

Adsorption of Picric Acid onto Granular Activated Carbon from Aqueous Solution: Parametric, Kinetic, Equilibrium and Thermodynamic Study

Praveen Kumar D.G¹, Kalleshappa C.M² and Aravinda H.B³

¹Assistant Professor, Department of Chemical Engineering, Bapuji Institute of Engineering and Technology, Davangere-Karnataka, India.

²Associate Professor, Department of Chemical Engineering, Bapuji Institute of Engineering and Technology, Davangere-Karnataka, India.

³Professor and Head, Department of Civil Engineering, Bapuji Institute of Engineering and Technology, Davangere-Karnataka, India.

Abstract: The present study aims to evaluate the influence of various experimental parameters viz., initial pH, adsorbent dose, contact time, initial concentration and temperature on the adsorptive removal of picric acid from aqueous solution by commercial grade granular activated carbon (GAC). Optimum conditions for picric acid removal were found to be $\text{pH}_0 \approx 3.8$, adsorbent dose ≈ 10 g/L of solution and equilibrium time 3.0 h. Picric acid adsorption onto GAC was found to be best represented by the Redlich-Peterson isotherm followed by Freundlich and Langmuir isotherm. The positive values of the change in entropy (ΔS^0); and the negative value of heat of adsorption (ΔH^0) and change in Gibbs free energy (ΔG^0) indicated feasible, exothermic, and spontaneous nature of picric acid adsorption onto GAC.

Keywords: Adsorption, picric acid, kinetics, isotherms, GAC

I. INTRODUCTION

An environmental problem is the presence of nitrophenols in wastewater streams. Nitrophenols are usually found in effluent wastes from explosive industries, textile industries, and photodegradation of pesticides, and so forth [1, 2]. Adsorption studies of phenols, nitrophenols and some of their derivatives from aqueous solutions using different adsorbents are well-documented [3, 4 and 5]. Among the nitrophenols, picric acid (2, 4, 6-trinitrophenol), which is synthesized with inherent stability until detonation, has been used in naval ordnance and was common in many other types of ordnance in the early part of this century [6, 7].

Due to the various applications of picric acid in dyes, explosives, analytical reagents, germicides, fungicides, tissue fixatives, photochemicals, and pharmaceuticals as well as for the oxidation and etching of iron, steel, and copper surfaces [8], it could enter the water table or environment and affect the health of humans because picric acid is toxic even at low concentrations [9, 10].

Exposure to picric acid dust and fume may cause eyes and skin irritation. The skin and hair maybe stained yellow. Inhalation of high concentration of dust has caused unconsciousness, weakness, muscle pain, and kidney problems. Swallowing picric acid may cause headache, dizziness, nausea, vomiting and diarrhea. High doses may causes disturbance of the red blood cells and damage to the kidneys and liver with blood in the urine [11].

On the other hand, the World Health Organization (WHO) reported 0.001 mg/L as the permissible phenolic concentration in potable water [12]. In addition, US Environmental Protection Agency issued a permissible limit of 0.1 mg/L in wastewater [13]. Because of these reasons, a systematic study on the removal of picric acid from wastewater is of considerable significance from an environmental point of view. Several methods have been proposed in literatures on techniques for removal of phenolic compounds from wastewater such as photocatalytic, microbial degradation, chemical-biological oxidation and catalytic oxidation process [14, 15, 16, and 17].

The adsorption process is one of the major methods for the removal of phenols, nitrophenols and some of their derivatives from aqueous solutions [18]. The potential of commercial grade granular and powdered activated carbon have been proven as an effective adsorbent used in adsorption technology over the century. It provides large surface area, high adsorption capacity and high degree of surface reactivity [19].

In this study, GAC is used for the adsorptive removal of picric acid from aqueous solutions. The GAC is characterized for its physicochemical characteristics. This study also reports the effect of operational factors such as solution pH (pH_0), adsorbent dose (m), initial concentration (C_0), contact time (t) and temperature (T) on the adsorption efficiency of picric acid from aqueous solutions onto GAC.

II. MATERIALS AND METHODS

2.1 Adsorbent and its Characterization

Commercial grade granular activated carbon (GAC) was purchased from Lobo Chemi Private Limited, Mumbai, India and was sieved using IS sieves (IS 437-1979). The size range of $-1000 +500 \mu\text{m}$ was used for the sorption of picric acid from the aqueous solutions. The physico-chemical characteristics of GAC were determined using standard methods. Proximate analysis of GAC was carried out using the standard procedure (IS: 1350-1984, part-I). Bulk density was determined using a MAC bulk density meter.

The structures of the different adsorbents were studied with the help of X-ray diffractometer (Rigaku Ultima IV, Japan). Field Emission scanning electron microscopy (FESEM) micrographs of GAC samples were obtained using scanning electron microscope (MIRA 3 TESCAN, USA). The specific surface area, total pore volume and mean pore diameter of the GAC particles were measured by nitrogen adsorption isotherm using Bellsorp II, Japan instrument by Brunauer–Emmett–Teller (BET) method using nitrogen as cold bath (77.15 K). The adsorption/desorption data analysis was carried out with Belsorp software-ver.6.4.0.0.

2.2 Adsorbate

Picric acid (2, 4, 6-Trinitrophenol) procured from Hi Media Laboratories Pvt. Ltd., Mumbai, India, was used as adsorbate. Stock solution of 1000 mg/L was prepared by dissolving accurate quantity of picric acid. Solution of required concentration was prepared by diluting the previously prepared stock solution with distilled water whenever required.

2.3 Analytical Measurement

The concentration of picric acid was determined by finding out the characteristic maximum absorbance wavelength using UV/VIS spectrophotometer (Schimadzu, UV-1800, Japan). A standard solution of known concentration was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined. The λ_{max} for picric acid is 355 nm. Calibration curve was plotted between the absorbance and the concentration of picric acid. Linear portion of this curve was used for determining the unknown concentration of picric acid solution.

2.4 Batch study

Batch experiments were conducted to study the effect of various parameters like adsorbent initial pH (pH_0), adsorbent dose (m), initial concentration (C_0), contact time (t) and temperature (T) on the adsorptive removal of picric acid by GAC. For performing an experimental run, 250 ml stoppered conical flask containing 100 ml of picric acid solution with known concentration (C_0), initial pH (pH_0) and adsorbent dose (m) were agitated at $303 \pm 1\text{K}$ in a temperature controlled orbital shaker (Remi- CIS 24 Plus, Mumbai) at a constant speed of 150 rpm. Samples were withdrawn from the shaker after appropriate time. These samples were filtered and analyzed for the residual picric acid concentrations.

Effect of pH_0 on removal picric acid was studied over a pH_0 range of 2 – 12. pH_0 was adjusted by addition of 0.1N H_2SO_4 or NaOH. The optimum dosage (m) was found by contacting different amounts of GAC with 50 mg/L picric acid solution till equilibrium was attained. For adsorption isotherms, picric acid solutions of $C_0 = 50 - 300 \text{mg/L}$ were agitated with a known amount of adsorbent (m) till equilibrium was achieved.

The effect of temperature on equilibrium adsorption was studied in the temperature range of 283 K - 323 K. Sorption equilibrium characteristics have also been studied. Various equilibrium isotherm (two and three parameters) equations viz. Langmuir, Freundlich, Temkin, and Redlich–Peterson (R–P) were tested for their applicability to represent the experimental sorption data. Thermodynamic studies were studied to understand the effect of temperature on the picric acid sorption, and to find out isosteric heat of adsorption. The percentage removal of adsorbate and the equilibrium adsorption uptake in solid phase, q_e (mg/g), were calculated as follows:

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

where q_e is equilibrium amount of adsorbate adsorbed (mg/g), C_0 is initial concentration of adsorbate in aqueous solution (mg/L), C_e equilibrium concentration (mg/L), V is volume of aqueous solution (L) and W is the weight of adsorbent (g).

III. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

The physico-chemical properties of GAC like, bulk density (mass per unit bed volume), BET surface area, total pore volume, mean pore diameter, moisture content, volatile matter, ash content, and fixed carbon were found to be 485.45 kg/m³, 258.42 m²/g, 0.213 cm²/g, 28.56 Å, 1.74%, 5.63%, 55.9%, and 36.71%, respectively. XRD pattern for GAC is shown in Fig. 1. The different peaks in the figure shows the presence of moganite [SiO₂], akdalaite [(Al₂O₃)₄·H₂O], tamarugite [NaAl(SO₄)₂·6H₂O], fersilicite [FeSi] and majorite [Mg₃(Fe,Al,Si)₂(SiO₄)₃] as major components in GAC. The broad peak in the XRD indicates the presence of amorphous form of silica.

The SEM micrographs as given in Fig. 2 (a) shows that the blank GAC has fibrous structure having large pore size with strands in each fiber and Fig. 2 (b) shows the SEM micrographs of the GAC loaded with picric acid. SEM at 2000X magnification does not show any difference in the texture of the blank and picric acid loaded GAC. It only shows that the GAC is crystalline in nature and with varying particle size. Blank GAC shows pore structure with pores of varying sizes. Numbers of pores observed in the loaded GAC are less as compared to that in blank GAC.

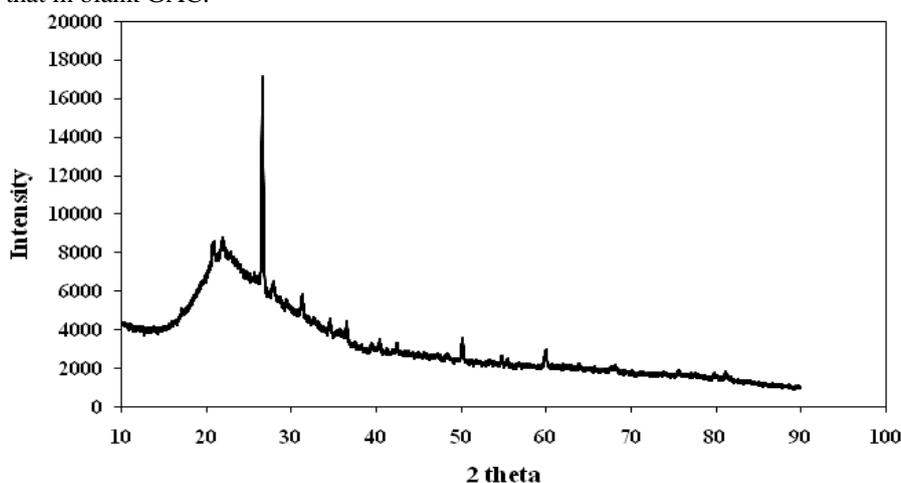
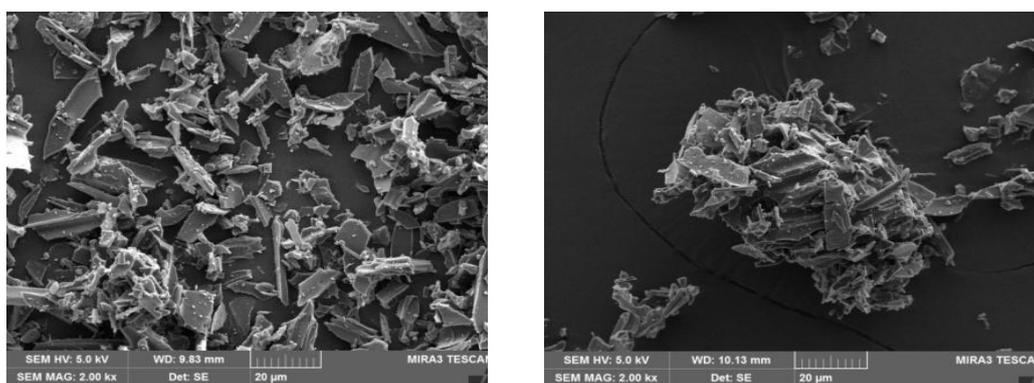


Fig. 1 X-Ray Diffraction of Blank of GAC.



(a)

(b)

Fig. 2 (a) SEM of Blank GAC, (b) Picric Acid Loaded GAC.

3.2 Effect of Initial pH (pH₀) of the Solution

Effect of pH₀ on the picric acid removal by GAC is shown in Fig. 3, for C₀ = 50 mg/L at 303 ± 1 K after 3 h of contact with m = 10 g/L. A maximum picric acid adsorption of ≈ 96% was found to occur at natural pH (pH₀ = 3.8) by GAC. The experimental results for adsorption in various pH suggested that there was an increase in the uptake of picric acid at a pH lower than 4 and decreases as the pH increase from 5 - 12. In other words, the solubility of picric acid diminishes as the pH value or H⁺ concentration decreases or increases, respectively, as the adsorption of phenolic compounds on activated carbon is inversely proportional to the solubility [20]. The picric acid dissociates to picrate anion at the higher pH values in which the surface functional groups are

either neutral or negatively charged. In these conditions, the electrostatic repulsion between the identical charges decreases the adsorption capacities. In addition, because picrate anions are more soluble in aqueous solution, the stronger adsorbate-water bonds must be broken before adsorption can occur [21, 22]. The further experiments were carried out with the natural pH of the solution.

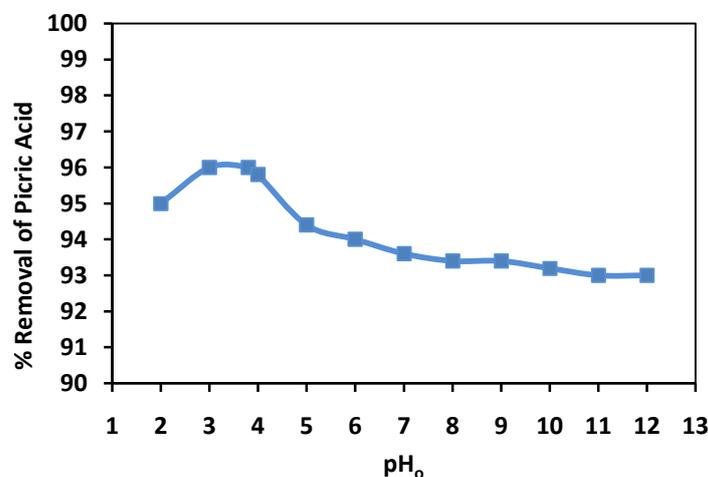


Fig. 3 Effect of Initial pH₀ of the Aqueous Solution on the Removal of Picric Acid by GAC. (T = 303 K, t = 3 hr, C₀ = 50 mg/L and m = 10 g/L).

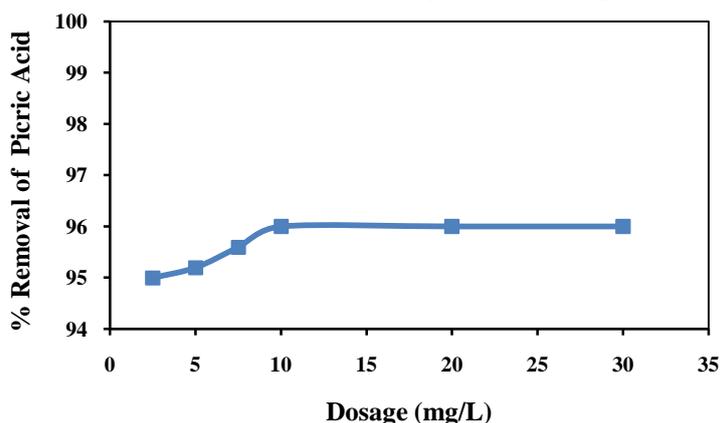


Fig. 4 Effect of Adsorbent Dose on the Adsorption of Picric Acid by GAC. (T = 303 K, t = 3.0 h, and C₀ = 50 mg/L).

3.3 Effect of Adsorbent Dose (m)

The effect of adsorbent dose (m) on the uptake of picric acid by GAC for C₀ = 50 mg/L is shown in Fig. 4. For GAC, the incremental picric acid removal for m between 2.5 g/L and 10 g/L is only marginal and beyond 10 g/L, the picric acid removal remains almost unaffected by the GAC dosage. An increase in the adsorption with an increase in the adsorbent dosage can be attributed to the increase in the availability of surface area of mesopores for adsorption and hence, the availability of more adsorption sites.

3.4 Effect of Initial Concentration (C₀) and Temperature

The effect of C₀ (50 - 300 mg/L) and temperature (283- 323 K) on the equilibrium uptake of picric acid by GAC at m = 10 g/L and t = 3 h was studied and a plot of the removal of picric acid and picric acid loading q_e versus C₀ with temperature as a parameter is given in Fig. 5. It is evident that the sorption of picric acid from the solution increases with an increase in C₀ and temperature. Picric acid removal is more than 73 % by GAC at the highest C₀ (300 mg/L) and for the lowest concentration C₀ (50 mg/L), 96 % of the removal is observed for all the temperature. It may, however, be noted that the picric acid loading onto GAC (i.e. q_e) increases with an increase in temperature. This means that the picric acid sorption capacity of the GAC increases significantly with an increase in C₀, but only weakly with an increase in temperature of the solution. This is attributed to the increase in the mass transfer driving force on account of an increase in C₀ [23, 24].

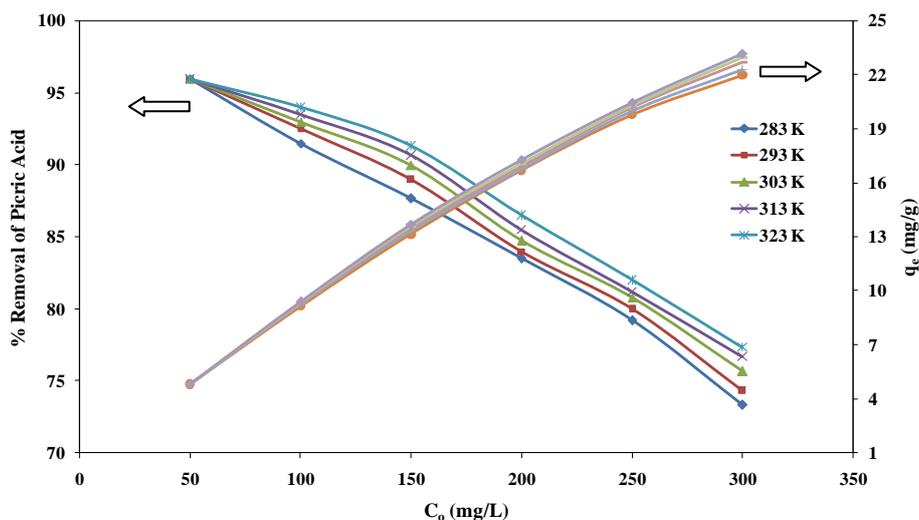


Fig. 5 Effect of C_0 and Temperature on the Removal of Picric Acid by GAC.
 ($m = 10 \text{ g/L}$, $\text{pH}_0 = 3.8$, $t = 3 \text{ h}$).

3.5 Effect of Contact Time and Kinetics of Adsorption

The effect of contact time on the removal of picric acid by GAC for $m = 10 \text{ g/L}$, for $C_0 = 50$ and 100 mg/L is shown in Fig. 6. Initially up to 1 hour, adsorption of picric acid was found to be increasing and thereafter, the adsorption rate decreased gradually. This was due to the fact that the adsorbates get adsorbed into the meso-pores during initial stages, thereafter, adsorbate have to travel deeper into the pores encountering larger resistance. This results in the slowing down of the adsorption during the later period of adsorption. The residual concentrations at 2 h contact time were found to be higher by a maximum of $\sim 1\%$ than those obtained after 3 h contact time. Therefore, after 3 h contact time, a steady state approximation was assumed and a quasi-equilibrium situation may be assumed. Accordingly all the batch experiments were conducted with a contact time of 3 h under vigorous shaking conditions.

3.6 Kinetics of adsorption

The rapid initial uptake is attributed to surface adsorption. When the picric acid adsorption at the exterior surface reached the saturation level, the picric acid begins to enter the pores of the adsorbents and is adsorbed at the interior surface of the adsorbent particles. The interior surface seems to be very active and has a very high affinity towards picric acid molecules. Hence, a very high uptake of picric acid by GAC was observed. As the surface saturates with picric acid molecules, the adsorption rate decreases due to an increase in the diffusion resistance as the molecules have to travel farther in to the interior pores. This means that at the later periods ($t > 1 \text{ h}$), the picric acid uptake is controlled by the micro pore diffusion.

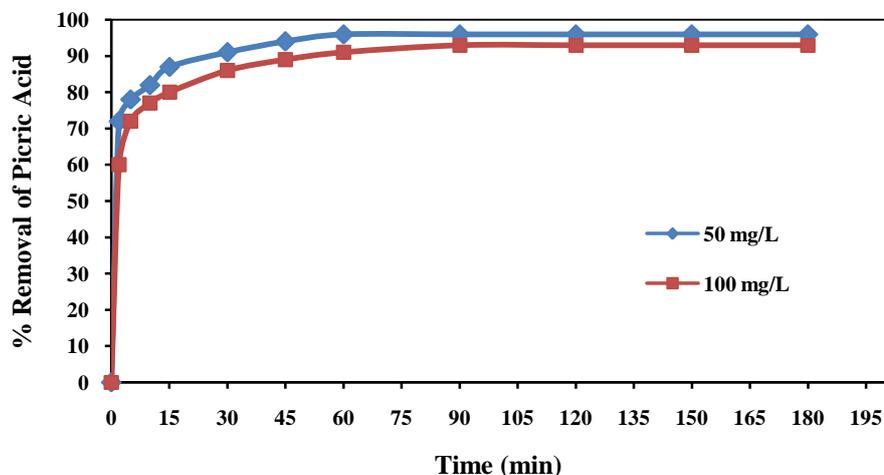


Fig. 6 Effect of Contact Time on the Removal of Picric Acid by GAC.
 ($C_0 = 50, 100 \text{ mg/L}$, $m = 10 \text{ g/L}$, $T = 303 \text{ K}$).

3.7 Adsorption equilibrium

Several equilibrium isotherm equations, namely, Langmuir [25], Freundlich [26], Temkin [27] and Redlich–Peterson [28], have been tested for their efficacy to represent the experimental sorption isotherm data. For low adsorbate loadings, Henry's law is valid. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [29]. The isotherm equations are explained by the following equations.

The Freundlich isotherm is given as $q_e = K_F C_e^{1/n}$ (2)

where, K_F is a constant indicating the adsorption capacity of the adsorbent (L/g) and $(1/n)$ is a constant giving the intensity of adsorption. These constants can be calculated from the plot of $\ln(C_e)$ versus $\ln(q_e)$.

The Langmuir isotherm is given as $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ (3)

where, q_m is the monolayer adsorption capacity (mg/g) and is a constant, and K_L is a constant related to the free energy of adsorption ($K_L = e^{-\Delta G/RT}$) and is the reciprocal of the concentration at which the adsorbent is half-saturated. C_e is the equilibrium liquid phase concentration (mg/L). A plot of either C_e/q_e versus C_e or the multiple regression fit of the equation with the experimental data enables the determination of the constants.

The Temkin isotherm is given as $q_e = B_T \ln K_T + B_T \ln C_e$ (4)

Where, $B_T = \frac{RT}{b}$ and is related to the heat of adsorption, b and K_T is the equilibrium binding constant

(L/mol) corresponding to the maximum binding energy. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants K_T and B_T .

The Redlich-Peterson isotherm is given as $q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$ (5)

Where, K_R (L/mg) and a_R (L/mg) are the R-P isotherm constants and β is the exponent which lies between 0 and 1.

Two different error functions of non-linear regression basin were employed in this study to find out the most suitable kinetic and isotherm models to represent the experimental data. The hybrid fractional error function (HYBRID) [30] and the Marquardt's percent standard deviation (MPSD) error function [31] have been used previously by a number of researchers in the field. These error functions are given as

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,\text{exp}} - q_{e,\text{calc}})^2}{q_{e,\text{exp}}} \right]_i \quad (6)$$

$$MPSD = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{(q_{e,\text{exp}} - q_{e,\text{calc}})}{q_{e,\text{exp}}} \right)_i^2} \quad (7)$$

Where, n is number of data points, P is number of unknown parameters, $q_{e,\text{exp}}$ is the experimental adsorption capacity (mg/g) and $q_{e,\text{calc}}$ is the adsorption capacity calculated by isotherm model (mg/g).

HYBRID was developed to improve the fit of the square of errors function at low concentration values. The MPSD is similar in some respects to a geometric mean error distribution modified according to the number of degrees of freedom of the system. The testing of the isotherm equations in correlating the experimental equilibrium sorption data for picric acid onto GAC are shown in Table 1. Fig. 7 shows the comparative fit of all the isotherms with the experimental data. It is found from the table by comparing the values of R^2 , HYBRID and MPSD values, and in Fig. 7 by comparing the experimental sorption data and isotherm equations data, the Redlich–Peterson equation followed by Freundlich and Langmuir equation best represented the experimental equilibrium sorption data.

Table 1. Isotherm Parameters and Error Analysis Values for the Adsorption of Picric Acid onto GAC ($C_0 = 50 - 300 \text{ mg/L}$, $m = 10 \text{ g/L}$, $t = 3 \text{ h}$, $\text{pH}_0 = 3.8$)

Isotherms	Constants	Temperatures (K)				
		283	293	303	313	323
Langmuir $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$K_L, \text{L/mg}$	0.071	0.077	0.079	0.083	0.089
	$q_m, \text{mg/g}$	25.641	25.641	26.316	26.316	26.316
	R^2 (Linear)	0.987	0.990	0.990	0.991	0.993
	R^2 (Non-Linear)	0.984	0.99	0.992	0.995	0.997
	HYBRID	2.198	2.759	1.777	2.447	2.296
	MPSD	18.264	15.505	13.907	12.16	9.74
Freundlich $q_e = K_F C_e^{1/n}$	$K_F, \text{L/mg}$	3.684	3.789	3.831	3.888	3.959
	n	2.370	2.358	2.320	2.299	2.283
	$1/n$	0.422	0.424	0.431	0.435	0.438
	R^2 (Linear)	0.995	0.99	0.987	0.983	0.976
	R^2 (Non-Linear)	0.998	0.995	0.994	0.991	0.988
	HYBRID	0.097	-0.011	-0.127	-0.348	-0.126
Temkin $q_e = (RT/b) \ln K_T C_e$	B	4.799	4.872	5.020	5.116	5.218
	$K_T, \text{L/mg}$	1.056	1.090	1.086	1.097	1.117
	R^2 (Linear)	0.974	0.983	0.987	0.99	0.994
	R^2 (Non-Linear)	0.987	0.992	0.994	0.995	0.997
	HYBRID	1.443	1.899	1.749	1.644	1.316
	MPSD	15.496	12.312	11.046	9.386	7.224
Redilich-Peterson $q_e = \frac{K_R C_e}{1 + \beta K_R C_e}$	$\beta, \text{L/mg}$	2.032	1.970	1.943	1.908	1.863
	$K_R, \text{L/mg}$	10	10	10	10	10
	β	0.643	0.641	0.635	0.632	0.629
	R^2 (Linear)	0.999	0.998	0.997	0.995	0.992
	R^2 (Non-Linear)	1.000	0.999	0.999	0.998	0.996
	HYBRID	-0.233	-0.389	-0.185	-0.190	-0.485
MPSD	2.901	3.463	4.519	5.615	7.166	

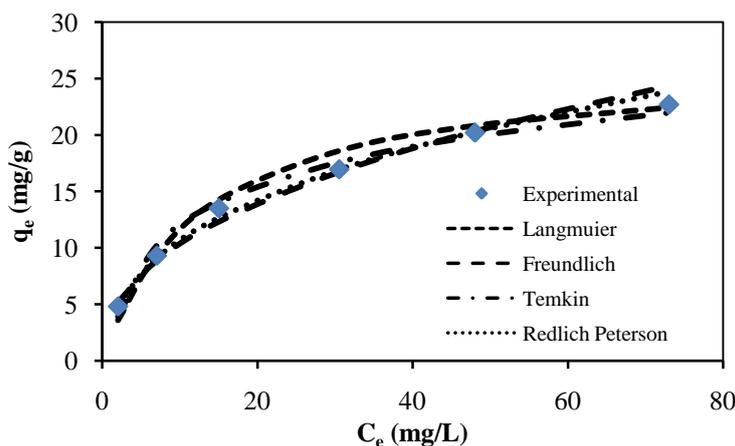


Fig. 7 Comparison of Fit of the Various Isotherm Equations with the Experimental Sorption Data for Picric Acid onto GAC at Temperature 303 K. ($m = 10 \text{ g/L}$, $\text{pH}_0 = 3.8$, $t = 3 \text{ h}$).

3.8 Estimation of Thermodynamic Parameters

The Gibbs free energy change of the adsorption process is related to the adsorption equilibrium constant by the classical Van't Hoff's equation:

$$\Delta G_{ads}^0 = -RT \ln K_{ads} \tag{8}$$

The Gibbs free energy change is also related to the change in entropy and heat of adsorption at a constant temperature as given by the equation:

$$\Delta G_{ads}^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

The above two equations give,

$$\ln K_{ads} = \frac{-\Delta G_{ads}^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \tag{10}$$

Where, ΔG_{ads}^0 is the free energy change (kJ/ mol), ΔH^0 is the change in enthalpy (kJ/ mol), ΔS^0 is the entropy change (kJ/ mol K), K_{ads} is the equilibrium constant of interaction between the adsorbate and the GAC surface, T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). Thus ΔH^0 can be determined by the slope of the linear Van't Hoff's plot i.e. as $\ln(K_{ads})$ versus $(1/T)$, using the equation:

$$\Delta H^0 = \left[R \frac{d \ln K}{d(1/T)} \right] \tag{11}$$

This ΔH^0 corresponds to the isosteric heat of adsorption ($\Delta H_{st,0}$) with zero surface coverage (i.e. $q_e = 0$) [32]. K_{ads} at $q_e = 0$ was obtained from the intercept of the $\ln(q_e/C_e)$ versus q_e plot [33]. Fig. 8 shows the Van't Hoff's plot for $\ln(q_e/C_e)$ versus q_e , from which ΔH^0 and ΔS^0 values have been calculated and presented in Table 2.

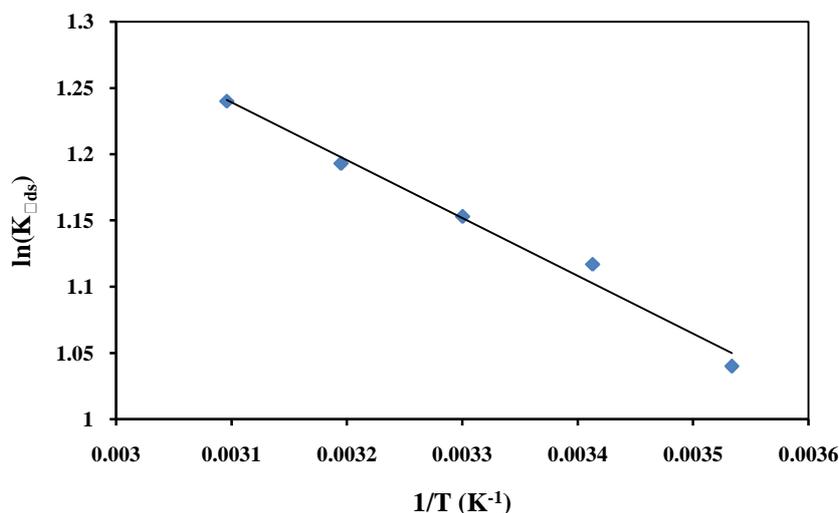


Fig. 8 Van't Hoff's Plot for the Determination of ΔH^0 , ΔS^0 , and ΔG^0 .

Table 2. Thermodynamic Parameters for the Adsorption of Picric Acid onto GAC.

Temperature (K)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol. K)	ΔG^0 (kJ/ mol)
283	3.6282	0.02155	-2.47
293			-2.69
303			-2.90
313			-3.12
323			-3.33

Adsorption of picric acid from an aqueous solution onto GAC is an endothermic process. The positive ΔH^0 value obtained in Table 2 indicates that the overall-sorption process is endothermic in nature. The positive ΔS^0 value suggests increased randomness at the solid/solution interfaces with some structural changes in the adsorbate and adsorbent at an affinity of the GAC towards picric acid. ΔG_{ads}^0 values were negative indicating that the sorption process led to a decrease in the Gibbs free energy and the adsorption process is spontaneous and feasible.

3.9 Isostatic Heat of Adsorption

Apparent isosteric heat of adsorption ($\Delta H_{st,a}$) at constant surface coverage (by considering the range of q_e values obtained in each experiment. e.g. for picric acid adsorption on GAC $q_e = 2, 4, 6, 8, 10$ mg/g) is calculated using Clausius - Clapeyron equation [34].

$$\frac{d \ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2} \tag{12}$$

$$\text{or} \quad \Delta H_{st,a} = R \left. \frac{d \ln C_e}{d(1/T)} \right|_{q_e} \tag{13}$$

For this purpose, the equilibrium concentration (C_e) at a constant equilibrium amount of adsorbed solute, q_e , is obtained from the adsorption isotherm data at different temperatures. Fig. 9 shows the extracted C_e at a constant q_e was plotted as $\ln(C_e)$ versus ($1/T$). $\Delta H_{st,\square}$ was calculated from the slope of the $\ln C_e$ versus ($1/T$) plot for different q_e of picric acid onto GAC.

The calculated $\Delta H_{st,\square}$ was plotted against the surface sorbate loading, q_e in Fig. 10. The plot showed that $\Delta H_{st,\square}$ increased as the surface sorbate loading increased. The variation in $\Delta H_{st,\square}$ with surface loading can be attributed to the possibility of having lateral interactions between adsorbed picric acid ions. $\Delta H_{st,\square}$ calculated from the Fig. 10 was found to be 4.649, 4.708, 4.779, 4.865 and 4.974 kJ/kg for $q_e = 2, 4, 6, 8$ and 10 mg/g, respectively. The positive values of $\Delta H_{st,\square}$ confirms that the adsorption of picric acid onto GAC is an endothermic process.

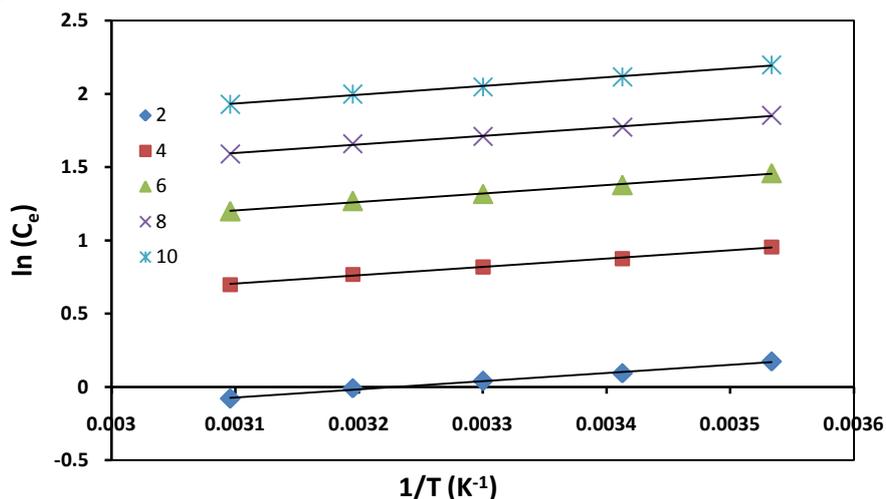


Fig. 9 Adsorption Isosters for Determining the Isosteric Heat of Adsorption q_e (mg/g).

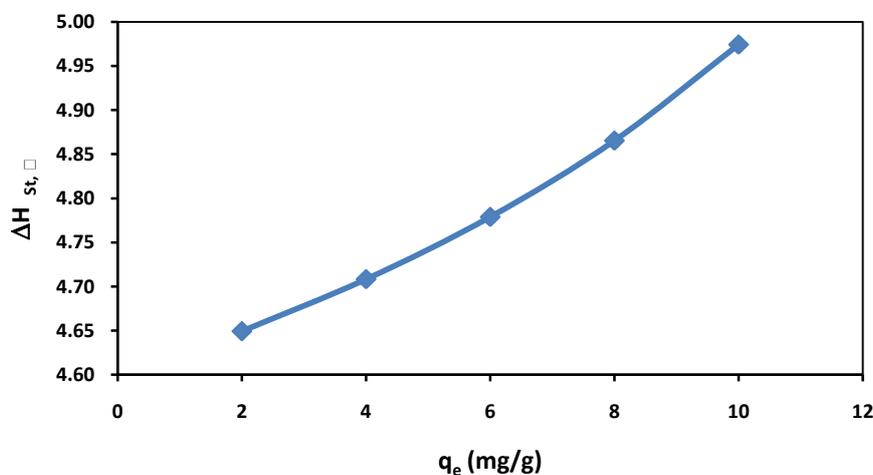


Fig. 10 Variation of $\Delta H_{st,\square}$ with respect to Surface Loading.

IV. CONCLUSIONS

The present study shows that picric acid can be effectively removed from aqueous solution by adsorption onto commercial granular activated carbon (GAC). Higher percentage of picric acid removal by GAC was possible provided that the C_0 in the solution was low. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 3.0 h. Adsorption of picric acid onto GAC was favorably influenced by increase in the temperature of the operation. Equilibrium isotherms were analyzed by different isotherm models. Redlich-Peterson, Freundlich and Langmuir isotherm was found to best represent the equilibrium data for picric acid adsorption onto GAC. ΔH^0 values indicated physical nature of the overall sorption process. The negative values of ΔG^0 indicated feasible and spontaneous adsorption of picric acid onto GAC.

REFERENCES

- [1]. Aggarwal, P. Misra, K. Kapoor, S. and K. Bhalla, A. K., Effect of surface oxygen complexes of activated carbon on the adsorption of 2, 4, 6-Trinitrophenol. *Def. Sci. J.* 48, 1998, 219–222.
- [2]. Sepehrian, H. Fasihi, J. Mahani, M. K., Adsorption behavior studies of picric acid on mesoporous MCM-41. *Ind. Eng. Chem. Res.* 48, 2009, 6772–6775.
- [3]. Srivastava, S. K. & Tyagi, Renu, Competitive effect of surfactants in the adsorption of phenols by activated carbon developed from the fertilizer waste slurry. *Chem. Engg. World*, 28(11), 1993, 83-86.
- [4]. Srivastava, S. K.; Gupta, V. K; Yadav, I. S. & Mohan, D., Removal of 2,4-dinitrophenol using bagasse fly ash-A sugar industry waste material. *Fresenius Environ. Bull.*, 4, 1995, 550-57.
- [5]. Meghea, Aurelia, Mihalache, Romina, Bumbac, G.H. & Costantinescu, I., Competitive adsorption of P-nitrophenol and O-cresol from aqueous solutions on activated carbon. *Sci. Technol. Environ. Prot.* 1(1), 1994, 10-17.
- [6]. Boileau J, Fauquignonon C, Napoly C. Explosives. In: Gerharts W, Tamamoto YS, Kaudy L, Rounsaviille JF, Schulz G, eds., *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim,145, 1987.
- [7]. Roth J. Picric Acid. In: Kaye SM, Herman HL, eds., *Encyclopedia of explosives and related items*, US Army Armament Research and Development Command, Dover, 285,1980.
- [8]. US Environmental Protection Agency, Ambient water quality criteria for nitrophenol, USEPA, Washington DC, (1980).
- [9]. Nipper M, Carr RS, Biedenbach JM, Hooten RL, Miller K., Fate and effects of picric acid and 2,6-DNT in marine environments: toxicity of degradation products. *Mar Pollut Bull*, 50, 2005,1205.
- [10]. Kavlock RJ, Oglesby LA, Hall LL, Fisher HL, Copeland F, Logsdon T, Ebron-McCoy M., In vivo and in vitro structure-dosimetry- activity relationships of substituted phenols in developmental toxicity assays. *Reprod Toxicol*, 5, 1991, 255.
- [11]. M.K.Dwivedi, I.P.Tripathi and Atul Kumar Dwivedi, Adsorptive removal of picric acid from wastewater using coal fly ash, *International Journal of Recent Scientific Research*, Vol. 5, Issue,10, , 2014, 1941-1945.
- [12]. World Health Organization, Guidelines for Drinking Water Quality. Vol. II: Health criteria and supporting information, WHO, Geneva, 1984.
- [13]. US Environmental Protection Agency, Technical support document for water quality based toxics control, EPA/440/485032, USEPA, Washington, DC ,1985.
- [14]. C. Canton, S. Esplugas and J. Casado, Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light, *Appl. Catal.*, 43, 2003, 139–149.
- [15]. Y.J. Feng and X.Y. Li, Electro-Catalytic Oxidation of phenol on several metal-oxide electrodes aqueous solution, *Water Res.*,37, 2003, 2399–2407.
- [16]. M. Ksibi, A. Zenzemi and R. Boukchina, Photocatalytic degradability of substituted phenols uv irradiated TiO_2 , *J. Photochem and Photobiol.*, 159, 2003, 61–70.
- [17]. G.B. Seetharam and B.A. Saville, Degradation of phenol using tyrosinase immobilized siliceous supports, *Water Res.*, 37, 2003, 436–440.
- [18]. Shen XE, Shan XQ, Dong DM, Hua XY, Owens G., Kinetics and thermodynamics of sorption of nitroaromatic compounds to as-grown and oxidized multiwalled carbon nanotubes. *J Colloid Interface Sci*, 330, 1, 2009.
- [19]. P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of acid yellow 36, *Dye. Pig.* 56, 2003, 239–249.
- [20]. Daifullah AAM, Girgis BS., Removal of some substituted phenols by activated carbon obtained from agricultural waste. *Water Res*, 32, 1998. 1169

- [21]. Tahermansouri H, Ahi RM, Kiani F., Kinetic, equilibrium and isotherm studies of cadmium removal from aqueous solutions by oxidized multi-walled carbon nanotubes and the functionalized ones with thiosemicarbazide and their toxicity investigations: a comparison. *J Chin Chem Soc*, 61, 2014, 1188.
- [22]. Terzyk A. P., Further insights into the role of carbon surface functionalities in the mechanism of phenol adsorption. *J Colloid Interface Sci*, 268, 2003, 301.
- [23]. I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, *Chemosphere* 61, 2005, 492– 501.
- [24]. D.H. Lataye, I.M. Mishra, I.D. Mall, Pyridine sorption from aqueous solution by rice husk ash (RHA) and granular activated carbon (GAC): Parametric, kinetic, equilibrium and thermodynamic aspects, *Journal of Hazardous Materials* 154 , 2008, 858–870.
- [25]. Langmuir I., The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.*, 40, 1918, 1361-1403.
- [26]. Freundlich H.M.F., Over the adsorption in solution, *J. Phys. Chem.*, 57, 1906, 385-471.
- [27]. Temkin M.I., Pyzhev V., Kinetics of ammonia synthesis on promoted iron catalysts, *Acta. Physiochim. URSS*, 12, 1940, 327–356.
- [28]. Redlich O., Peterson D.L., A useful adsorption isotherm. *J. Phys. Chem.*, 63, 1959, 1024–1026.
- [29]. Hasley G.D. Jr., Taylor H.S., The adsorption of hydrogen on tungsten powders, *J. Chem. Phys.*, 15, 1947,624.
- [30]. Porter J. F., McKay G., Choy K. H., The prediction of sorption from a binary mixture of acidic dyes using single- and mixed isotherm variants of the ideal adsorbed solute theory, *Chem. Eng. Sci.*, 54, 1999, 5863-85.
- [31]. Marquardt D. W., An algorithm for least-squares estimation of nonlinear parameters, *J. Soc. Ind. Appl. Math.*, 11, 1963, 431-441.
- [32]. Suzuki M., Adsorption engineering, Kodansha-Elsevier, Tokyo, 1990.
- [33]. Khan A. A., Singh R. P., Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H⁺, Na⁺ and Ca²⁺ forms. *Colloid Surface*, 24, 1987, 33-42.
- [34]. Young D.M., Crowell A. D., Physical adsorption of gases, Butterworths, London, 1962.