



Silver nanoparticles treated activated carbon as effective sorbent for the removal of acid Red 1 dye from aqueous media: Kinetic and equilibrium studies

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Silver nanoparticles (AgNPLs) impregnated onto activated carbon (AC) as an effective solid adsorbent has been used for the uptake of acid red 1 (AR) from aqueous solution. In acid medium at $pH \leq 4.0$, the removal of AR is found favourable than at $pH \geq 4.0$. The data approve well with Freundlich model and pseudo second-order kinetic. Adsorption capacity calculated from Langmuir is 107.5 mg/g. Thermodynamic activation parameters suggest endothermic and spontaneous process. Silver nanoparticles enhanced uptake of AR by AC. The liquid-film and intra-particle diffusion types examined the adsorption mechanism. Removal of AR from AC-AgNPLs surface carried out to illustrate the recapture of the adsorbent and adsorbate for the economic value of the remediation system. The solid phase extractor is excellent recovered for six consecutive sorption-adsorption round elucidate its rise reused.

Keywords: Acid red 1, Activated carbon, AgNPLs, Adsorption, Kinetics models

Water is very important in our daily life and polluted by the action of domestic and industrial wastes. The continuous increase of using synthetic dyes in textile industries may cause many problems¹ for the reproductive organs and develop toxicity and neurotoxicity², which necessitates their efficient removal from wastewater. The synthetic dyes are toxic and carcinogenic compounds; causes a dangerous harmful for human, animals and environment even at low concentrations³. Environmental pollution caused by organic dyes due to its formation of hazardous aromatic amines through metabolic action in animals and plants. In addition, when dye mixed with water prevents the penetration of sunlight and causes oxygen deficiency in water⁴. Remediation of dyes from aqueous solution by sorption is the most effective method⁵. This technique depends on the uptake of organic dyes from the aquatic system to a solid adsorbent to reduce the effluent percentage from aquatic medium.

Adsorption process is one of the most important mechanisms for remediation of dyes from aquatic system⁶. Therefore, the modification and development of solid adsorbent become necessary for the sorption of dye from the textile effluents. AC is the most

common and important adsorbent in the sorption of dyes from wastewater due to large surface area and adsorption capacity⁷. Several techniques used for remediation of organic pollutants from wastewaters have been reported as easy, effective fast and low-cost technique in water treatment field⁶⁻⁸. According to the versatility and effectiveness of AC used as public solid phase extractor in remediation process. Adsorption of acid red by AC prepared from some agriculture wastes such as poplar wood⁹, rice bran¹⁰ and palm kernel¹¹ were investigated.

Metal nanoparticles as efficient adsorbents used in remediation system because of unique properties and large surface area of nanoparticles^{12,13}. The nanoparticles impregnated onto AC as an effective and conventional material, which increases the number of active site and adsorption capacity. The nanoparticles of Fe_2O_3 immobilized on AC are more effective than free AC in the sorption of dyes from aquatic medium¹⁴. Silver nanoparticles (AgNPs) coated AC was used in the adsorption of methyl orange (MO) from water has been reported¹⁵. The preparation and characterization of nanosilver by reaction of Ag(I) with maltose sugar in presence of CTAB was studied¹⁶. The role of surfactants as a

capping agent in the preparation of nanosilver to increase the stability of silver sols and gave a better size of nanoparticles was investigated¹⁶.

In this work, studying the effect of nanosilver immobilized onto AC as efficiency sorbent in the sorption of acid red 1 from aquatic medium was investigated. Adsorption isotherm, kinetics model, thermodynamic parameters and intra-particle diffusion are studied to give the significant role in the remediation of organic dyes from aquatic system.

Experimental Section

Materials and reagents

The chemicals, solvent and reagents used in this work purchased from Merck and BDH. All aqueous solutions were prepared using doubly distilled water. Acid red 1 solution was prepared by diluting its stock solution. The preparation and characterization of silver nanoparticles and activated carbon loaded nanosilver were studied in the reported methods^{16,17}. The pH of the reaction medium was controlled by adding small portions of 0.1 mol dm⁻³ NaOH and 0.1 mol dm⁻³ HCl.

Instruments

Absorption determents were recorded using Perkin Elmer EZ-150 spectrophotometers. XRD patterns of the activated carbon, activated carbon loaded nanosilver before, and after adsorption, using a Bruker D8 advance X-ray diffraction was investigated. TEM and SEM photographs of the adsorbent were examined using a LEO 440i and JEOL, JEM-1011 instruments, respectively. The temperature of the reaction mixture was fixed, using Gallen Kamp Griffen, BGL 240 V series automatic thermostat. The determination of pH was done using a (ATC- G353) pH-meter.

Batching experiment

Adsorption of AR by AC-AgNPLs from aqueous solution was carried out at different optimal conditions. The effect of pH, time, temperatures, adsorbent dose and concentration of dye on the adsorption of AR were investigated. In an experiment run, the amount of adsorbent (10-50 mg) and the AR solution for the concentration range (10-50 mg/L) were added in conical flask. The pH (2.0-10.0) ranges were adjusted by using 0.1M HCl or 0.1M NaOH and completing the total volume up to 50 mL by adding second distilled water. The resulting solution was agitated (100-300 rpm) at temperature (15-35 °C) for time intervals (1-20 min.). The mixtures after reached

to the equilibrium time were separated using Whatmann No.1 filter paper and the final concentration of AR remains in the filtrate was determined by measuring absorbance at 520 nm.

The AR removal percentage (R %) and the amount of adsorbate adsorbed on AC-AgNPLs, q_e (mg/g) was illustrate by equations (1, 2) as follow:

$$\% \text{ removal} = 100 (C_o - C_e) / C_o \quad \dots (1)$$

$$q_e = (C_o - C_e) \times V / m \quad \dots (2)$$

where m (g) is the mass of solid adsorbent, V is the volume (L) of solution, and C_o and C_e are the initial and equilibrium concentrations of AR (mg/L).

The results were measured three times and the reported data is the average value with standard deviation = $\pm 4.0\%$.

Results and Discussion

Nanomaterials play a significant role in the remediation of the organic dyes and heavy metals from aquatic system and environments. Impregnation of nanosilver onto solid phase extractor such as activated carbon, silica gel, graphene increases its activity towards adsorption of organic dyes¹⁷⁻¹⁹. This is may be due to the unique properties of nanoparticles which increases the active sites and adsorption capacity of solid adsorbent. The individual properties of nanosilver in morphology have been expanded into a large scale of using in remediation studies. Integration of nanosilver with other substances is an effective technique for the modification of its applications. Nanosilver with small size was characterized by high surface area, which increases the efficiency between adsorbate and adsorbent.¹⁵ Activated carbon has an effective solid phase extractor in the adsorption of organic dyes from aquatic medium. Adsorption process is more effective tools in the remediation of organic dyes from aqueous solutions^{16,17}.

Characterization of AC-AgNPLs before and after sorption

It's interesting to investigate the capacity of AC immobilized with nanosilver for adsorption of AR from aqueous medium compared to AC. Nanosilver loaded on AC increases the surface area and active site of AC-AgNPLs than AC. Therefore, the removal percentage of AR from water by activated carbon loaded nanosilver is more than that free activated carbon. The X-ray patterns of activated carbon loaded nanosilver was investigated before and after adsorption of AR measured to indicate that, the AR

adsorbed on AC-AgNPLs (Fig. 1). Figure 1, shows that the decrease of peak intensity of activated carbon modified with nanosilver after adsorption than before adsorption, confirming that removal of AR by AC-AgNPLs.

TEM image for AC-AgNPLs before and after removal of AR was investigated (Figure 2 (a & b)). Figure 2b, shows that AR adsorbed on and the unequal distribution of the AR on atypical part of the AC-AgNPLs. Active site of nanosilver immobilized on activated carbon adsorbed AR. The removal of AR in presence AC-AgNPLs occurs in a short time and at $pH \leq 4.0$.

Removal study

The effect of pH plays a significant role on the sorption of dye onto solid phase extractor, which influences on the charged of surface adsorbent. The acidic and basic medium involved H^+ and OH^- which are adsorbed on the solid adsorbent and thus the sorption of ions or other species is influenced by pH of solution²⁰. The influence of pH on the removal of AR was carried out at $[AR] = 25 \text{ mgL}^{-1}$, $[AC-AgNPLs] = 20 \text{ mg}$, $T = 25 \text{ }^\circ\text{C}$, $t = 20 \text{ min}$, $\text{rpm} = 200$ for pH s range (2.0 –10.0). Figure 3 shows that the removal % of AR decreases when the pH values increase from 2.0 to 10. At highly acidic pH , the number of positive charge sites of adsorbent that causes the strong electrostatic attraction between positively charged AC-AgNPLs surface and negatively charged of anionic AR dye, which increases the sorption of dye²⁰. In alkaline solution, the removal % of AR decreases when pH increases, this may be due to the repulsion between OH^- ions of medium and anionic dye²⁰.

The effect of time in the sorption of AR by AC-AgNPLs from aqueous medium was studied. The

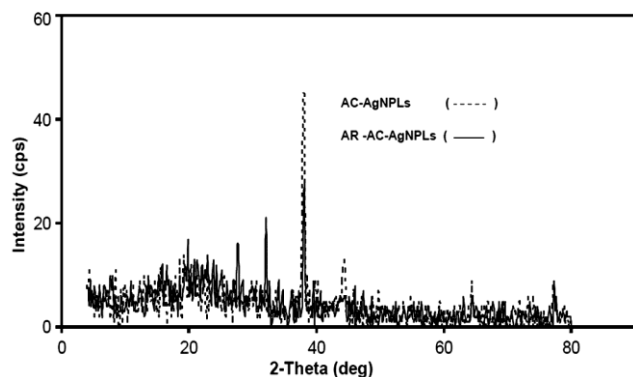


Fig. 1 — XRD spectrum of AC-AgNPLs (...) and AC-AgNPLs-AR (—)

removal% of AR increases from 45.0 to 98.0 % when the agitation times increase from 1.0 to 20.0 min. In the beginning, (1- 7min) the removal rate of AR was very high due to the excess active sites on the surface of AC-AgNPLs. After 20 min the adsorption of dye nearly remains constant. The contact time for removing AR to reach equilibrium was best found at 20 min. The removal % of AR is very slow at the final stage of agitation time due to decreasing the number of active sites which is agreement the previous study²¹.

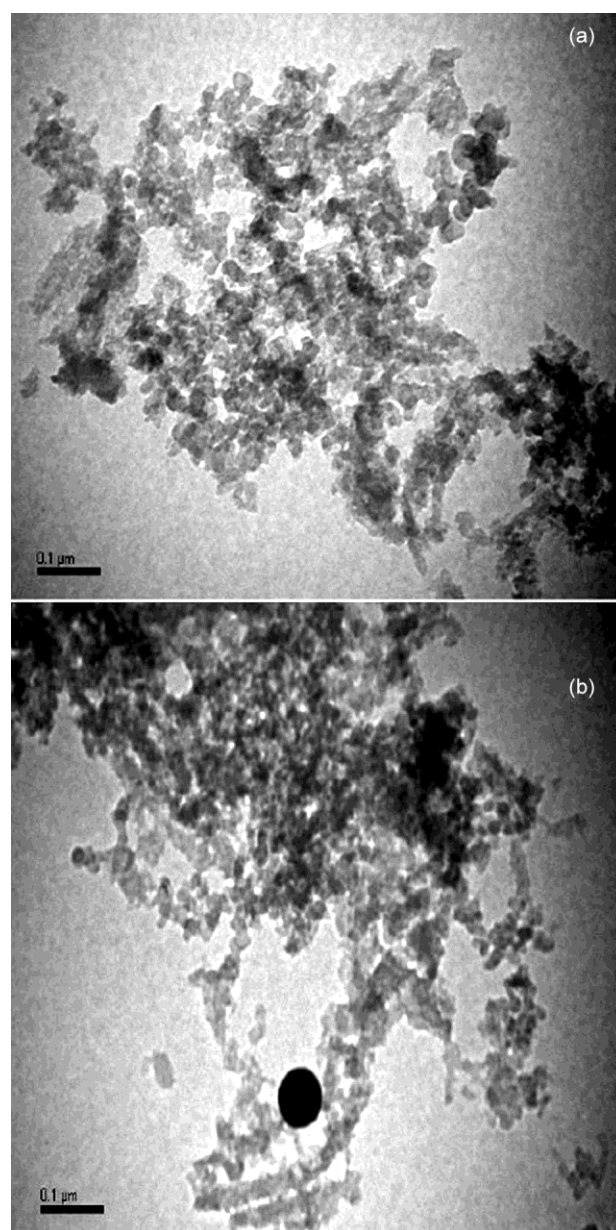


Fig. 2 — (a) TEM image of AC-AgNPLs and (b) TEM image of AR adsorbed onto AC-AgNPLs

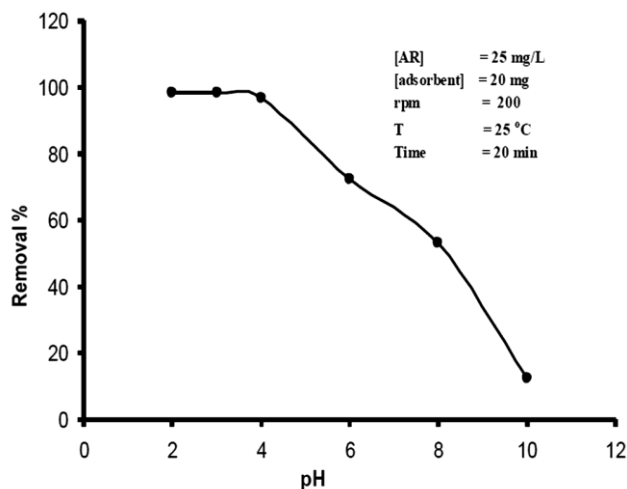


Fig. 3 — pH effect on the adsorption of AR

The role of rotation speed on the percentage of the adsorption of AR indicated that the removal percentage of AR is increased with increasing the rotation per min (rpm). The removal percentage was raised from 89 % to 99 % when the rotation speed increased from (100-300) rpm. The speed of rotation enhanced the distribution of adsorbate in the bulk of solution and the outside boundary layer²². The removal % of AR gradually increases up to reach a maximum value at 200 rpm, refers to strong mobility of medium and decreases the resistance of boundary film²³. Thus, we choice 200 rpm as optimum speed of rotation in the removal study.

It is evident that the dosage of the adsorbent has an effective role in the sorption of AR from aqueous medium. Influence of different quantities of AC and AC-AgNPLs on the removal % of AR is illustrated in Fig. 4. Figure 4, indicates that with the rise of the solid adsorbent dosage from 5.0 to 30 mg the removal % rise from 37.6 to 98.23 % and above 20 mg the removal % nearly kept unchanged. The high value of the removal % is explained by the existence of more availability active sites on the AC-AgNPLs and AC surface²⁰. Thus; the amount of adsorbent (20 mg) was used to be the suitable optimum dose of adsorbent for this work. This phenomenon can also be the amount of active sites on the surface of solid adsorbent, which act as the available surface and allow the highest AR adsorption²⁴. The removal percentage of AR by activated carbon loading nanosilver is higher than free activated (Fig. 4). This is may be the silver nanoparticles lead to the increase of the number of available active sites on activated carbon treated with nanosilver surface than free AC, which can give rise to the higher adsorption of AR²⁵.

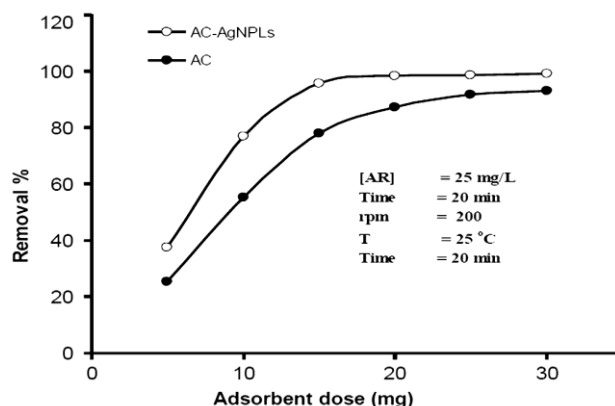


Fig. 4 — Effect of adsorbent dose on the removal of AR

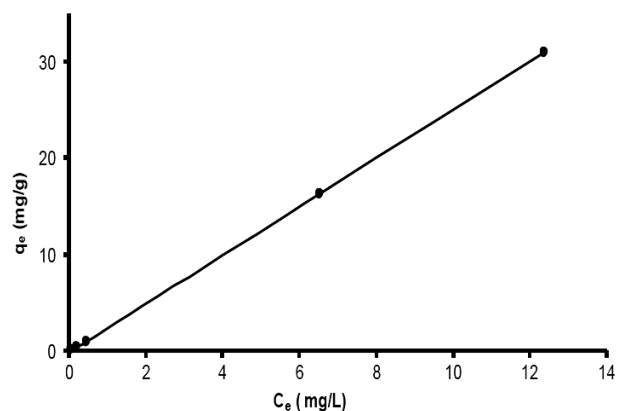


Fig. 5 — Plot of q_e versus C_e for removal of AR

The variation of dye concentration on the sorption % of AR from aqueous medium was investigated. It was found that the removal % of AR decreased from 99.23 to 75.26% with decreasing of [AR] from 5.0 to 50 mg/L. Because of the fixed amount of effective sites on the AC-AgNPLs surface to sorb is more than AR species.³² The adsorption capacity of AR into AC-AgNPLs was determined from the adsorption isotherm and has the value 49.2 mg of AR per one gram of AC-AgNPLs. Plot the adsorbed amount of AR per gram of adsorbent, q_e , against [AR] residue in the solution, C_e , illustrated in Fig. 5. The data in Fig. 5, indicates that increases of the q_e values when C_e increases, due to higher amount of effective sites on the solid adsorbent²². The uptake of AR is high due to the change of concentration as reported.²³

Equilibrium isotherm and kinetic study models for AR removal by AC-AgNPLs

Freundlich isotherm assumes that the sorption process takes place through the multilayer adsorption mechanism and the capacity of adsorption is concerned to the concentration of AR dye at equilibrium.²⁶ Freundlich model is given by equation (3):

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad \dots (3)$$

where C_e is the equilibrium concentration of dye (mgL^{-1}), q_e is the adsorbed quantity of dye per gram of solid adsorbent (mgg^{-1}), n and K_f are Freundlich isotherm constants concerning to adsorption intensity and the adsorption capacity, respectively. Plot $\ln q_e$ vs. $\ln C_e$ is linear as represented in Fig. 6. K_f and n values were determined from intercept and slope of Fig. 6 and summarized in Table 1. Langmuir isotherm model was usually used for homogenous sorption, since AC-AgNPs surface and that once AR species cover the sites no further sorption will be occurring at that site, leading to the sorption process is monolayer.²⁷ The Langmuir isotherm model is given by equation (4):

$$C_e/q_e = 1/q_m K_L + 1/q_m C_e \quad \dots (4)$$

where q_m (Lmg^{-1}) and K_L (mgg^{-1}) are the Langmuir constants concerning to the adsorption energy and adsorption capacity, respectively. Plotting of C_e/q_e against C_e is linear as represented. The values K_L and q_m and were determined from the intercept and slope of Figure 7 and collected in Table 1. Table 1, shows that the linear regression (R^2) of the Freundlich model is more than Langmuir isotherm, this indicates that the Freundlich isotherm provides that a good model of the sorption system. Therefore, the AR dye sorption on

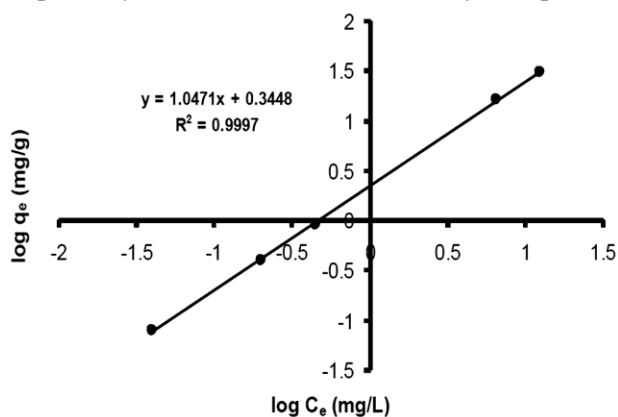


Fig. 6 — Freundlich isotherm graph for AR removal

Table 1 — Adsorption isotherm data for the sorption of AR on AC-AgNPLs

Isotherm model	Parameters	Unit	Values
Langmuir	K_L	L/g	0.02
	q_m	mg/g	107.5
	R^2		0.8564
	R_L		0.67
Freundlich	K_f	mg/g	2.21
	n	g/L	1.05
	R^2		0.9997

activated carbon loaded nanosilver occurs via a multilayer form. The fundamental characteristic of Langmuir isotherm can be determined by the dimensionless constant separation term (R_L) to detected high affinity adsorption as represented in equation (5):

$$R_L = 1 / (1 + K_L C_o) \quad \dots (5)$$

The R_L value clears that type of isotherm to be acceptable ($0 < R_L < 1$), unfavourable ($R_L > 1$), irreversible ($R_L = 0$) and linear ($R_L = 1$). From Table 1, it is noticed that R_L value lie between 0 and 1, clear that AR has been desirably adsorbed on activated carbon loaded nanosilver^{21,28}. Other workers in study of AR adsorption have reported similar data with activated carbon produced from agriculture waste and multiwall carbon nanotubes^{9,20,29}. The adsorption capacity for AR dye sorbed per unit weight of AC-AgNPLs from the aqueous medium in this work equal to 107.5 mg/g (Table 1). The comparison the adsorption capacity (q_m) of this work with other previous studies of various adsorbent for the adsorption of AR from aqueous medium is summarized in Table 2. Table 2, shows that AgNPLs

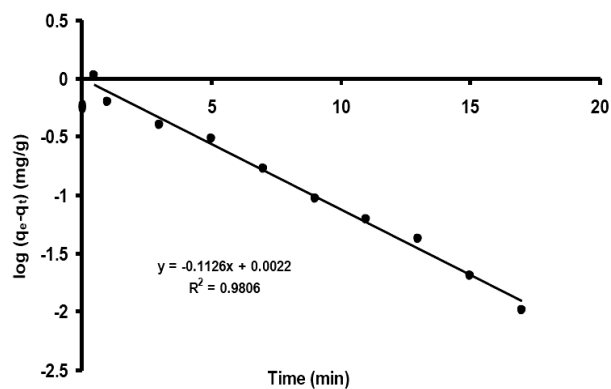


Fig. 7 — Pseudo first order kinetic model for AR removal

Table 2 — Comparison of the adsorption capacities (q_m) of AR onto AC-AgNPLs and other adsorbents

Adsorbent	q_m (mg/g)	Reference
AC-AgNPLs	107.5	This work
AC (Poplar wood)	3.91	Shokoohi (2010)
AC (Plast waste)	105.6	Manimekalai <i>et al.</i> (2015)
Chitosan-carbon nanotube	810	Chatterjee <i>et al.</i> (2009)
Kaolinite	29	Halak and Yaviz (2004)
Monotmorillonite	19	Halak and Yaviz (2004)
Granular AC	31	Hameed (2009)
Activated Plant(Biomass eichorma crassipes)	112.3	Rajamohan <i>et al.</i> (2013)
Rice bran	0.06	Hashemian <i>et al.</i> (2008)
Palm Kernel	38.6	Ofomaja and HO (2007)

treated AC has a higher adsorption capacity than other adsorbents. This comparison shows the importance and role of nanosilver in the adsorption of AR by activated carbon loaded nanosilver from aqueous medium.

The dynamics of sorption represent the way of controlling the efficacy of the removal process and the equilibrium time of the removal of AR onto AC-AgNPLs. In this process, three kinetics models included pseudo first, second-order and intra-particle diffusion models were investigated to identify the rate of the sorption of AR on AC-AgNPLs under optimum condition. Pseudo-first order kinetic model can be calculated using Lagergren Equation³⁰:

$$\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad \dots (6)$$

where; K_1 is the pseudo first-order rate constant ($\text{gm g}^{-1} \text{min}^{-1}$) and q_e and q_t are the amounts of adsorbate (mg/g) at equilibrium and at time t (min.), respectively. Plotting of $\log (q_e - q_t)$ against t , is linear with intercept as illustrated in Fig. 7. Values of q_e and K_1 were calculated from the intercept and slope of Fig. 8 as shown in Table 3. The pseudo-second-order kinetic is expressed by the following³¹:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad \dots (7)$$

where; K_2 = pseudo second-order kinetic ($\text{gm g}^{-1} \text{min}^{-1}$).

Plotting of t/q_t vs. t is linear with intercept as shown in Fig. 8. The values of q_e and K_2 were

Table 3 — Kinetic parameters for the removal of AR by AC-AgNPLs.

Kinetic model	Parameters	Values
Pseudo-first-order	q_e (mg/g)	1.0
	K_1 (min^{-1})	0.26
	R^2	0.9806
Pseudo second-order	q_e (mg/g)	2.05
	K_2 (min^{-1})	0.62
	R^2	0.9991

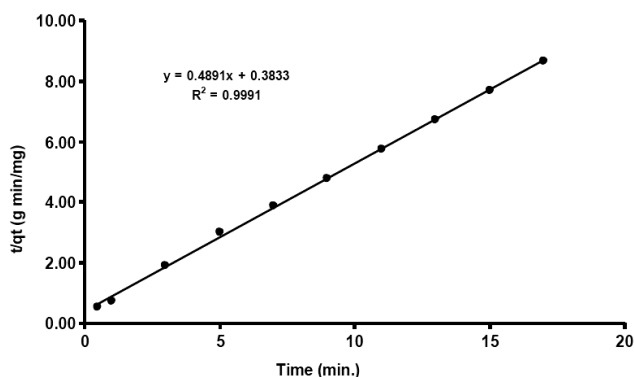


Fig. 8 — Pseudo second order kinetic model for AR removal

calculated from the slope and intercept of Fig. 8 as shown in Table 3. The linear regression for the pseudo-first-order kinetic model ($R^2 = 0.9806$) is lower than the linear regression for the pseudo second-order one ($R^2 = 0.9991$). This is clear that the pseudo-second-order kinetic model is favorable to express the sorption process of AR on AC-AgNPLs, suggesting that sorption process was controlled by chemisorptions²¹ as the previous studies on the adsorption of AR by solid adsorbents^{22, 23}.

Interpretation of the mechanism of AR sorption by AC-AgNPLs, the kinetic results had a furthermore treatment by intra-particle diffusion model equation (8)³²:

$$q_t = k_{\text{diff}} t^{1/2} + C \quad \dots (8)$$

where; k_{diff} is the diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C is the intercept. Plotting of q_t vs. $t^{1/2}$ not linear for full time with correlation coefficient ($R^2 = 0.8657$) and values of k_{diff} and C were calculated from slope and intercept of Figure 9 as 0.27 ($\text{mg/g min}^{1/2}$) and 0.99 mg/g , respectively. The Value of an intercept (C) gave an interpretation about the boundary layer thickness. When the adsorption mechanism obeys the intra-particle diffusion, plotting q_t vs. $t^{1/2}$ is linear passes into origin therefore, intra-particle diffusion is rate determining step furthermore the sorption process occurs by the film diffusion controls. Figure 9 plot is not giving a straight line over the whole time, shows that there are more than one model of adsorption controlling in the sorption of AR. From Fig. 9, it has noticed that there are two parts—the first section is refers to diffusion film and the second one is assign to the intra particle diffusion. Therefore, that the intra particle diffusion is not only the rate controlling steps but also some other mechanism might involve.

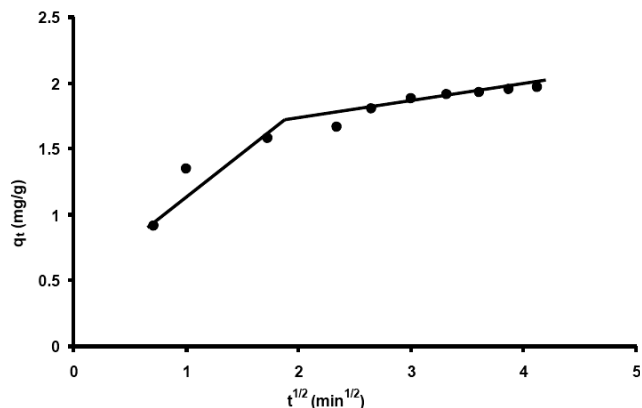
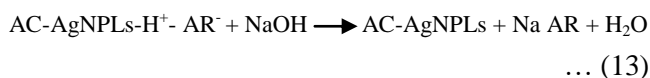


Fig. 9 — Plot of q_t vs. $t^{1/2}$ for AR removal

From the effect of pH in acid and alkaline medium and other parameters, the proposed mechanism of the sorption and desorption of AR was investigated. Formation of AgNPLs by the reduction of Ag^+ using maltose (R-CHO) as reducing agent in aqueous micellar media was investigated (Eq. 9)¹⁶. Nanosilver loaded into AC by impregnation process (Eq. 10). In acid medium the protonation of solid adsorbent, AC-AgNPs, occur to give AC-AgNPLs- H^+ . The sorption of AR on AC-AgNPLs take place through the strong electrostatic attraction between the positively charged AC-AgNPLs- H^+ and anionic AR. From the previous argumentation, the sorption and desorption mechanism of AR is illustrate by equations. (9 – 13):



The de-sorption operation of AR^- by sodium hydroxide is illustrated by Eq. (13):



Temperature effect

The role of temperature on the remediation process is the most important parameter that the effect of dye uptake by solid adsorbent. Thus, in separate batch experiments the effect of solution temperature at a wide range (15-35°C) on AR extraction, clear that the AR uptake increased with the elevation of temperature supported the endothermic process of AR adsorbed. The change of temperature from 15°C to 35°C, the removal percentage of AR is raised from 96.4 % to 99.2 %. This is attributed to the mobility of AR inside pores of AC-AgNPLs and through the outer boundary layer increases with elevation of temperature, which leads to the most penetration of AR across the inside structure of the solid adsorbent by the bulge effect.

The thermodynamic values of the sorption of AR by AC-AgNPLs were performed for a temperature range (288-308 K). The enthalpy of activation, ΔH° , the entropy of activation, ΔS° , and free energy change, ΔG° , can be determined using the equations (14-16):

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad \dots (14)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots (15)$$

$$K_d = q_e/C_e \quad \dots (16)$$

Table 4 — Thermal parameters of the AR adsorption onto AC-AgNPLs.

Temp. (K)	$\ln K_d$	ΔG° (kJ/mol ⁻¹)	ΔH° (kJ/mol ⁻¹)	ΔS° (J/mol ⁻¹ .K)
288	4.22	-10.00		
293	4.59	-11.20		
298	4.92	-12.77	58.4	237.5
303	5.42	-13.56		
308	5.77	-14.75		

where, K_d is the equilibrium constant for adsorption, R is the general gas constant and T is the absolute temperature. Plotting of $\log K_d$ vs. $1/T$ gave a straight line according to linear equation: $y = mx + c$ with linear regression ($R^2 = 0.9951$) at the temperature study. The thermodynamic values for the sorption of AR by AC-AgNPLs were determined from the intercept, slope $\ln K_d$ against $1/T$, and illustrated in Table 4. The positive values of ΔH° confirmed the endothermic nature of interaction between AR and AC-AgNPLs. The entropy of activation ΔS° determines the disorderliness of the sorption of solid-liquid interface.³³ Negative value of ΔG° , indicates that the spontaneous nature for the adsorption process. Higher temperature leads to the strong interaction between the active sites and adsorbent of the AC-AgNPLs, which gives a high AR sorption. ΔG values shifted from -10.0 kJmol⁻¹ to more negative value (- 14.75 kJmol⁻¹) from 288 to 308 K, reveals the adsorption to be more favourable at higher temperature.

Regeneration and reusability studies

Desorption process was carried out to elucidate the efficiency of solid adsorbent for adsorption of AR from aqueous medium. The regeneration and reusability of adsorbent in the adsorption and desorption of AR from the aqueous medium at the same optimum condition using 0.01N NaOH was investigated. The data indicate that the removal % of AC-AgNPLs is almost the same after six sorption–desorption cycles. Consequently, the AC-AgNPLs is the best reusable adsorbent for the adsorption of AR from aquatic medium.

Conclusion

Activated carbon loading nanosilver has been used for removal of AR. Silver nanoparticles increase activity for the adsorption of AR from aqueous medium. Nanosilver increases the active site on the activated carbon surface and so; uptake of AR by AC-AgNPLs is very high. Adsorption capacity value of AR is found to be 107.5 mgg⁻¹. The experimental data confirm well Freundlich isotherm model with pseudo

second-order kinetic. Positive values of ΔH° confirm the endothermic process of interaction between AR and AC-AgNPLs. Removal percentage of AR from aqueous solution by AC-AgNPLs is more than AC. Indeed, the developed AgNPLs-treated AC could be utilized for routine pre-concentration and /or separation of AR in natural water. The adsorption mechanism has been examined and obeys the liquid-film and intra-particle diffusion models. The adsorbent, AC-AgNPLs, is successfully completed recycled for six consecutive sorption-desorption round elucidate its highly reused.

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