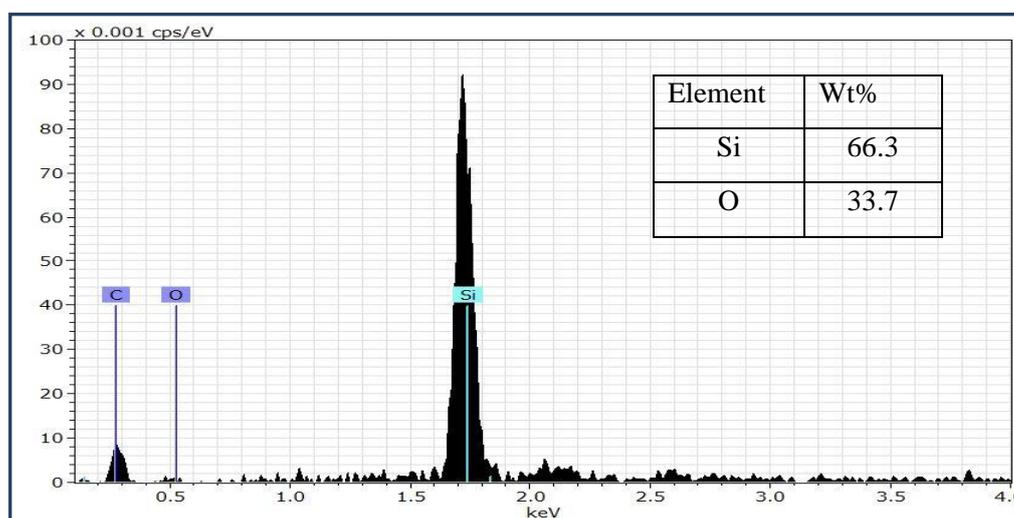**Figure2. FT-IR of Nanosilica sample**

Element	Wt%
Si	66.3
O	33.7

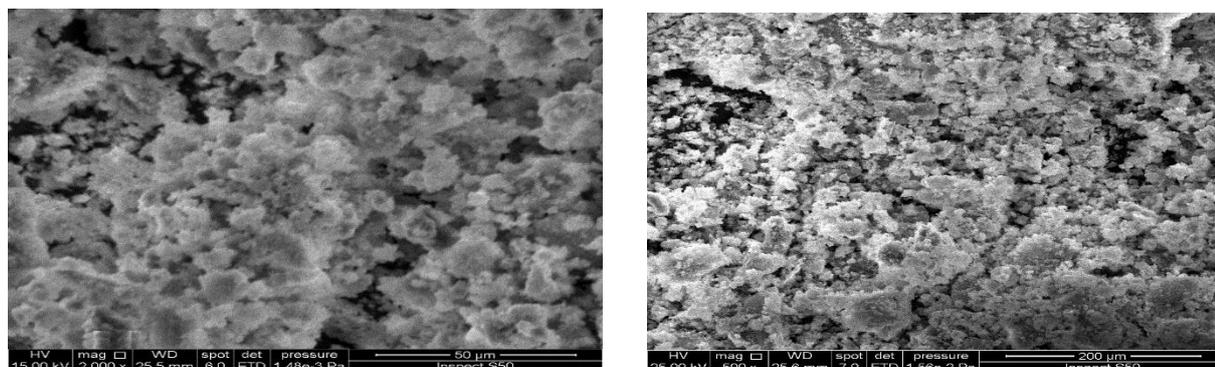**Figure3. EDX pattern of nanosilica sample**

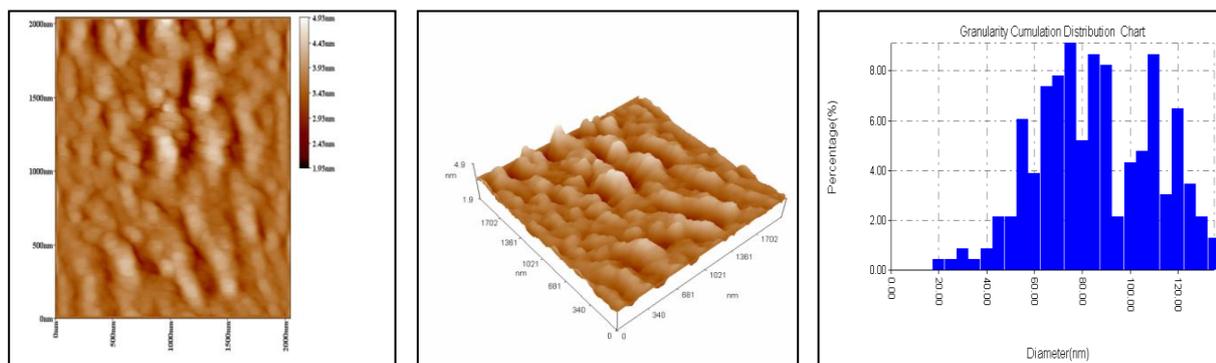**Figure4. Scanning electron microphotographs of Nanosilica sample**

Figure5. AFM images and granularity cumulating distribution of nanosilica.

Adsorption Study
Effect of Nanosilica dosage

In order to study the effect of adsorbent dosage on adsorption process, different amount of nanosilica (0.05, 0.1, 0.15, 0.2 and 0.25 g) per 50 mL of solution were examined at 25^0C and 25mg/L as initial concentration of dye. The percentage removal of CR dye was calculated according the following equation:

$$\% \ Removal = \frac{C_0 - C_e}{C_0} x \ 100 \ ... ... (2)$$

Figure 6 shows the results of dye removal and reveals that the amount of Congo red adsorbed increased with increasing the adsorbent dosage and reached a maximum value at 0.2 g /50 ml of solution. When the dosage was 0.25 g of nanosilica, decreasing in the percentage removal of CR was noticed. This is may be due to increase the adsorption sites which leads to the unsaturation of these sites during adsorption process (16).
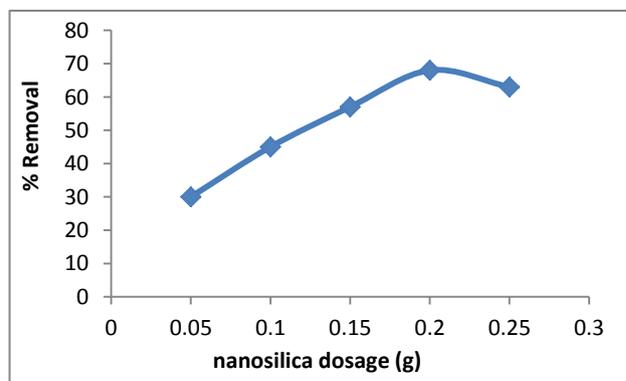

Figure 6. Effect of NS dosage on adsorption of CR dye

Effect of contact time and initial concentration on the adsorption process

The effect of contact time was studied at 25 ^0C using range of initial concentration of CR dye (5-40) mg/L in different time periods. From Fig.7 it can be seen that the removal was increased rapidly during the first hour of adsorption process, and then it slows down with the increase in contact time. The time necessary to reach the equilibrium for the removal of the Congo red molecules at different concentrations by nanosilica was established to be 60 min.
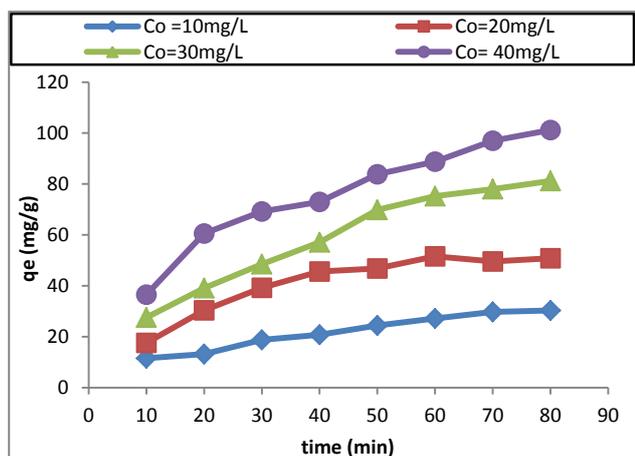
Figure 7. Effect of contact time and initial concentration on removal of CR dye

Figure 8. Adsorption isotherm of Congo red on Nanosilica

Also, the effect of initial concentration of CR dye (5-40 mg/L) was shown in Fig. 7 and revealed that the amount adsorbed of CR increases with increasing initial concentration, so the removal of CR depends on the concentration of the dye. At low concentration, the active adsorption sites are relatively high so CR dye molecules can easily find the accessible adsorption sites, but at higher concentrations the available site of adsorption decreased with more time. In addition, at high concentration CR dye molecules have the ability to aggregate in aqueous media under different shapes and sizes (17). These aggregations may be preventing easily accessible of CR dye molecules in vacant sites of adsorbent.

Adsorption Isotherms of Process

Adsorption isotherms describe the mechanisms, surface properties and the affinity of adsorbent towards adsorbate. Figure 8 represents the relation between the concentration of dye at equilibrium (C_e) and the amount of dye adsorbed at equilibrium (q_e). The graph shows that the isotherm is of S type according to Giles classification (18) which indicates high affinity of NS to adsorb CR dye. Sharp rise increasing in the plateau was noticed as the concentration of CR increased until reaching maximum capacity at high concentration of CR dye. This is due to strong self-assembly tendency of CR dye molecules which lead to difficulty in access empty sites on the surface of NS.
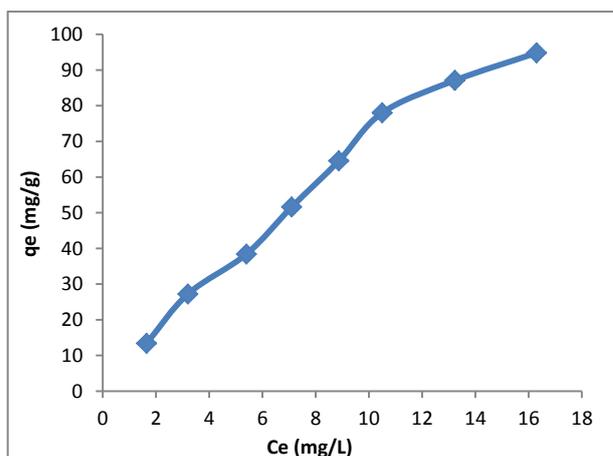
Adsorption experimental data must be fitted into an appropriate isotherm model. Thus, the most widely known, Langmuir and Freundlich isotherms, were used to evaluate the relationship between the amount of dye adsorbed and the remained concentration of dye at equilibrium.

Langmuir isotherm (19) assumes homogeneous monolayer adsorption on the surface of adsorbent which contains finite number of sites, so no further adsorption may take place on these sites, the linear form of Langmuir equation can be written as follow:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q^\circ} + \frac{C_e}{Q^\circ} \dots \dots \dots \dots (3)$$

Where, Q° (mg/g) and K_L (L/mg) are the Langmuir constants. Q° is the maximum adsorption capacity and K_L is the constant related to the energy adsorption constant. The Langmuir constants Q° and K_L were determined from the slope and interception when C_e/q_e was plotted linearly against C_e. Figure 9 represents applying of Langmuir isotherm equation on experimental results of adsorption of CR dye on NS adsorbent.
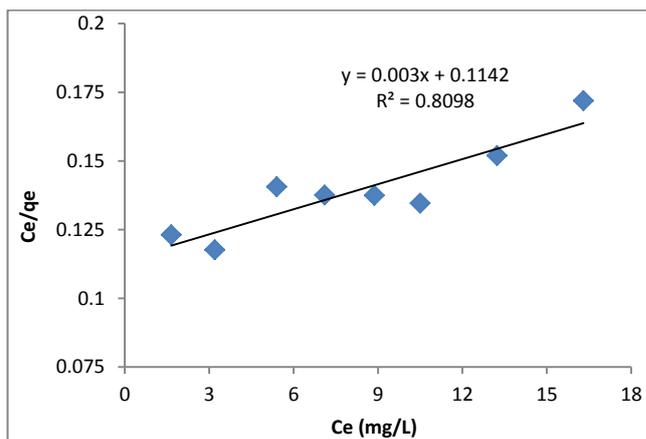

Figure 9. Langmuir Isotherm of Adsorption of CR dye on NS adsorbent.

Freundlich isotherm (20) model is derived from Langmuir isotherm and assumes a heterogeneous surface of adsorption capacity and can be applied to multilayer adsorption process and is given by:

$$\ln q_e = \ln K_f + \frac{1}{n} \, lnC_e \dots \dots \dots \dots . (4)$$

Where, K_f is the Freundlich constant correspond to adsorption capacity (mg/L); n is a dimensionless constant related to the intensity of adsorption. The value of n reflects the degree of nonlinearity between adsorption process and concentration of dye. Values of K_f and n respectively are obtained from intercept and slope of the linear plot of lnq_e versus $ln \, C_e$ as in Fig. 10.
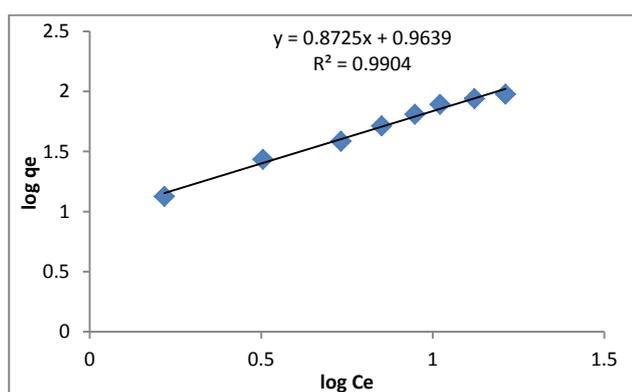

Figure 10. Freundlich isotherm of adsorption of CR dye on NS adsorbent.

From the results presented in Table 1, it is clear that the R^2 (regression coefficients) value of Freundlich isotherm (0.9904) was greater than that estimated from Langmuir (0.898) which reveals the well fitness of adsorption isotherm with Freundlich equation. Value of n is 1.15 indicates positive cooperatively in binding and a heterogeneous nature of adsorption. Also, the value of maximum monolayer capacity (Q^0) estimated from Langmuir equation was higher comparison with many studies which were used nanomaterials as adsorbents (21, 22).

Table 1. Equilibrium adsorption parameters for Langmuir and Freundlich isotherm

Estimated values of Langmuir equation			Estimated values of Freundlich equation		
R^2	Q^0 (mg/g)	K_L (Lmg^{-1})	R^2	K_f (Lmg^{-1})	n
0.898	333.3	0.026	0.9904	9.2	1.15

Kinetics of Adsorption

Many kinetics models were applied to study the mechanism of dye adsorption process on the surface of adsorbents. The most widely used kinetic models are Lagergren-first-order equation, and pseudo-second-order equation. These equations have been used to study the adsorption kinetic behavior of Congo red (25 mg/l) onto nanosilica at 25^0C. The best fit model was selected based on the linear regression correlation coefficient values (R^2). The linear form of the pseudo-first order kinetic model of (23) can be expressed as follows:

$$\log(q_e - q_t) = logq_e - (k_1/2.303) \, t \dots \dots \dots (5)$$

where k_1 is the rate constant of the pseudo-first order kinetics (min^{-1}), q_e is the amount of CR adsorbed on the surface of NS at equilibrium, q_t is the amount of CR adsorbed on the surface of NS at any time. The q_e and k_1 are calculated from the intercept and the slope of plots of log (q_e - q_t) vs t, respectively. The result of such plot is illustrated in Fig. 11.
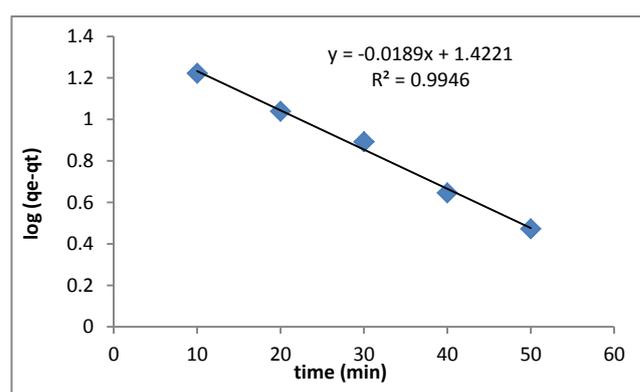

Figure 11. Pseudo first order plot of kinetics adsorption of CR dye on NS

The linear form of the pseudo-second order kinetic model (24) is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \dots \dots \dots \dots (6)$$

where k_2 is the rate constant of the pseudo-second order kinetics (g mg^{-1} min^{-1}). k_2 and q_e are calculated from the intercept and the slope of plots of t/q_t against t, respectively as shown in Fig. 12.
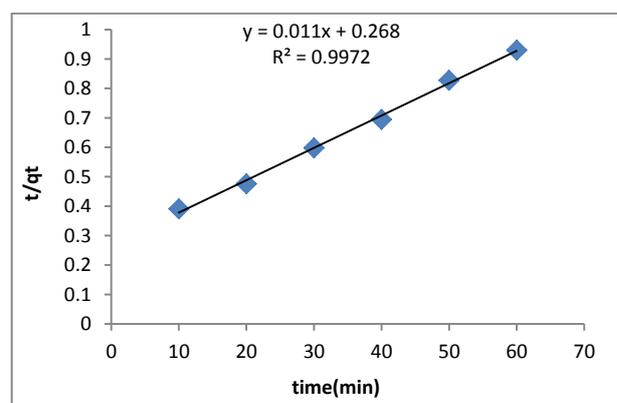

Figure 12. Pseudo second order plot of kinetics adsorption of CR dye on NS

From the kinetics parameters in Table 2, the values of correlation coefficients ($R^{2)}$ of the two

equation(0.9946 for first order and 0.9972 for second order) are closely even the value of R^2 of pseudo second order equation is slightly higher. This means that pseudo second order kinetics equation gave well-fitting with adsorption kinetics data.

Table 2. Kinetics parameters of adsorption of CR dye on NS adsorbent

Kinetics equations	R^2	k	$q_{e\ (mg/g)}$
Pseudo First order	0.9946	4.3×10^{-2} (min^{-1})	26.34
Pseudo Second order	0.9972	4.5×10^{-4} $(g\ mg^{-1}\ min^{-1})$	90.9

Conclusions:

Cheap and ecofriendly sample of nanosilica shows good affinity for removing pollutant dyes from wastewater. Congo red dye as adsorbate material proves the high adsorptive efficiency of the prepared sample of nano silica. The different factors studied to get optimum conditions of adsorption CR dye on NS surface to reach equilibrium reveal highly efficient of NS as adsorbent. The best fitting of equilibrium parameters to Freundlich model indicates positive cooperatively in binding and a heterogeneous nature of adsorption. According to their correlation coefficient, both kinetics equations (pseudo first and pseudo second order reaction) fit well with the results of kinetics adsorption data but the results are followed by second order more than first order equation.

Author's declaration:

- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Besides, the Figures and images, which are not mine, have been given the permission for re-publication attached with the manuscript.
- The author has signed an animal welfare statement.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

References:

1. Jing Y, Niu H, Li Y. Improved ethylene-propylene rubber/silica interface via in-situ polymerization. Polym. J. 2019;172:117-125.
2. Elkady M, Hassan SH, Hashim A. Immobilization of Magnetic Nanoparticle onto Amine-Modified Nano-Silica Gel for Copper Ions Remediation. Materials. 2016; 9 (460):1-24.
3. Basheer A. New generation nano-adsorbents for the removal of emerging contaminants in water. J. Mol. Liq. 2018; 261:283-293.
4. Peng B, Zhang L, Luo J, Wang P, Ding B, Zeng M, et al. A review of nanomaterials for nanofluid enhanced oil recovery. RSC Adv. 2017; 7: 32246-32254.
5. Madadi A, Eskandari-Naddaf H, Nejad M. Evaluation of Bond Strength of Reinforcement in Concrete Containing Fibers, Micro-silica and Nano-silica. J. Stress Anal. 2018; 3(1)11-19.
6. Waring D, Hallas G. The Chemistry and Applications of Dyes. 1990. p
7. Viswanathan B. Photocatalytic Degradation of Dyes: An Overview. Curr. Catal. 2018;7(1)99-121.
8. Darvishmanesh S, Pethica BA, Sundaresan S. Forward osmosis using draw solutions manifesting liquid-liquid phase Separation. Desalination. 2017;421:23–31
9. Khan AM, Khan IM, Zafar S. Removal of different anionic dyes from aqueous solution by anion exchange membrane. Membr Water Treat. 2017; 8(3): 259-277.
10. Shena J, Shahida S, Amuraa I, Sarihana A, Tiana M, Emanuelsson EA. Enhanced adsorption of cationic and anionic dyes from aqueous solutions by polyacid doped polyaniline. Synth. Met. 2018; 245:151–159
11. Alam M, Khanom R, Rahman M. Removal of Congo Red Dye from Industrial Wastewater by Untreated Sawdust. Am. J. Environ. Protect. 2015; 4(5):207-213.
12. Farias RS, Buarque H, Cruz M. Adsorption of Congo Red Dye from Aqueous Solution onto Amino-functionalized Silica Gel. Eng Saint Ambeint. 2018; 23(6): 1053-1060.
13. Zhang J. Adsorption of Congo red from aqueous solution using ZnO-modified SiO_2 nanospheres with rough surfaces. J. Mol. Liq. 2018; 249:772-778.
14. Ryouya H, Yasuhiro T, Makoto O. The synthesis of thin layers of organosilica by the co-condensation of tetraethoxysilane and phenyl triethoxysilane in the presence of cationic surfactant .J. Mater. Sci.2012; 47:2195-2200.
15. Agnieszka K, Waldemar B, Jacek G. The porosity and morphology of mesoporous silica agglomerates. J. Porous Mater. 2010;17:669-676.
16. Silva F, Nascimento L, Brito M, Silca K, Paschoal W, Fujiyama R. Biosorption of Methylene Blue Dye Using Natural Biosorbents Made from Weeds. Materials. 2019; 12(15):2468-2476.
17. Zhou Y, Ge L, Fan N, Xia M. Adsorption of Congo red from aqueous solution onto shrimp shell powder. Adsorpt. Sci. Technol. 2018; 36:1310-1330.
18. Giles CH, Smith DA .General treatment and classification of the solute adsorption isotherm. J Colloid Interface Sci. 1974; 47(3):755-765.
19. Langmuir I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. J. Amer. Chem. Soc. 1918; 40(9):1316-1403.
20. Freundlich HMF. Over the adsorption in solution. J. Phys. Chem. 1906; 57: 385-470.
21. Wang L, Wang A. Adsorption characteristics of Congo red onto the chitosan/montmorillonite

nanocomposite. J. Hazard Mater. 2007; 147(3): 979-985.

22. Fkhami A, Moosavi R. Adsorptive removal of Congo red, a carcinogenic textile dye from aqueous solutions by maghemite nanoparticles. J. Hazard Mater. 2010; 174(1-3):398-403.

23. Lagergren S. For the theory so-called adsorption of dissolved substances. Kungliga Svenska Vetenskapsakademiens. Handlingar. 1898; 24(4):1-39.

24. McKay G ,Ho YS. Pseudo-second order model for sorption processes. Process Biochem. 1999; 34: 451-465.

إزالة صبغة الكونغو الحمراء من محاليلها المائية بأستخدام سطح صديق للبيئة محضر من النانوسيليكا

انعام حسين علي

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق

الخلاصة:

أصبح تطوير مواد مازة جديدة ورخيصة وصديقة للبيئة مطلبا مهما لمعالجة مياه الصرف، وتعتبر النانوسيليكا (NS)ا خيارا جيدا. في هذا البحث تم تحضير نموذج من النانوسيليكا باستخدام سيليكات الصوديوم كمصدر سيليكوني والسطح الفعال غير الايوني (Tween 20) كقالب. تم تشخيص النموذج المحضر باستخدام عدة تقنيات مثل EDX, SEM, AFM, FT-IR ، حيث أكد طيف FT-IR على وجود السيليكا في العينة ، اما تحليل SEM فأظهر وجود هياكل نانوية تتراوح مساميتها من (20-100 نانوميتر). تم دراسة الخواص الامتزازية لهذا النموذج عن طريق إزالة صبغة الكونغو الحمراء من محاليلها المائية في درجة حرارة الغرفة (25م)باستخدام طريقة الدفعات لدراسة تأثير مختلف المتغيرات على عملية الامتزاز مثل كمية المادة المازة والتركيز الابتدائي وزمن الاتزان واعطت النتائج افضل كمية للمادة المازة 0.2 غم من النانوسيليكا لكل 50 مل من محلول الصبغة و60 دقيقة هو الزمن اللازم للوصول الى حالة الاتزان. تم تحليل النتائج العملية المستخرجة بأستخدام معادلتي لانكماير وفرندلج والتي اظهرت تطابقا كبيرا مع معادلة فرندلج التي تكشف عن عدم تجانس السطح الماز. كذلك تم دراسة حركية عملية الامتزاز بتطبيق معادلتي الدرجة الاولى والثانية الكاذبة واعطت المعادلتان تطابقا كبيرا مع النتائج الا ان معادلة المرتبة الثانية الكاذبة كانت الافضل لتفسير حركية الامتزاز.

الكلمات المفتاحية: الكونغو الحمراء، معادلة فرندلج، معادلة لانكماير، نانوسيليكا، سيليكات الصوديوم، توين 20 .