Original Article

Investigation and Optimization of Some Parameters Influencing Brilliant Green (Dye) Removal Using Activated Carbon

Farnush Horriat

MS.c, Master student of chemistry department, Islamic Azad university, Iran

Abstract

The present study evaluates the performance of activated carbon modified by silica nanoparticles (SiO_2) for remoing brilliant green dye from aqueous environments. At first, silica nanoparticles (SiO_2) was prepared as the adsorbent which was subsequently stabilized on active carbon. Then, the various parameters influencing the absorption process such as PH of the dye solution (1-10), adsorbent contact time (0.5-30 minutes), amount of the adsorbent (0.005-0.02 grams) and the initial concentration of the dye (10-40 milligrams/liter) were evaluated. After investigating the effect of the parameters influencing the absorption process, the optimum solution PH rate, optimum contact time, optimum adsorbent amount and optimum preliminary dye concentration were respectively obtained equal to 6, 18 minutes, 0.02g and 15mg/l; under the foresaid setup, the silica nanoparticles-modified active carbon adsorbent was found capable of removing more than 95% of the brilliant green dye. This is while the maximum capacity of the SiO_2 nanoparticle-modified active carbon's absorption was also found above 250.0 milligram per gram of the adsorbent.

Keywords: surficial absorption, silica nanoparticles (SiO_2), active carbon, brilliant green

INTRODUCTION

The followings are the methods applied for successful removal of the dye existent in the wastewater flowing out of the dyeing industry: biodegradation, electrochemical methods, chemical methods and physicochemical methods. Absorption occurs in two forms of surficial and internal. One of the methods most frequently utilized for driving dyes and metal ions out of the wastewater of the various industries' factories is the surficial absorption on the solid adsorbent particles. Many materials can be employed as adsorbent but active carbon is essentially a lot effective due to its absorption properties. The general stages during which a soluble material can infiltrate into carbon particles for attaching to their internal surfaces are generally called absorption. The absorption properties of the activated carbon are more effective physically than chemically [1].

Active carbon which is one of the most widely applied chemical materials in the surficial absorption processes is a crystal and non-graphitic material which is applied due to the possession of a large number of internal pores as the adsorbent in various industries like oil and gas, water and industrial wastewater purification, pharmaceutics and food industry and so forth. Carbon has various factor groups, including hydroxyl, carboxyl, amine and carboxylic acid with Van Der Waals and hydrogen bonds, capable of absorbing the various dyes. Carbon's physical absorption ability is more than its chemical absorption capability. Due to such properties like vast surface area, large surface interaction, general absorption effects and optimal pore sizes, activated carbon can better act as an adsorbent. Quantitatively, active carbons are classified based on scales like total carbon surface area, carbon density, particle sizes' distribution and absorption capacity and all these factors influence the absorption speed and absorption capacity. Active carbons are prepared from the initial carbon-bearing materials based on chemical or physical methods. Various parameters like initial material, activation method, soaking ratio and type of soaker, activation temperature, time of retention in the final temperature and temperature increase speed intervene in the

Address for correspondence: Farnush Horriat, MS.c, Master student of chemistry department, Islamic Azad university,iran
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active carbon's properties. Besides the carbon production conditions, the type of the initial material is effective in the properties of the produced active carbon. The followings are the applications of the active carbon: A) water (drinkable water, aquarium water and industrial water) treatment in terms of color and odor and taste; B) dye removal from sugar and sugar cube; C) improving the color and flavor of the beverages and juices; D) use in devices like air purifier, air freshener and industrial filters. Active carbon has a low absorption capacity for industrial applications and it is not proper for the elimination of the colors in large scale. Thus, the thought about the use of an alternative adsorbent with industrial application, high flexibility, proper output and economic cost-effectiveness has always been existing and seeming necessary [2].

PH is considered as one of the most important analytical parameters. In every adsorbent-adsorbed system, the solution's PH influences the nature of the adsorbent surface's charge, absorption capacity of the absorbable molecules, properties of the adsorbent's surface, ionization rate of the adsorbed and adsorbent groups, ion state and molecule's hydrophilicity and lipophilicity. There are two mechanisms for getting the dye adsorbed on the nanoparticles and activated carbon: 1)electrostatic between the adsorbent and the dye and 2) chemical reaction between the dye and the adsorbent. Stirring time is one of the parameters influencing the amount of dye absorption on one preservative and it determines the test kinetics and period. The reaction time required for absorption depends on various factors like nanoparticle size, pore volume, porosity diameter, type of activated carbon, apparent shape of the activated carbon (powder or granulated), type of the adsorbent as well as the texture of the solution. The amount of the adsorbent and the existent active sites on its surface constitute a significant variable that influences the efficiency of the removal action. In the investigation of the effect of the adsorbent amount, it is usually necessary to have an idea about the efficiency of an adsorbent and the capability of its dye removal in the lowest usable amount for cost-effectiveness concerns, especially for adsorbent made using expensive nanoparticles. In the process of the surficial adsorption, the initial concentration of the dye is an important parameter. The reason for this parameter's importance is that the amount of the driving force required for transferring the dye particles to the adsorbent's surface depends on the amount of dye existent in the solution.

Gha'edi et al (2013) investigated the adsorption of methylene blue and brilliant green dyes in a dual mixture on the macro-size natural cerevisiae adsorbent [3]. The biomass adsorption capability was maximum in PH=6 which is close to the PH of the natural aqueous solutions [3]. In order to develop a systematic method for removing anionic and dangerous eosin yellow dyes from aqueous solutions, Mittal et al (2012) used soya residues as adsorbent and noticed in the course of the studies that the adsorption of eosin yellow dye is reduced with the increase in PH but it is increased with the increase on the concentration and amount of the adsorbent as well as the elevation of the temperature [4]. Yi Huang et al (2011) used chitosan attached to ethylene diamine as adsorbent for removing anionic eosin yellow dyes from aqueous solutions. They applied FT-IR methods and zeta potential analysis for describing their adsorbent and investigated the effects of various parameters, including the particles' size, solution's PH, stimulation rate, temperature, adsorbent dosage (5-50mg/l) and contact time (1min-24h) and initial dye concentration (30-50mg/l) [5]. Santhi et al (2010) used activated carbon as an adsorbent for removing the malachite green dyes and evaluated the effects of the various parameters, including the adsorbent's dosage, initial PH, temperature, initial dye concentration and contact time. The optimum PH for the adsorption of the dye was 7 and the maximum adsorption was equal to 99.4% for a gram of adsorbent [6]. Hameed et al (2007) investigated the methylene blue dyes' removal from aqueous solutions using activated carbon prepared of the sawdust of bamboo wood. For a concentration of 1g/l, the increase in dye concentration from 100mg/l to 500mg/l caused an increase in the dye adsorption rate from 96mg/g to 294mg/g [7]. In this study, some of the effective parameters like PH, contact time, adsorbent amount and initial dye concentration that influence the removal of the brilliant green dyes using activated carbon were investigated and optimized.

MATERIALS AND METHODS:

In this study, in order to prepare a 1000mg/l solution of the brilliant green dye, 0.5g of the dye was dissolved in an amount of double distilled water and the mixture's volume was increased in a 500-milliliter balloon. The next standard solutions were prepared by diluting a given volume of this mother solution. In this study, the maximum adsorption wavelength was set for measuring the amount of the brilliant green (BG) dye. Then, the solutions of this dye were prepared in such concentrations as 10mg/l, 15mg/l, 20mg/l, 30mg/l and 40mg/l and the solutions were set in PH values in a range from 1 to 10 (PH setting was carried out using sodium hydroxide and hydrochloric acid). The initial adsorption of every solution was read in the same PH and, then, a given amount of the adsorbent was added to that solution which was stirred in an identical time and speed. The dye adsorption and removal rate of every solution by this new adsorbent was measured using the signal and adsorption rate read by UV-Vis device. The optimum point was determined for each adsorbent by the delineation of the removal percentage in respect to the studied variable. In order to access the maximum removal process output, the effects of various factors like PH, contact time, stirring speed and the adsorbent amount were optimized and the efficiency of the new adsorbent was evaluated for removing the brilliant green dye.

In order to stabilize the silica nanoparticles on the activated carbon, a mixture of this nanoparticle and activated carbon was seminally prepared in a 1:3 ratio. Then, it was dispersed inside 50ml of a mixture made of water and ethanol for one hour. After this stage, the silica nanoparticle-active carbon mixture was placed in an ultrasonic bath for two hours.

Resultantly, the silica nanoparticles were deposited on the active carbon surfaces. The silica nanoparticle-modified activated carbon was filtered and intensively washed using deionized distilled water. Next, it was dried in 25C for 24 hours. The obtained compound was in a completely uniform powder form. The prepared adsorbent was identified and analyzed by SEM and TEM techniques.

In order to obtain the optimum PH of the brilliant green dye's removal, 50.0ml of a 20mg/l solution of brilliant green was prepared in various PH values in a range from 1 to 10 (using nitric acid and diluted sodium hydroxide) and it was placed in 25°C in contact with 10mg and 15mg of the activated carbon modified using silica nanoparticles (SiO_2) and the solution was stirred after 30 minutes of contact with the adsorbent in a speed of 400 round per minute so that the dye adsorption can take place [8]. In order to determine the best contact time suitable for maximum adsorption in every concentration by means of each amount of the foresaid adsorbent in a series of similar experiments, 50ml of the brilliant green dye was prepared in such concentrations as 10mg/l, 15mg/l, 20mg/l, 30mg/l and 40mg/l in a PH=6 with silica nanoparticles (SiO_2) and the mixture made of each amount of the adsorbents (namely, 0.005g, 0.01g, 0.015g and 0.02g) was stirred in 400rpm for various periods, namely 0.5min, 1min, 1.5min, 2min, 3min, 5min, 7min, 12min, 15min, 18min, 21min, 24min, 27min and 30min so that the dye adsorption can occur on the adsorbent. In order to determine the best amount of the adsorbent suitable for maximum adsorption in each concentration for a fixed time of 30 minutes in a series of similar experiments, 50ml of the brilliant green solution was prepared in various 10mg/l, 15mg/l, 20mg/l and 30mg/l concentrations with a PH=6 for silica nanoparticles (SiO_2) and the mixture made of each amount of the adsorbents (namely, 0.005g, 0.01g, 0.015g and 0.02g) was stirred in 400rpm for 30 minutes so that the dye adsorption can occur on the adsorbent. After performing the similar experiments with different concentrations, it was observed that the brilliant green dye adsorption is maximum when using 0.02g of adsorbent for a 15mg/l concentration thereof. In order to investigate the initial dye concentration, similar solutions of the brilliant green (50.0ml with various dye concentrations in a range from 10 to 40mg/l) was prepared and placed in contact with various adsorbent amounts (0.005-0.02g). After 30 minutes, an equilibrium was achieved and the maximum dye adsorption took place. Then, each of the solutions was filtered and their adsorption rates were obtained in 623nm wavelength which was used for calculating the dye elimination percentage.

STUDY RESULTS:

Figures (1) and (2) display the SEM and TEM images of silica nanoparticles. The images are expressive of the idea that the silica nanoparticles stabilized on the prepared activated carbon have pore distribution about 20 to 30 (table 1) which enable entrapment of a vast spectrum of ions and molecules and/or adsorbing the organic molecules on their surfaces thereby to adsorb and entrap various ingredients and different functional groups on their surfaces. Furthermore, due to the high specific surface, they can be also applied in industrial scales as well as bioenvironmental applications. SEM is one of the common techniques used for determining the morphology and dimensions and structure of the objects' surfaces. The SEM structure of the silica nanoparticles stabilized on the prepared activated carbon is indicative of the idea that firstly the prepared nanoparticles feature homogenous and uniform structures and, secondly, there is a vast spectrum of the pores with various dimensions and sizes and nearly all these prepared nanoparticles also feature a high purity and it is due to these pores of different sizes that the activated carbon can trap various molecules in the interior and exterior surfaces of them. In the meanwhile, the investigation of this adsorbent is reflective of the idea that the functional groups, including carboxyl, hydroxy and carbonyl groups, on the nanoparticle surfaces of these groups enable them as active sites trap various metal ions and molecules of dye through Van Der Waals forces (with π bonds in hydrocarbon chains), hydrogen bonds with various functional groups and chemical bonds by soft-soft and hard-hard interactions.

Table 1: specifications of silica nanoparticle adsorbent

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Silicon Oxide Nanoparticles (SiO2)	
Nanoparticles (SiO2) Purity	99+%
Nanoparticles (S1O2) APS	20-30nm
Nanoparticles (S1O2) SSA	180-600m2/g
Nanopartides (SiO2) Color	white
Nanoparticles (SiO2) Bulk Nanopartides (SiO2) True Density	<0.10g/cm3
Nanopartides (SiO2) True Density	2.4 g/cm3

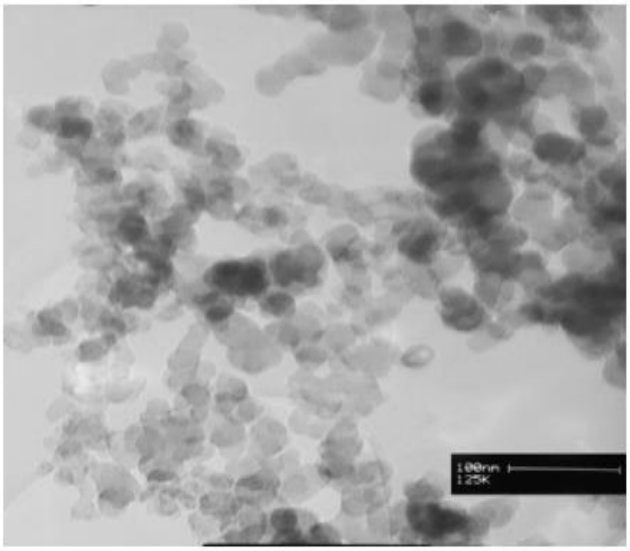

Figure (1): SEM image of SiO_2-AC nanoparticle (nanoparticle size between 20nm and 30nm)

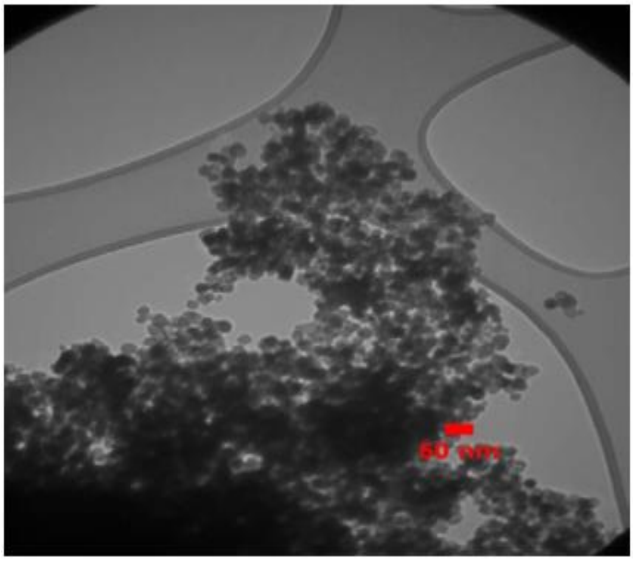

Figure (2): TEM image of SiO_2-AC nanoparticle

As it is evident from the results in diagram (1), the optimum PH for the two adsorbent amount is equal to 6. Considering the structure of brilliant green (BG) dye and the structural and charge changes of this dye in various PH values, it is expected that the adsorption charge and site in the BG dye's structure be extremely dependent on PH. According to BG dye's cationic nature, the interaction between the adsorbent surface and the dye is in the form of the interaction between the aromatic chain and π electrons of the adsorbent structure. In low PH values, the positive charge existent on the surface of the adsorbent prevents the dye adsorption due to the similar charge and electrical repulsion hence the adsorption rate is reduced. Contrarily, in high PH values, the opposite occurs. Considering the presence of the nitrogen atoms and positive charge in the dye structure, both the adsorbent and the adsorbed have positive charges due to the protonation of the active carbon and silica nanoparticles' functional groups as well as the dye's nitrogen atoms and this prevents the adsorption of the dye onto the adsorbent as a result of the produced electrostatic repulsive force. The increase in PH causes the functional groups to lose proton and the dye becomes neutral in charge and it is subsequently absorbed on the adsorbent with such mechanisms as hydrogen bond, formation of the electron donating-receiving complexes and π- π bond or soft-soft interaction.

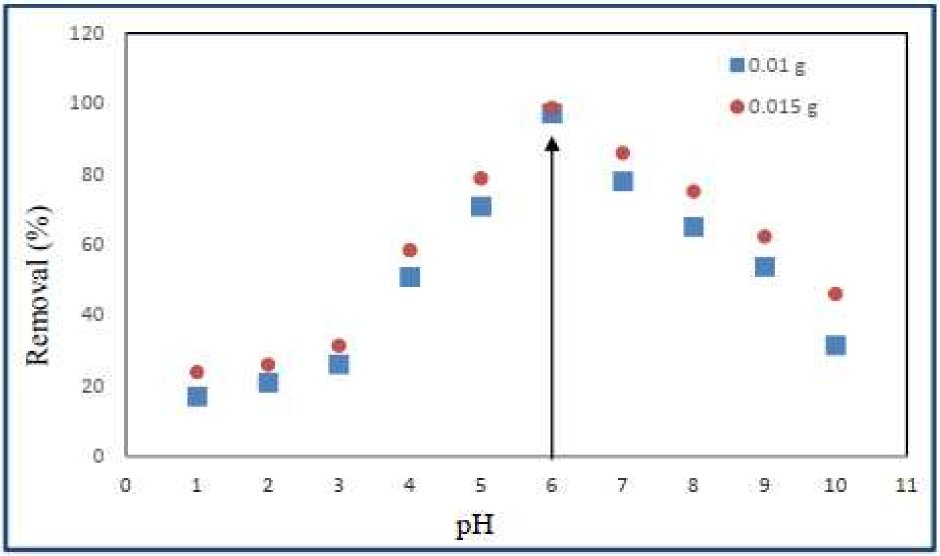

Diagram (1): investigating the effect of the environment's PH on the BG dye's removal (in a dye concentration of 20mg/l in various PH values on 0.015g and 0.01g of silica (SiO_2) nanoparticle-modified activated carbon in 400rpm for 30 minutes in 25.0±0.5°C

The results of the silica (SiO_2) nanoparticle-modified activated carbon's contact time effect for the removal of BG dye have been given in diagrams (2) to (7) for various concentrations. The results of these diagrams are indicative of the idea that the maximum dye removal in each concentration is achieved by the increase in time till the arrival at the optimum time after which the dye removal does not undergo much of a change. After an equilibrium time (18 minutes), the percentage of the BG dye's removal is fixed. This finding originates from this reality that there are many empty spaces in the beginning of the surficial adsorption process for dye adsorption on the surface of the adsorbent but, upon getting close to the steady-state, these empty spaces can be barely occupied by dye molecules for such a probable reason as the existence of counteracting forces in the mass in the vicinity of the adsorbent. Diagrams (2) to (7) can well show this issue in such a way that about 80.0% of the dye removal occurs in the first five minutes. According to these diagrams, after the first several minutes were spent, the dye removal percentage changes with a small slope which is indicative of the intraparticle infiltration. 18 minutes was selected as the optimal dye removal time. In each of these curves, there are three stages in the form of the linear diagrams. The first linear part (fastest adsorption stage) pertains to the dye infiltration onto the adsorbent's surface; the second linear part is pertinent to the intraparticle infiltration and the third stage is related to the dye's infiltration into the smaller pores of the silica nanoparticle-modified activated carbon adsorbent at the time of the equilibrium's establishment. With the increase in the concentration slope between the adsorbed in the solution and the adsorbent's surface, the maximum removal is achieved for the existence of empty and unoccupied sites in the early stages. Increase in the concentration slope leads to the increase in dye adsorption. The concentration is reduced with the pass of time and the accumulation of the dye molecules in the empty and unoccupied sites.

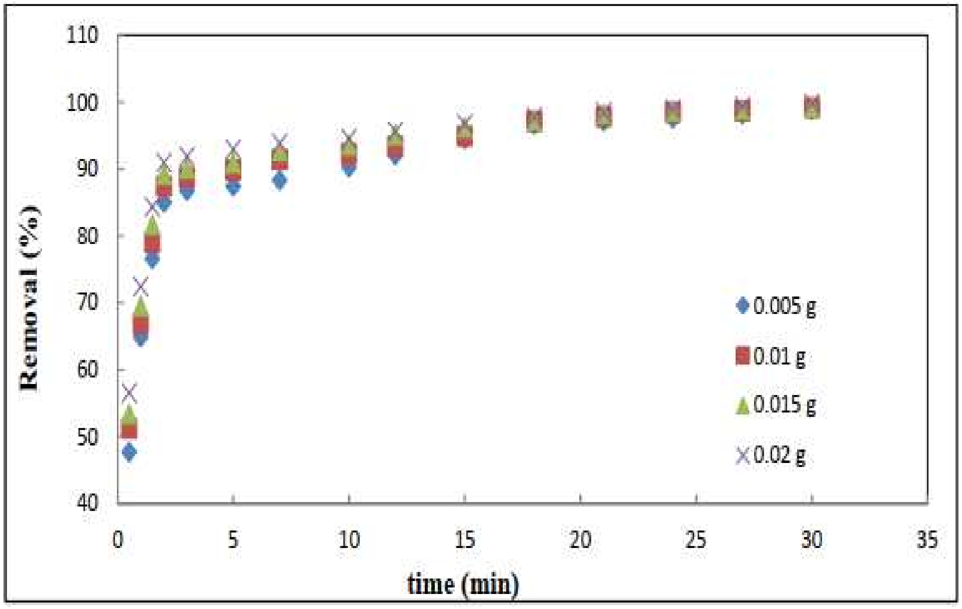

Diagram (2): the effect of the contact time on the elimination of BG dye in a concentration of 10mg/l (various amounts of adsorbent: 0.005g-0.02g) in different times (0-30 minutes) with a 400rpm speed in PH=6 and in a temperature of 25.0±0.5°C

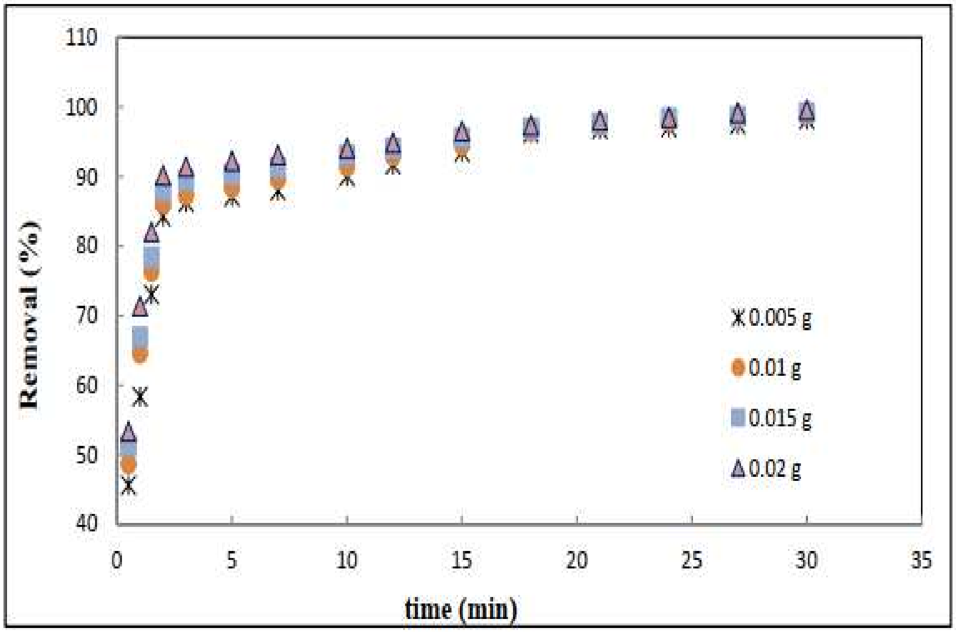

Diagram (3): the effect of the contact time on the elimination of BG dye in a concentration of 15mg/l (various amounts of adsorbent: 0.005g-0.02g) in different times (0-30 minutes) with a 400rpm speed in PH=6 and in a temperature of 25.0±0.5°C

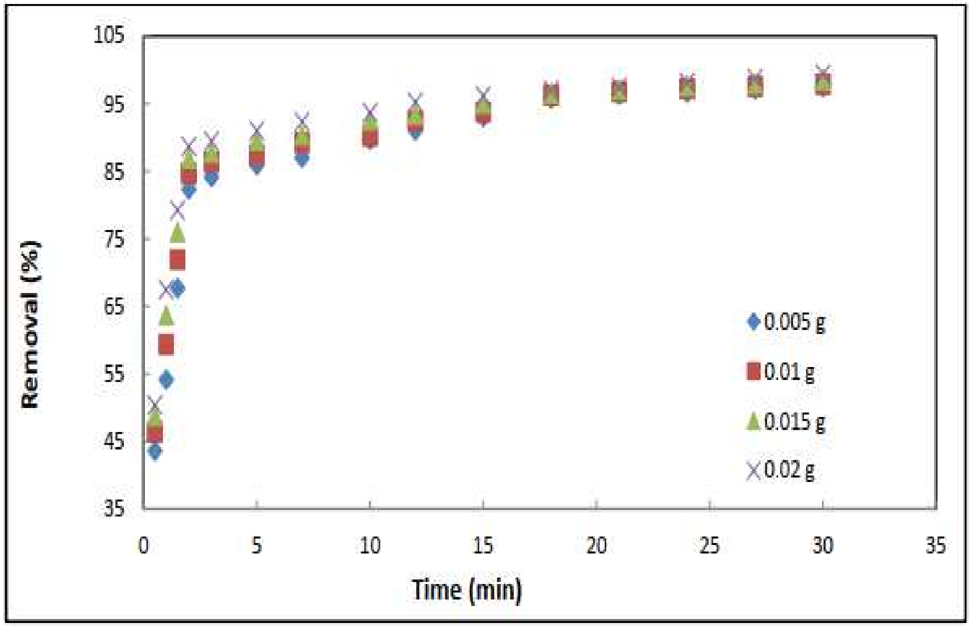

Diagram (4): the effect of the contact time on the elimination of BG dye in a concentration of 20mg/l (various amounts of adsorbent: 0.005g-0.02g) in different times (0-30 minutes) with a 400rpm speed in PH=6 and in a temperature of 25.0±0.5°C

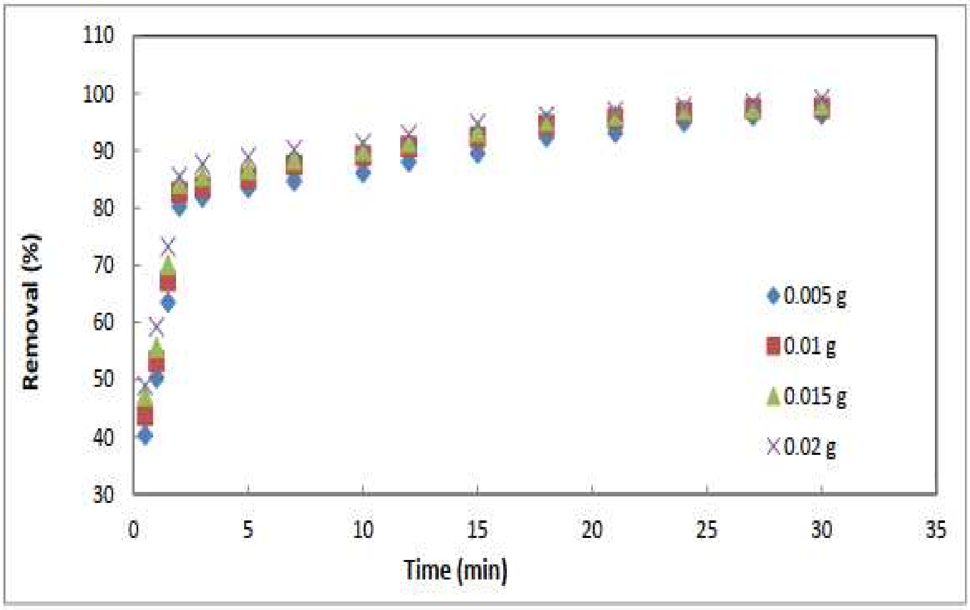

Diagram (5): the effect of the contact time on the elimination of BG dye in a concentration of 25mg/l (various amounts of adsorbent: 0.005g-0.02g) in different times (0-30 minutes) with a 400rpm speed in PH=6 and in a temperature of 25.0±0.5°C

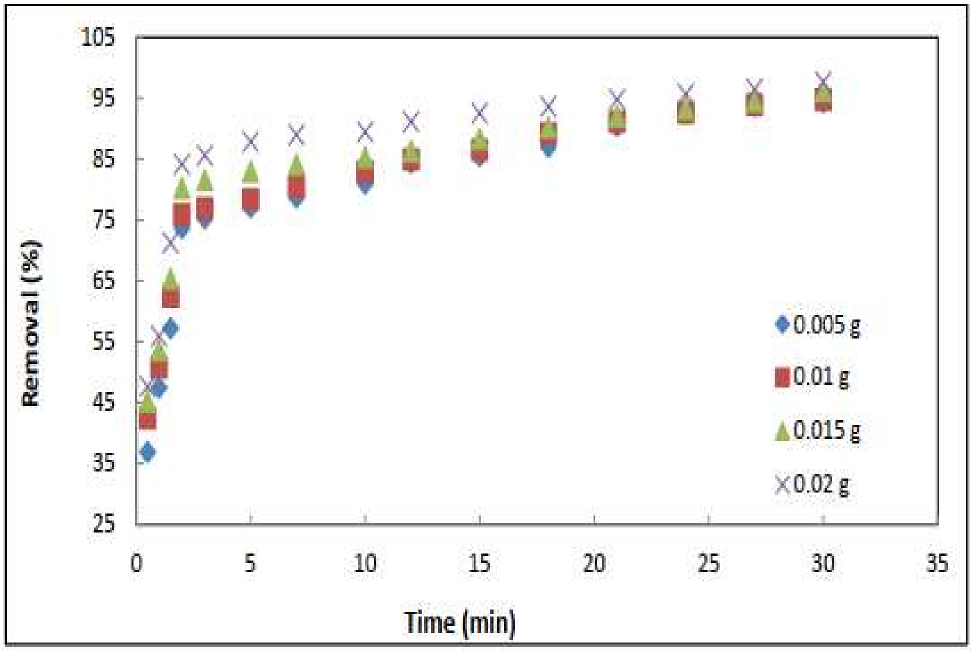

Diagram (6): the effect of the contact time on the elimination of BG dye in a concentration of 30mg/l (various amounts of adsorbent: 0.005g-0.02g) in different times (0-30 minutes) with a 400rpm speed in PH=6 and in a temperature of 25.0±0.5°C

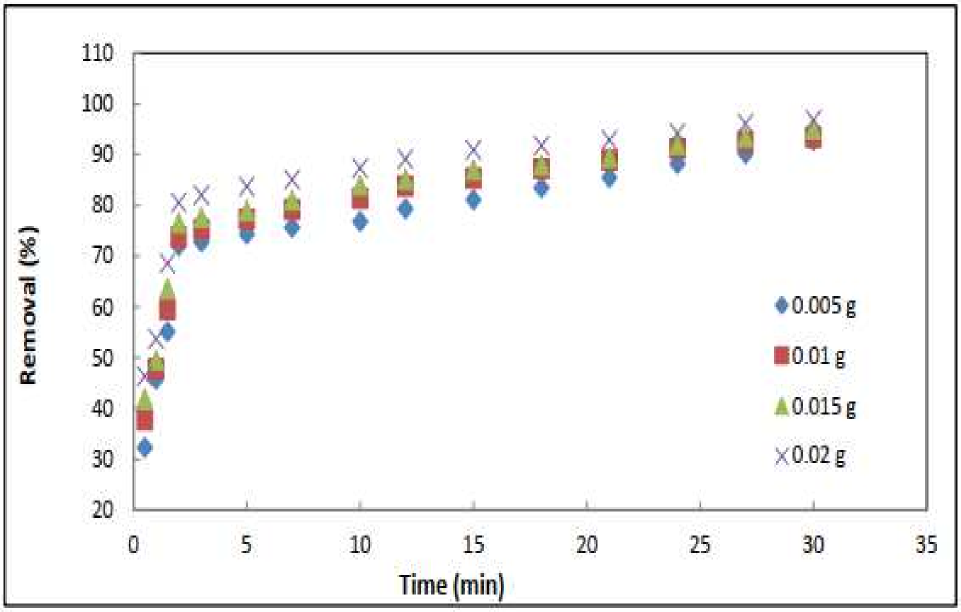

Diagram (7): the effect of the contact time on the elimination of BG dye in a concentration of 40mg/l (various amounts of adsorbent: 0.005g-0.02g) in different times (0-30 minutes) with a 400rpm speed in PH=6 and in a temperature of 25.0±0.5°C

The amount of the adsorbent (silica nanoparticle-modified activated carbon) and the rate of the active sites on its surface are effective on the amount and percentage of the BG dye's adsorption. As it is observed in diagram (8), the increase in the amount of the adsorbent causes increase in the dye removal in different concentrations; the increase in the adsorbent amount from 0.005g to 0.02g causes an increase in the adsorbent's removal of dye with a steeper slope. Any further increase in the adsorbent amount above 0.01g, the dye removal changes with a slighter slope. The increase in the dye removal rate with the increase in the amount of the adsorbent is for the reason that the number of the empty active sites of the adsorbent's molecules available for adsorbing the dye molecules is increased. Generally, the adsorption capacity increases in the course of time and it reaches a fixed amount at a given time and no dye molecule is removed anymore. At this time, the amount of the adsorbed dye reaches dynamic equilibrium with the amount of desorbed dye. As it is seen in diagram (8), the increase in the amount of the adsorbent to above 15mg causes an increase in the number of the adsorbent's active sites but these sites are not saturated hence the BG dye's removal percentage does not undergo much of a change. The other reason for this phenomenon can be the intraparticle interactions. For example, the accumulation of a large amount of the adsorbent causes reduction in the surface area of the adsorbent hence increase in the length of the infiltration path. In addition, a repulsion is created between the molecules adsorbed on the solid's surface and the molecules that are in solution phase. In order to obtain the maximum dye adsorption and removal capacity, the surface area of the loading (the ratio of the dye mass to the adsorbent rate) should be less than optimum. The reason for the reduction in the adsorbent's capacity with the increase in its amount is that although the number of the adsorbent's active sites is increased, they are left unoccupied due to the fixed concentration of the dye hence the adsorbent's adsorption capacity is decreased.

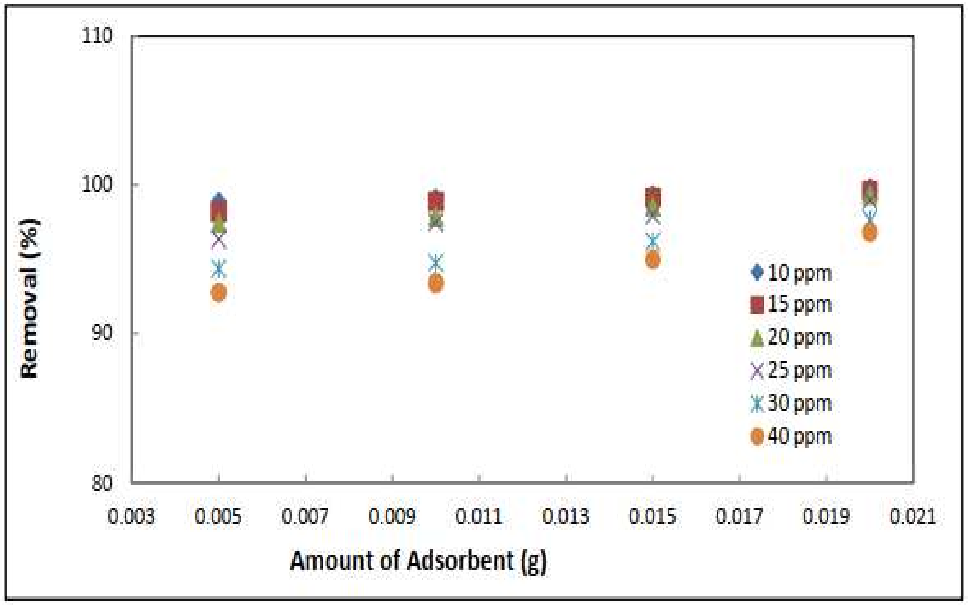

Diagram (8): investigating the effect of the amount of silica (SiO_2) nanoparticle-modified activated carbon adsorbent on the amount of BG dye's removal in various concentrations and times with 400rpm speed in PH=6 and 25.0±0.5°C

The results offered in diagram (9) are indicative of the higher BG dye's removal percentage in lower concentrations. However, the real amount of the dye adsorbed onto the adsorbent will be increased with the increase in the dye concentration. This reality is for the reason that the number of the available empty spaces on the adsorbent surface is very large for the dye molecules in low dye concentrations but the number of these empty spaces is reduced with the increase in the dye concentration and the adsorbent will be saturated. On the other hand, a repulsion force is created in higher dye concentrations due to the charged dye molecules between the dye molecules existent in the solution and the surface-adsorbed molecules and this prevents the dissolved dye molecules' approach to the adsorbent's surface. Thus, 15mg/l was chosen as the optimum concentration. Considering the fact that the various wastewaters have different temperatures and various dye concentrations, it is necessary to design and develop efficient methods featuring high adsorption capacity and ability for the removal and extraction of various dyes. The results of the diagram (9) showed that the dye removal rate is reduced with the increase in the initial dye concentration for a fixed amount of the adsorbent due to the adsorbent's surface saturation and/or inadequacy of the active sites. The figure's results are reflective of this reality on the other hand that the amount of the dye concentration can be reduced for all the different dye concentrations by optimizing the time and the adsorbent amount following which the water and wastewater treatment and keeping the concentration below the allowed limit for the production of water with better quality can be feasible. The increase in the dye concentration for the low adsorbent amounts causes a considerable increase in the adsorbent capacity (q_m, milligram per gram).

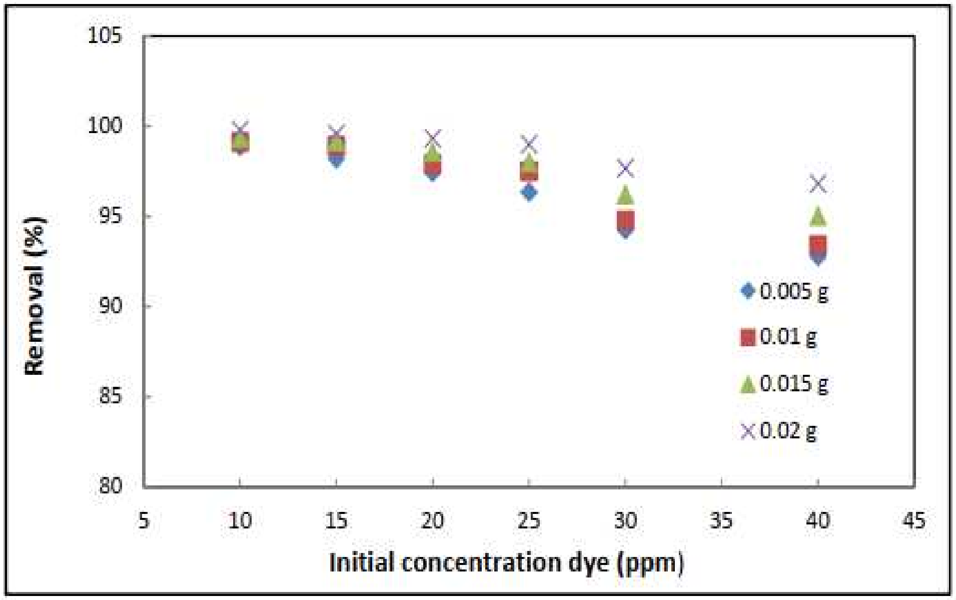

Diagram (9): the effect of the BG dye's initial concentration on the amount of its removal by silica (SiO_2) nanoparticle-modified activated carbon for various amounts of the adsorbent (0.005g-0.02g) in various times (0-30 minutes) in a 400rpm speed in PH=6 and 25.0±0.5°C

DISCUSSION AND FINAL CONCLUSION:

Fluids containing dye are produced like all the other wastewaters rapidly. As an example, in dying industries, 100l of the wastewater is produced per every kilogram of the dye substances. Thus, there is a need for an efficient system capable of maximally removing the dye from the wastewater in the lowest possible time. Dye removal from the wastewater is feasible by the use of economically cost-effective adsorbents. The primary goal of the present study is achievement of a simple, cheap, low-cost and environment-friendly method applicable in larger scales for the removal of dyes from the aqueous environments. In line with this, the present study sought producing and using silica nanoparticle-modified activated carbon adsorbent for eliminating dye. The dye removal from the wastewater is feasible using adsorbents that are economically cost-effective, including activated carbon and nanoparticles.

The results presented in the current research paper indicated that the silica nanoparticle-modified activated carbon features a high efficiency and output and lowest use of chemical materials and is capable of removing the maximum BG dye under proper thermal conditions. In this research paper, the effect of the various parameters influencing the adsorption process such as PH of the dye solution (1-10), adsorbent's contact time (0.5-30), amount of adsorbent (0.005g-0.02g) and the dye's initial concentration (10-40 mg/l) were evaluated. The optimum amount of the adsorbent was found equal to 0.02, 18 minutes was figured out as the optimum contact time for an initial dye concentration of 15mg/l and the optimum solution's PH was found equal to 6.

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