

Gold nanoparticle loaded activated carbon as novel adsorbent for the removal of Congo red

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Abstract

The present investigation assesses the applicability efficiency and performance of gold nano particle loaded activated carbon (Au-NP-AC) adsorbent for remove the Congo red (CR) from wastewater. The adsorption characteristics and dye removal efficiency of adsorbent have been determined by investigating the influence of variables including pH, contact time, concentration of the dye, amount of adsorbent and temperature. The graphical correlation of various adsorption isotherm models like Langmuir, Freundlich and Tempkin have been used to evaluate the ongoing adsorption. Calculation of various thermodynamic parameters such as, Gibb's free energy, entropy and enthalpy of the on-going adsorption process indicate feasibility and endothermic nature of CR adsorption onto Au-NP-AC. The kinetic studies suggest that the process follows pseudo second order kinetics and involvement of particle diffusion mechanism.

Keywords: Congo red, Dye, Gold nano particle, Activated carbon, Pollution

Introduction

The dyeing effluent discharged from textile industries is one of the largest contributors to textile effluent and is comprised mainly of residual dyes and auxiliary chemicals (Blackburn, 2004). Dyeing effluent has a serious environmental impact because disposal of this effluent into the receiving water body damages aquatic biota or humans by mutagenic and carcinogenic effects (Crini, 2006). Such colored effluent can affect photosynthetic processes of aquatic plants, reducing oxygen levels in water and, in severe cases, resulting in the suffocation of aquatic flora and fauna (Hu & Wu, 2001; Cheung *et al.*, 2009). Treatment of effluent containing synthetic dyestuffs is very difficult, since the dyes are stable in conditions of light and heat, the presence of oxidizing agents and are resistant to aerobic digestion (Sun & Yang, 2003; Yee & Chin, 2005; Chatterjee *et al.*, 2009).

Because of the low biodegradability of dyes, the conventional biological wastewater treatment processes were not efficient in the treatment of dyes contaminated wastewater (Mondal, 2008). Therefore, dyes wastewater was usually treated by physical and/or chemical methods, such as coagulation and flocculation (Zonoozi *et al.*, 2009), membrane separation (Sachdeva & Kumar, 2009), activated carbon adsorption (Tan *et al.*, 2008), electrochemical removal (Gupta *et al.*, 2007a), and photochemical degradation (Gupta 2007b). However, for the developing countries, these methods are still too expensive to be used widely. Developing economical adsorbents to treat dyes wastewater has attracted great interest in recent years (Kavitha & Namasivayam, 2007; Hua *et al.*, 2010).

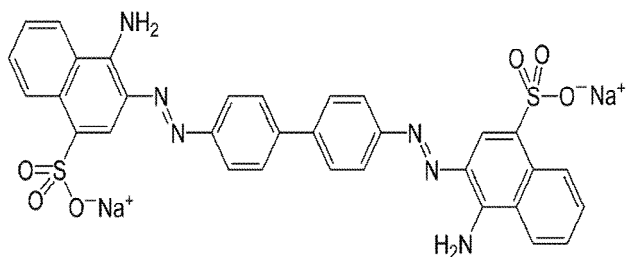
Congo red (CR) (sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid, formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol) is a

secondary diazo dye that have complex chemical structure and high solubility in aqueous solution. CR is metabolized to benzidine, a known human carcinogen and exposure to this dye can cause some allergic responses. CR mainly occurs in the effluents discharged from textile, paper, printing, leather industries, etc (Han *et al.*, 2008). There are many processes to remove CR molecules from colored effluents and the treatment methods can be divided into three categories: (1) physical methods such as adsorption (Namasivayam & Kavitha, 2002; Mall *et al.*, 2005; Chatterjee *et al.*, 2009); (2) chemical methods such as ozonation (Gharbani *et al.*, 2008; Khadhraoui *et al.*, 2009), photo degradation (Wahi *et al.*, 2005) and electrochemical process (Elahmadi *et al.*, 2009); and (3) biodegradation (Gopinath *et al.*, 2009). Adsorption techniques have potential for removing organics from water due to their high efficiency and ability to separate a wide range of chemical compounds (Slejko, 1985; Suffet & McGurie, 1985; Jain & Sikarwar, 2008; Sari & Tuzen, 2008; Uluozlu *et al.*, 2010).

Nanoparticles have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area. It is a common behavior that nano particles would easily aggregate because of the magnetic property of nano particles themselves, so most of the particles exist in chain-like aggregates (Arami *et al.*, 2005; Ardejani *et al.*, 2007).

The objective of the present work is to investigate the potential feasibility of AuNP-AC for the adsorption of Congo red (Fig. 1). The kinetic and equilibrium data were analyzed so that we can understand the adsorption mechanism and different models were applied to fit the experimental data.

Fig. 1. Chemical structure of Congo red



Experimental

Instruments and reagents

Stock CR solution was prepared by dissolving its appropriate amount in double distilled water and the test solutions were prepared by diluting stock solution to the desired concentrations, while its concentration was determined at 497 nm. The pH measurements were done using pH/Ion meter model-686, and absorption measurements were carried out using Jasco UV-Visible spectrophotometer model V-570 using a quartz cell with an optical path of 1 cm. The shape and surface morphology of the Au nanoparticles were investigated by field emission scanning electron microscope (FE-SEM, Hitachi S4160) under an acceleration voltage of 15 kV. For TEM, the samples were prepared by dropping diluted solutions of Au nanoparticles onto 400-mesh carbon-coated copper grids with the excessive solvent immediately evaporated. A Hitachi H-800 TEM at an operating voltage of 200 kV determined the morphology and electron diffraction pattern of the Au nanoparticles. All chemicals including NaOH, HCl and KCl with the highest purity available are purchased from Merck, Darmstadt, Germany.

Measurements of dye uptake

The concentrations of dye in solution were estimated quantitatively using the linear regression equations obtained by plotting its calibration curve over CR concentrations. The efficiency of CR removal was determined at certain time intervals in the range of 0-17 min and the equilibrium was established after 15 min. The effect of pH on CR adsorption was studied by adjusting pH of dye solutions (25 mg L^{-1}) in the pH range of 2-8 using 0.1 g L^{-1} of Au-NP-AC for 9.5 min, while the initial pH of solution was adjusted by addition of HCl or NaOH. Dye adsorption experiments were also accomplished to obtain isotherms in the range of $10\text{-}40 \text{ mg L}^{-1}$ CR concentrations.

The amount of dye adsorbed on adsorbent (q_e (mg g^{-1})) was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e) V/W, \quad (1)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium dye concentrations in solution, respectively, V the volume of the solution (L) and W is the mass (g) of the adsorbent.

Preparation of Au-NP-AC

The Au nanoparticles were synthesized in a one-step reduction process in an aqueous solution. In a typical preparation, a $200 \mu\text{L}$ aliquot of a $0.05 \text{ M HAuCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution was added into 50 mL of an aqueous solution containing $0.2 \text{ wt } \%$ of the soluble starch and vigorously stirred for 1 h . The pH of resulting solution was adjusted to desired values by adding a 0.05 M NaOH solution. After about 1 h the solution turned light pink, which indicated the initial formation of the Au nanoparticles. The mixture was maintained at $70 \text{ }^\circ\text{C}$ for 6 h and the color of the reaction solution became winy red.

Determination of the zero point charge pH (pH_{ZPC})

The pH corresponding to the point of zero charge, pH_{ZPC} for this new solid phase was determined by the final pH drift method previously reported elsewhere. The pH was adjusted to initial values between 2 and 8 by adding HCl or NaOH and the pH_{ZPC} of Au-NP-AC used for the adsorption experiment is determined by using solid to liquid ratio of 1:1000. For this, 0.05 g of Au-NP-AC is added to 50 mL of dye solution with varying pH from 2 to 8 and stirred for 15 min . The difference between the final pH and initial pH of the solution is plotted against the initial pH of the solution. The surface of the material is neutral when aqueous solution pH is equal to pH_{ZPC} . The surface is negatively charged at pH values greater than pH_{ZPC} , and positively charged at pH values lower than pH_{ZPC} (Kiefer *et al.*, 1997; Nandi *et al.*, 2009).

Result and discussion

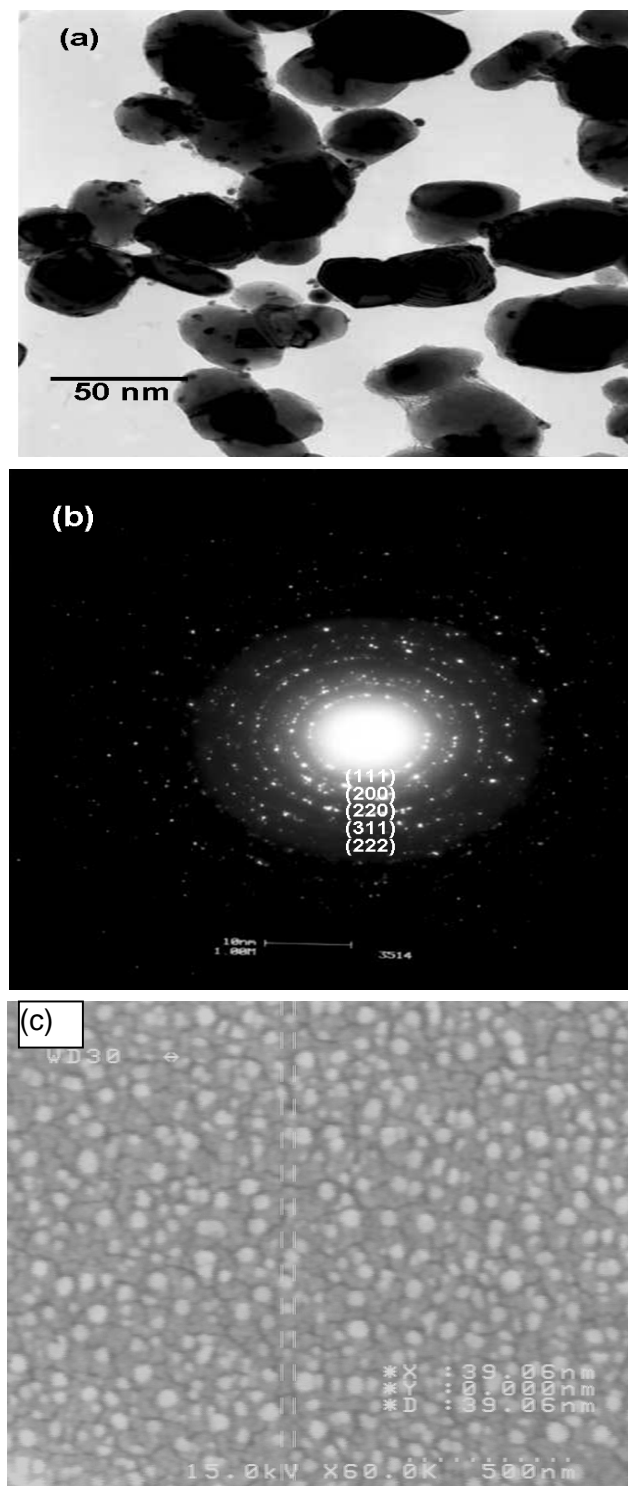
Characterization of adsorbent

Soluble starch can effectively reduce Au^{3+} ions into Au^0 upon the addition of a small amount of NaOH aqueous solution; both of visual observation and accurate UV-Vis determination confirmed this.

The reduction of Au^{3+} ions with starch aqueous solution at $70 \text{ }^\circ\text{C}$ leads to the formation of Au nanoparticles that are stable in solution for several months. This indicates that the soluble starch serves as both reducing and stabilizing agent.



Fig. 2. (a) Typical TEM image of the starch-stabilized Au nanoparticles, (b) The electron diffraction (ED) pattern of the Au nanoparticles and (c) FESEM image of the Au nanoparticles loaded activated carbon.



A typical TEM image of the Au nanoparticles is displayed in (Fig. 2a). As we anticipated from the FESEM image, the Au nanoparticles are observed with a relatively narrow particle size distribution (25-55 nm range). To clarify the exact crystal structure of the Au nanoparticles, electron diffraction (ED) measurements were carried out. The diffraction rings of the Au nanoparticles ED pattern (Fig. 2b) correspond well to the crystalline planes of the cubic structured Au, suggesting the nanocrystalline nature of these Au nanoparticles.

The rings in electron diffraction pattern can be assigned to the [111], [200], [220], [311], and [222] crystal planes of a face-centered-cubic (fcc) lattice structure of gold nanoparticles, respectively (Wang & Chen, 2008). The FESEM image of the Au nanoparticles (Fig. 2c) reveals the Au nanoparticles are semi-spherical in shape and quite uniform in size distribution (in the range of 20-60 nm) and agrees with that determined by the TEM image.

Effect of contact time

Equilibrium time is one of the most important parameters in the design of economical wastewater treatment system. The adsorption of dyes onto Au-NP-AC was studied as a function of contact time in order to determine the necessary adsorption equilibrium time. Rapid uptake and quick establishment of equilibrium time imply the efficiency of particular adsorbent in terms of usage in wastewater treatment. Fig. 3 shows the effects of contact time on adsorption of dye by Au-NP-AC and it was observed that the adsorption rate is rapid at the initial stages and then gradually increases with the progress of adsorption until the equilibrium is reached. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of Au-NP-AC and the slow rate of dye adsorption is probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent. It was found that more than 80 % of removal of CR occurred in the first 7.5 min and thereafter the rate of adsorption was found to be slow till up 98 % at 15 min.

Fig. 3. Effect of contact time on CR removal by 0.025 g of Au-NP-AC, pH 4, at room temperature and CR concentration 15 mg L⁻¹.

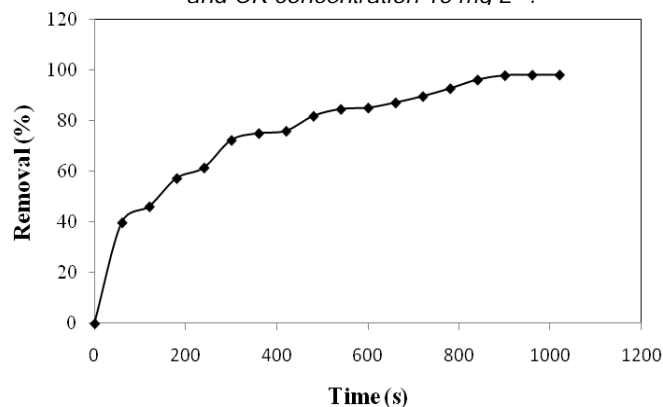
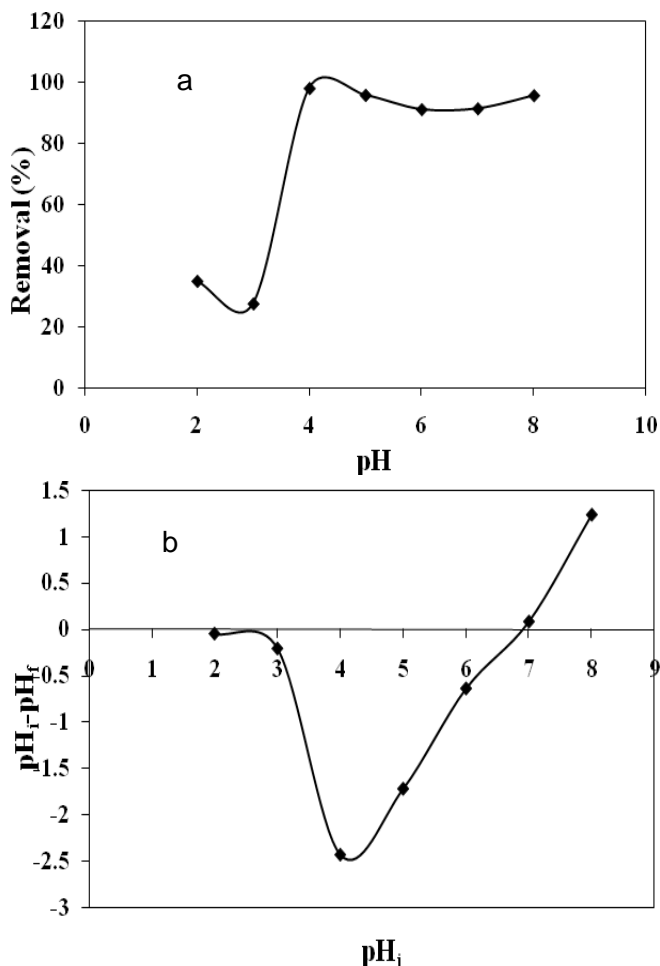


Fig. 4. (a) Effect of pH on the removal of CR by AuN-AC at room temperature, contact time of 15 min, adsorbent dosage of 0.025 g and dye concentration of 15 mg L⁻¹ and (b) pH_{ZPC} of gold nanoparticle loaded activated carbon (AuN-AC)



Effect of pH

The wastewater from textile industries usually has a wide range of pH values. Thus pH of the system plays an important role in the textile wastes treatment. The value of pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of initial pH on the adsorption of CR was studied in the pH range of 2 to 8 at room temperature at initial dye concentration of 15 mg L⁻¹, adsorbent dose of 0.025 g and contact time of 15 min and respective results are presented in (Fig. 4a). As it can be seen, the maximum uptake of the CR is obtained at pH of 4.0. It was observed, that the pH significantly affects the extent of adsorption of dye over the adsorbent and a decrease in the adsorption efficiency further this value was observed. At lower pH, probably surface of Au-

NP-AC has positive charge (protonation of functional group of Au-NP-AC in highly acidic solution) which favors the adsorption of CR over Au-NP-AC and lead to increase in adsorption.

The pH_{ZPC} of Au-NP-AC used for the adsorption experiment is determined as pH 2.0 and 7.0 (Fig. 4b).

Effect of adsorbent dosage

One of the most critical parameter for rapid and efficient dye removal is size and amount of adsorbent which must be optimized. The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. The effect of adsorbent dose on the dye removal percentage is shown in Fig. 5a. It was observed that initially the removal percentage increased rapidly with the increase in adsorbent dose till 0.025 g and after the critical dose the removal percentage almost reached a constant value. This can be attributed to increased adsorbent surface area and availability of more adsorption sites with the increasing dosage of the adsorbent, while the adsorption density of dye decreased with increase in adsorbent dosage. Therefore, for subsequent work 0.025 g of Au-NP-AC has been selected.

Effect of temperature

Various textile dye effluents are produced at relatively high temperature; therefore temperature influence as an important factor for the real application of the Au-NP-AC as adsorbent for CR removal must be investigated. In to determine whether the ongoing CR adsorption process on Au-NP-AC was endothermic or exothermic in nature, a set of similar experiments were carried out in the temperature range of 283.15-333.15 K at constant initial dyes concentration of 25 mg L⁻¹ in pH of 4.0, adsorbent dose of 0.025 g and contact time of 15 min and results are presented in Fig. 5b. Results show that the adsorption of CR increased with an increase in temperature that indicates the process is endothermic and can be explained by the endothermic spontaneity of the adsorption process.

Effect of initial dye concentration on adsorption of CR

Effect of CR initial concentration on the efficiency of its adsorption was investigated in range of 10 to 40 mg L⁻¹ and results are shown in Fig. 5c. It was seen that the CR adsorption efficiency increases with increase in its concentration and tends to attain saturation at higher concentrations. Although, by increasing the initial dye concentration the percentage of dye removal decreased, the actual amount of dye adsorbed per unit mass of Au-NP-AC increased.

In the process, the CR molecules have to first encounter the boundary layer effect and then diffuse from boundary layer film onto adsorbent surface and finally diffuse into the porous structure of the adsorbent that will take relatively longer contact time. On the other hand, the percentage removal of dye was higher at lower initial dye concentrations and smaller at higher initial concentrations, which clearly indicate that the adsorption of CR from its aqueous solution was dependent on its initial concentration. For subsequent analysis the initial concentration of CR was adjust at 15 mg L^{-1} .

Adsorption equilibrium study

Adsorption isotherms are prerequisites to understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants. Successful application of the adsorption technique demands studies based on various adsorption isotherm models (Mittal *et al.*, 2009) because adsorption isotherm models clearly depict the relationship of amount adsorbed by a unit weight of adsorbent with the concentration of adsorbent remaining in the medium at equilibrium. There are many equations for analyzing experimental adsorption equilibrium data. The equation parameters of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent for adsorbate.

The parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and the three important isotherms, the Langmuir, Freundlich and Temkin isotherms are applied in this study.

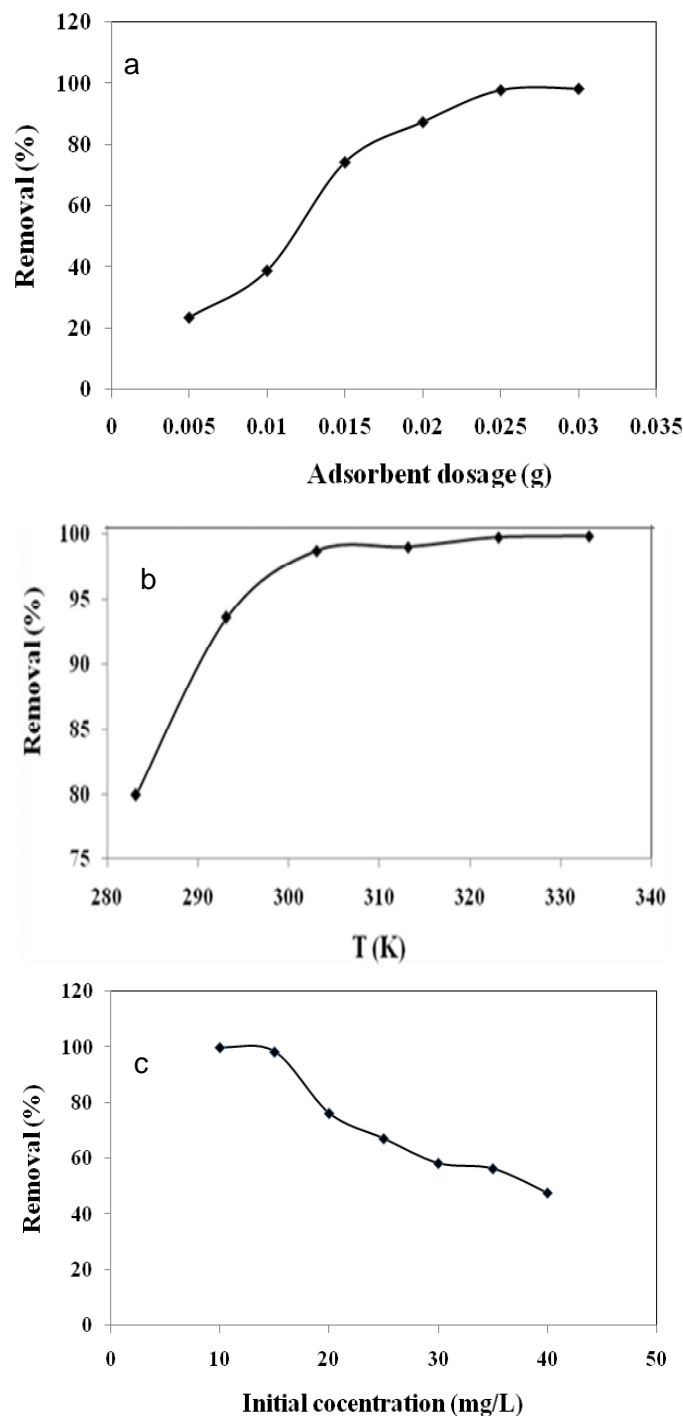
Langmuir isotherm: The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature.

The Langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites with negligible interaction between adsorbed molecules, is represented in the linear form as follows (Langmuir, 1916; Amin, 2009):

$$C_e/q_e = 1/k_L Q_m + C_e/Q_m \quad (2)$$

where K_L is the Langmuir adsorption constant (L mg^{-1}) and Q_m is the theoretical maximum adsorption capacity (mg g^{-1}). The value of Q_m and K_L constant obtained by The Langmuir plots (C_e/q_e vs. C_e) that these values and the correlation coefficient of this model is presented in Table 1. The isotherms of CR on Au-NP-AC was found to be linear over the whole concentration range studies and the correlation coefficients were extremely high ($R^2 > 0.99$) as shown in Table 1.

Fig. 5. (a) Effect of AuN-AC dosage on CR removal at dye concentration of 15 mg L^{-1} in 200 mL, at pH 4 and room temperature, (b) Effect of temperature on removal of CR at 0.025g of AuN-AC, pH 4, dye concentration of 15 mg L^{-1} and (c) Effect of initial dye concentration on removal of CR at 0.025 g of AuN-AC, pH 4 and room temperature



Freundlich isotherm: The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of sorption heat over the surface was

Table 1. Isotherm parameters and correlation coefficients calculated by various adsorption models onto 0.025 g of Au-NP-AC, pH 4, and room temperature.

Langmuir-1: $C_e/q_e = (1/K_a Q_m) + C_e/Q_m$	Q_m (mg g ⁻¹)	71.43
	K_a (L mg ⁻¹)	0.56
	R^2	0.992
Freundlich: $\log q_e = \log K_F + (1/n) \log C_e$	1/n	0.077
	K_F (L mg ⁻¹)	29.58
	R^2	0.909
Tempkin: $q_e = B_1 \ln K_T + B_1 \ln C_e$	B_1	2.176
	$K_T \times 10^{+5}$ (L mg ⁻¹)	11.84

presented in the linear form as follows (Freundlich, 1906):

$$\log q_e = \log K_F + 1/n_F \log C_e, \quad (3)$$

where K_F ((mg g⁻¹)/(mg L⁻¹)^{1/n}) is the Freundlich constant related to the bonding energy and can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent. The 1/n_F factor is heterogeneity factor and n_F is a measure of the deviation from linearity of adsorption, which its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of $n = 1$, the adsorption is linear; $n < 1$, the adsorption process is chemical; if $n > 1$, the adsorption is a favorable physical process (Crini *et al.*, 2007). Slope and intercept plot of $\log(q_e)$ versus $\log(C_e)$ indicate the value of K_f and the slope of 1/n_F (Table 1). As it can be seen Freundlich is unsuitable model for interpreting whole isotherm interpretation.

Tempkin isotherm: Heat of adsorption and the adsorbent-adsorbate interaction on adsorption isotherms were studied by Tempkin and Pyzhev (Tempkin & Pyzhev, 1940) and its equation is given as:

$$q_e = RT/b \ln(K_T C_e). \quad (4)$$

Eq. (4) can be linearized as:

$$q_e = B_T \ln K_T + B_T \ln C_e, \quad (5)$$

where $B_T = RT/b$, T is the absolute temperature in K, R the universal gas constant, 8.314 Jmol⁻¹ K⁻¹, K_T the equilibrium binding constant (L mg⁻¹) and B_T is related to the heat of adsorption. Values of B_1 and K_T were calculated from the plot of q_e against $\ln C_e$ (Table 1). Low correlation coefficient of this model show it's inapplicably for total isotherm analysis of data.

Kinetic study

The rate as well as mechanism of adsorption process can be elucidated on the basis of kinetic study (Rengaraj *et al.*, 2004; Anayurt *et al.*, 2009). Dye adsorption on solid surface may be explained by two distinct mechanisms; (i) an initial rapid binding of dye molecules on the adsorbent surface followed by (ii) relatively slow intra-particle diffusion. The adsorption kinetic data were described by the Lagergren pseudo-first-order model that is the earliest

known equation describing the adsorption rate based on the adsorption capacity. The Lagergren equation is commonly expresses as follows (Sari, 2008):

$$dq_t/dt = k_1(q_e - q_t), \quad (6)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g⁻¹), k_1 is the rate constant of pseudo-first order adsorption (l min⁻¹). Integrating Eq. (6) for the boundary conditions $t=0$ to $t = t$ and $q_t=0$ to $q_t = q_t$ gives:

$$\log(q_e/q_e - q_t) = (k_1/2.303) t. \quad (7)$$

Eq. (9) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303) t. \quad (8)$$

By plotting the values of $\log(q_e - q_t)$ versus t to give a linear relationship from which k_1 and q_e can be determined from the slope and intercept (Table. 2). If the intercept dose not equal q_e then the reaction is not likely to be first-order reaction even this plot has high correlation coefficient. The variation in the rate of adsorption should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process.

Experimental data show high degree of nonlinearity and poor correlation coefficients for pseudo first-order model. The adsorption kinetic may be described by the pseudo-second order model (Lagergren, 1898), which is generally given as following:

$$dq_t/dt = k_2(q_e - q_t)^2, \quad (9)$$

where k_2 (g mg⁻¹ min⁻¹) is the second-order rate constant of adsorption. Integrating Eq. (9) for the boundary conditions $q_t=0$ to $q_t = q_t$ at $t=0$ to $t = t$ is simplified as can be rearranged and linearized to obtain:

$$(t/q_t) = 1/k_2 q_e^2 + 1/q_e(t). \quad (10)$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following Eq.:

$$h = k_2 q_e^2. \quad (11)$$

It was mentioned above that the curve fitting plots of $\log(q_e - q_t)$ versus t (Table. 2) does not show good results for the entire sorption period, while the plots of t/q_t versus t give a straight line confirming the applicability of the pseudo-second-order equation. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t , respectively. The values of R^2 and q_e also indicated that this equation produced better results (Table 2). R^2 values for pseudo-second-order kinetic model were found to be high (0.993), and the calculated q_e values are mainly near to the experimental data. This indicates that the CR -Au-NP-AC adsorption system obeys the pseudo-second-order kinetic model for the entire sorption period. Transportation of the dyes from the solution phase into the pores of the adsorbent may also be considered as the rate controlling stage in batch experiments under rapid stirring condition.



Another alternative method for kinetic evaluation of an adsorption process is intra-particle-diffusion model that is based on the phenomena that dye adsorption on sorbent material take place through four steps: (a) migration of dye molecules from bulk solution to the surface of the adsorbent through bulk diffusion, (b) diffusion of dye molecules through the boundary layer to the surface of the adsorbent via film diffusion; (c) the transport of the dye molecules from the surface to the interior pores of the particle occur through intra-particle-diffusion or pore-diffusion mechanism and (d) the adsorption of dye on the surface of material by chemical reaction via ion-exchange, complexation and/or chelation.

If the adsorption experiment is a batch system with rapid stirring, there is a possibility that the transport of sorbate from solution into pores (bulk) of the adsorbent is the rate-controlling step (Ho, 1998). This possibility was tested in terms of a graphical relationship between the amount of dye adsorbed and the square root of time (Mall *et al.*, 2005). The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model as:

$$q_t = k_{id}t^{1/2} + C. \quad (12)$$

In this equation K_{dif} ($mg\ g^{-1}\ min^{-1/2}$) is the intra-particle diffusion rate constant. The values of K_{dif} were calculated from the slopes of q_t versus $t^{1/2}$. C is the intercept which is related to the thickness of the boundary layer i.e., the larger intercept the greater is the boundary layer effect and their obtained value is reported in Table. 2. The deviation of straight lines from the origin may be because of the difference between the rate of mass transfer in the initial and final stages of adsorption.

It was reported that if the intraparticle diffusion is the sole rate-limiting step, it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin that means if the value of C was equal to zero, indicating that the intraparticle diffusion model may be the controlling factor in determining the kinetics of the process (Rengaraj *et al.*,

2004). The R^2 values given in Table 2 is far from the unity indicating not applicability of this model, which show that the rate-limiting step is not the intraparticle diffusion process, but the intraparticle diffusion model may be the controlling factor in determining the kinetics of the process.

The Elovich equation is another rate equation based on the adsorption capacity is given as follows (Basar, 2006; Mittal *et al.*, 2007; Senturk *et al.*, 2010);

$$dq_t/dt = \alpha \exp(-\beta q_t), \quad (13)$$

where α is the initial adsorption rate ($mg\ g^{-1}\ min^{-1}$) and β is the de-sorption constant ($g\ mg^{-1}$) during any one experiment. It is simplified by assuming $\alpha\beta \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (13) rewrite as followed:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t). \quad (14)$$

Plot of q_t versus $\ln(t)$ should yield a linear relationship if the Elovich is applicable with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The Elovich constants obtained from the slope and the intercept of the straight line which are reported in Table 2, show that the correlation coefficients R^2 is 0.976 for this model.

Thermodynamic study

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process (Chatterjee *et al.*, 2007; Sari & Tuzen, 2008). The variation of dye removal efficiency with respect to temperature can be explained by thermodynamic parameters, which were evaluated from following equations (Lagergren, 1898; Temkin & Pyzhev, 1940; Rengaraj *et al.*, 2004):

$$\Delta G = -RT \ln K, \quad (15)$$

Table 2. Adsorption kinetic parameters at different initial CR onto 0.025 g of Au-NP-AC in 50 ml at pH 7, room temperature and CR concentration of 15 mg L⁻¹

Model	Linear equation	Parameter (units and their criterion)	Parameter value
First-order kinetic	$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t$	$k_1 \times 10^{-3}$ q_e (calc) R^2	2.30 21.77 0.98
Second-order kinetic	$dq_t/dt = k_2(q_e - q_t)^2$	$k_2 \times 10^{-4}$ q_e (calc) R^2 h	1.59 34.50 0.99 0.19
Intraparticle diffusion	$q_t = k_{id}t^{1/2} + C$	K_{dif} C R^2	0.74 7.25 0.97
Elovich	$dq_t/dt = \alpha \exp(-\beta q_t)$	B α R^2	0.15 0.51 0.98
		q_e (exp)	29.38

Table 3. Thermodynamic parameters for adsorption of CR onto 0.015 g of Au-NP-AC in 50 ml at pH 7 and initial dye concentration of 15 mg L⁻¹

Adsorbent	C ₀ (mg/L)	Parameter	Temperature (K)					
			283.15	293.15	303.15	313.15	323.15	333.15
Carbon-Au	15	k _c	11.99	35.87	254.64	1901.67	2576.78	2277.33
		ΔG ⁰ (kJ/mol)	-5.85	-8.72	-13.96	-19.66	-21.10	-21.41
C ₀ (mg/L)			ΔS ⁰ (J/mol K)		ΔH ⁰ (kJ/mol)		E _a (kJ/mol)	S [*]
15			380.36		104.12		101.05	4.30×10 ⁻²⁰

where ΔG is the free energy change (kJ mol⁻¹), R is the universal gas constant (8.314 Jmol⁻¹ K⁻¹), K_o the thermodynamic equilibrium constant and T is the absolute temperature (K). Values of K may be calculated from the relation $\ln q_e/C_e$ vs. q_e at different temperatures and extrapolating to zero. The thermodynamic parameters are listed in Table 3. The negative ΔG values confirm the spontaneous nature and feasibility of the adsorption process. The ΔG values were decreased as the temperature was increased from 283.15 to 333.15 K, which is an indication of the physical adsorption nature of the process. The values of other parameters such as enthalpy change (ΔH), and entropy change (ΔS), may be determined from Van't Hoff equation:

$$\ln K = \Delta S/R - \Delta H/RT. \quad (16)$$

ΔH and ΔG⁰ can be obtained from the slope and intercept of Van't Hoff plot of $\ln K$ vs. $1/T$. The data are presented in Table 3. The positive value of ΔH suggested that the endothermic nature of adsorption while the positive value of ΔS indicated that the increasing randomness at the solid/solution interface during the adsorption of CR onto Au-NP-AC. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions. In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^{*}) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage (θ) as follows:

$$S^* = (1 - \theta)e^{-(E_a/RT)}. \quad (17)$$

The sticking probability, S^{*}, is a function of the adsorbate/adsorbent system under investigation, its value lies in the range 0 < S^{*} < 1 and is dependent on the temperature of the system. The parameter S^{*} indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinite. The surface coverage (θ) can be calculated from the following equation:

$$\theta = [1 - C_e/C_0]. \quad (18)$$

The activation energy and sticking probability were estimated from a plot of $\ln(1-\theta)$ vs. $1/T$. The activation energy, E_a, calculated from the slope of the plot was found to be kJ/mol for adsorption of CR onto Au-NP-AC.

Conclusion

The gold nanoparticle loaded activated carbon is identified to be an effective adsorbent for the removal of CR from aqueous solutions. It was observed that batch sorption using Au-NP-AC was dependent on parameters such as initial concentration of dye, time, pH, dose of adsorbent and type of dye. The equilibrium and kinetic studies were made for the adsorption of dyes from aqueous solutions onto CR. Adsorption parameters for the Langmuir, Freundlich and Temkin isotherms were determined and the equilibrium data were best described by the Langmuir model. The process is endothermic in nature and its kinetics can be successfully fitted to pseudo-second-order kinetic model. The results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate controlling step.

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