



Batch adsorption of 4-nitrophenol by acid activated jute stick char: Equilibrium, kinetic and thermodynamic studies

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ABSTRACT

The article describes the performance of acid activated jute stick char (AAJSC) for the adsorption of 4-nitrophenol (4-NP) from aqueous solution in batch mode. Jute stick, a bulk volume agricultural waste, was utilized for adsorption. The char of jute stick prepared at 773 K was activated with phosphoric acid and adsorption experiments were carried out at 298, 308 and 318 K. Equilibrium adsorption data were analyzed using two-parameter models—Langmuir, Freundlich, Temkin, Dubunin-Radushkevich and three-parameter-Redlich-Peterson model. The goodness of the fit was measured using linear regression coefficient (R^2) value and five different error functions. The adsorption data was found to be well described by Langmuir model. The equilibrium time for adsorption was achieved within 4 h. Studies showed that adsorption decreases with the increasing temperature. pH studies were also performed to obtain the equilibrium pH for adsorption. The pseudo-first-order, pseudo-second-order and Elovich kinetic models were applied to test the kinetic data, and were found to closely follow the pseudo-second-order kinetic model. The thermodynamic constants of the adsorption process; ΔG° , ΔH° and ΔS° were evaluated as -18.79 kJ/mol at 25 °C, 3917.4 J/mol, 76.21 J/mol K⁻¹ respectively. These showed that the adsorption process was endothermic and spontaneous.

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1. Introduction

Phenols are a threat to the environment and health, due to their relative high toxicity and persistence in aqueous media [1]. Among the phenolic derivatives, 4-nitrophenol (4-NP) is an important intermediate used in organic synthesis. It is used in pesticide production, as fungicide for leather [2,3] in dyes/pigment production, engineering polymers, pharmaceutical and organic synthesis [4] and also in specialty products for military applications [5]. Among the mononitrophenols, 4-NP is produced in the highest quantities worldwide, highest toxicity and is more water-soluble [6,9] and hence is selected in the present study. Nitrophenols are listed as toxic pollutants by United States Environmental Protection Agency (USEPA) [6]. The major use of 4-NP is in the production of pesticides, namely methyl- and ethyl parathion and are often encountered in the environment as degradation products of pesticides such as nitrofen, methyl paraoxon, methyl parathion and ethyl parathion [7–9].

Traditional methods of water purification [10] such as chemical oxidation and microbial degradation [11] are not able to remove

phenols efficiently as they remain persistent. Among the numerous techniques, adsorption using solid adsorbents is an effective separation process for treating domestic and industrial effluents [12,13]. Commercial activated carbons and organic resins have been used with success. However, their widespread use is restricted due to high cost [14]. Alternative non-conventional material including natural materials such as clays, siliceous materials, zeolites, lignin [15], yellow bentonite [16], waste materials and by-products from agriculture and industry (sugarcane bagasse, tea leaves, rice husk, straw, chitin, fly ash, etc.) [17,18] have been studied. Recently, polymeric adsorbents [19] and carbon nanotubes [20] due to their more varied functionality, surface area and porosity [21,22] have been employed to remove phenolic compounds from aqueous solutions [23–27]. In spite of their advantages, low-cost adsorbents still represent an interesting and attractive alternative due to their easy availability and good adsorption properties towards a wide range of pollutants. In the present study, phosphoric acid activated jute stick char is used as an adsorbent for the removal of 4-NP. Phosphoric acid is preferred over $ZnCl_2$ because of the environmental disadvantage associated with the later. Jute stick is a cheap and an abundant agricultural waste and its adsorption capacity can be increased by activating the char with phosphoric acid. The present study therefore utilizes acid activated jute stick char (AAJSC) for the adsorption of 4-nitrophenol from aqueous system.

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Nomenclature

q_L	Langmuir isotherm constants (mg/g)
A	Temkin isotherm constant (L/g)
ARE	the average relative error
B	Temkin isotherm constants (J/mol)
C_e	equilibrium 4-NP concentration (mg/L)
C_0	Initial 4-NP concentration (mg/L)
EABS	the sum of absolute errors
ERRSQ	the sum of squares of errors
HYBRID	the fractional error function
K_F	Freundlich constants (mg/g)
MPSD	Marquardt's percent standard deviation
q_e	amount of 4-NP adsorbed at equilibrium (mg/g)
q_t	amount of 4-NP adsorbed at time t (mg/g)
q_{max}	maximum adsorption capacity of the adsorbent (mg/g)
m	mass of the adsorbent (g)
n_F	Freundlich isotherm exponent
q_{DR}	Dubunin-Radushkevich constant (mol/g)
E	free energy value of adsorbent-adsorbate system
R^2	linear regression coefficient of determination
k_1	First order rate constant in (h^{-1})
k_2	Second order rate constant (g/mg h)
t	time (h)
T	temperature (K)
x	amount of dye adsorbed in mg
p	number of data points
n	number of parameters

2. Experimental

2.1. Preparation and characterization of the adsorbent

Jute stick used for the preparation of adsorbent was obtained locally. The precursor was first washed with distilled water, dried, cut and sieved to the desired mesh size of 100–200 BSS. It was activated by treating with phosphoric acid in 1:1(w/w) at 383 K for 2 h and finally at 773 K for 4 h. The purpose of chemical activation is to increase the surface area of the adsorbent. The mixture was then dried in an overnight at 378 K. The activated product was then washed with deionized water several times to remove the excess acid until the pH of the solution reaches almost neutral. The final product was kept in oven for 12 h at a temperature of 333–353 K to remove moisture. Table 1 shows the analysis of the prepared adsorbent.

2.2. Methods and analysis

A stock solution of 4-NP (1000 mg/L) was prepared in deionized water and all working solutions were prepared by diluting the stock solution to the desired concentrations. The pH of the solution was adjusted using 0.1N HCl and 0.1N NaOH. All chemicals used were of analytical grade (Merck). The concentrations of 4-NP

Table 1
Analysis of the adsorbent, AAJSC.

Moisture (%)	9.88
Volatile matter (%)	50.17
Ash (%)	12.76
Carbon (%)	22.65
Hydrogen (%)	3.02
Nitrogen (%)	0.27

were determined spectrophotometrically (UV-spectrophotometer, Model: Cary 100 Bio UV visible spectrophotometer) by monitoring the absorbance at 315 nm, where maximum absorption was observed. The method involved agitating different amounts of the adsorbent (0.2–2 g) with 20 mL of 1000 ppm 4-NP aqueous solution. Equilibrium studies were carried out at three different solution temperatures at 298, 308 and 318 K in its natural pH condition. The contact time was kept for 24 h, which was more than sufficient to reach the equilibrium. The supernatant solutions were used to measure the amount of 4-NP adsorbed at equilibrium by the adsorbent and the amount adsorbed was calculated by the mass balance equation given by Eq. (1)

$$q_e = \frac{V(C_0 - C_e)}{m \times 1000} \quad (1)$$

where q_e is the adsorption capacity in mg/g, C_0 and C_e are the initial, and equilibrium concentration of 4-NP in mg/L, V is the volume of 4-NP solution in mL and m is the total amount of prepared jute stick char in g.

2.3. Determination of pH_{ZPC}

pH_{ZPC} is the pH when the charge on the activated carbon surface is zero. The pH drift method [28] was used to determine the pH_{ZPC} of the carbon surface using 50 mL of 0.1 M NaCl in a series of Erlenmeyer flasks whose pH were adjusted using 0.1 M NaOH and 0.1 M HCl in the range between 2 and 12. The initial pH of the solutions were determined and 0.15 g of the adsorbent was added to each of the flasks and after completion of 48 h, the final pH of the solutions were measured. pH_{ZPC} was noted at the pH in which the initial pH equals the final pH.

2.4. Desorption studies

Desorption and regeneration studies are important in the field of adsorption studies. The desorption of 4-NP loaded adsorbent was carried out by using various strengths of NaOH (1–0.3 M), HNO₃ (0.001–0.3 M) and water by taking 0.2 g of AAJSC pre-adsorbed with 20 mL of 1000 ppm 4-NP and shaken continuously at 150 rpm for 2 h. Desorption efficiency was calculated using the following equation:

$$\% \text{ Desorption} = \frac{C_d \times V_d}{w \times q_e 1000} \times 100 \quad (2)$$

where C_d is the desorbed adsorbate concentration (mg/L), V_d is the volume of the desorption solution, w is the mass of the pre-adsorbed adsorbent (g), q_e is the amount of the adsorbate pre-adsorbed on the adsorbent (mg/g).

3. Results and discussion

3.1. FTIR spectra

FTIR spectra of AAJSC were obtained in order to understand the nature of functional groups present. Fig. 1(a) and (b) shows the FTIR spectra of AAJSC before and after 4-NP adsorption displaying the complex nature of the adsorbent. Bands appearing at 3429.43 and 3332.99 cm^{-1} were assigned to OH stretching while those at 2966.52 and 2904.80 cm^{-1} were due to C–H stretching of alkane. The increase in intensity of the bands at 3429.43 and 3332.99 cm^{-1} in Fig. 1(b) shows the adsorption of 4-NP. The bands at 2112.05, 1703.14, 721.38, and 630.72 cm^{-1} were due to C≡C stretching, C=O stretching of carboxylic group, methylene rocking band and ≡C–H bending mode respectively. Out of these, carboxylic and hydroxyl groups played a major role in the removal of 4-NP. The band at 3332.99 cm^{-1} is responsible for H-bonding of the phenol unit to

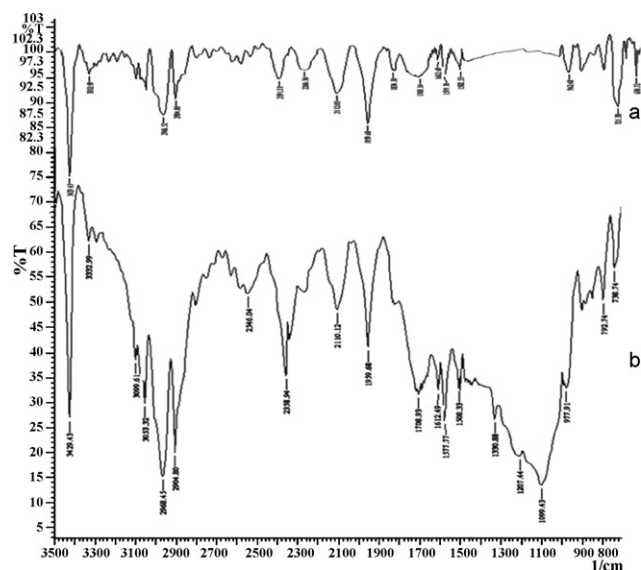


Fig. 1. (a) FTIR spectrum of AAJSC before adsorption of 4-NP. (b) FTIR spectrum of AAJSC after adsorption of 4-NP.

the adsorbent. As depicted in Fig. 1(b), the band position due to aliphatic C–H group was shifted by +2 and became sharper. The band due to C=O stretching of carboxylic group has also shifted by +5.79. Bands at 1508.33 and 1330.88 cm^{-1} were typical of NO_2 group indicating the adsorption of 4-NP. The presence of a medium peak at 792.74 cm^{-1} in Fig. 1(b) further confirmed the adsorption of para-substituted benzene product.

3.2. Adsorption equilibrium

3.2.1. Isotherm models and error analysis

In order to adequately correlate the experimental data, several isotherm equations were tested to find the best fit using linear regression coefficient and five different error functions. An accurate mathematical description for the equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems. The different equilibrium adsorption isotherms that were used to investigate the experimental data are given below:

Isotherms	Equation	Parameters	Refs.
Langmuir	$\frac{C_e}{q_e} = \frac{1}{a_1 b} + \frac{C_e}{a}$	a_1, b	[29]
Freundlich	$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$	n_F, K_F	[30]
*Temkin	$q_e = \left(\frac{RT}{b_T}\right) \ln K_{Tem} + \left(\frac{RT}{b_T}\right) \ln C_e$	B, K_{Tem}	[31]
Dubunin-Radushkevich	$\ln q_e = \ln q_{DR} - \left(\frac{RT}{E}\right)^2 \left(\ln \frac{C_0}{C_e}\right)^2 q_{DR}, E$		[32]
Redlich-Peterson	$q_e = \frac{q_m \beta C_e}{1 + \beta C_e^{1-n}}$	q_m, n, B	[33,34]

Fig. 2 depicts the adsorption isotherm (C_e vs q_e) at three different temperatures (298, 308 and 318 K) and shows that the adsorption capacity, which is mass (mg) of the total 4-NP removed per unit mass of adsorbent, increases with increasing equilibrium 4-NP concentrations and eventually attained a constant value. It also shows that removal of 4-NP is favourable at lower temperature and decreases with the increase in temperature. A detailed error analysis was undertaken to investigate the best fit adsorption isotherm which describe the adsorption process. The five different error functions studied are as follows:

1. *The sum of the squares of errors (ERRSQ)*: This is the most common error function [35] but it has the drawback of biasing the fit

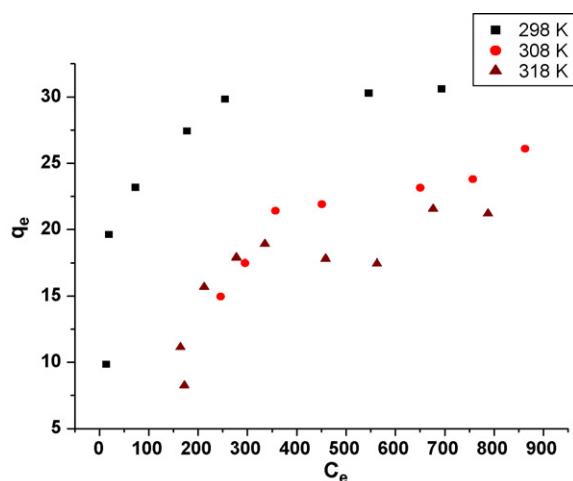


Fig. 2. Equilibrium adsorption isotherm of 4-NP onto AAJSC at 298, 308 and 318 K ($C_0 = 1000$ ppm).

towards the data obtained at higher concentration range.

$$\sum_{i=1}^p (q_{e,calc} - q_{e,meas})_i^2 \quad (3)$$

2. *The hybrid fractional error function (HYBRID)*: Ho et al. [36] developed this error function in order to improve the fit of ERRSQ method at low concentration.

$$\frac{100}{p-n} \sum_{i=1}^p \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i \quad (4)$$

3. *Marquardt's percent standard deviation (MPSD)*: This error function [36] is a modification of geometric mean error distribution to allow for the number of degrees of freedom of the system.

$$100 \left(\sqrt{\frac{1}{p-n} \sum_{i=1}^p \left[\frac{q_{e,meas} - q_{e,cal}}{q_{e,meas}} \right]^2} \right) \quad (5)$$

4. *The average relative error (ARE)*: Fractional error distribution across the entire concentration range is being attempted to minimize in this error function [36].

$$\frac{100}{p} \sum_{i=1}^p \left| \frac{q_{e,calc} - q_{e,meas}}{q_{e,meas}} \right|_i \quad (6)$$

5. *The sum of absolute errors (EABS)*: This error function [36] also biases the fit towards higher concentration.

$$\sum_{i=1}^p |q_{e,calc} - q_{e,meas}|_i \quad (7)$$

On the basis of the lowest value of various error functions and from correlation coefficient R^2 value i.e. the isotherm

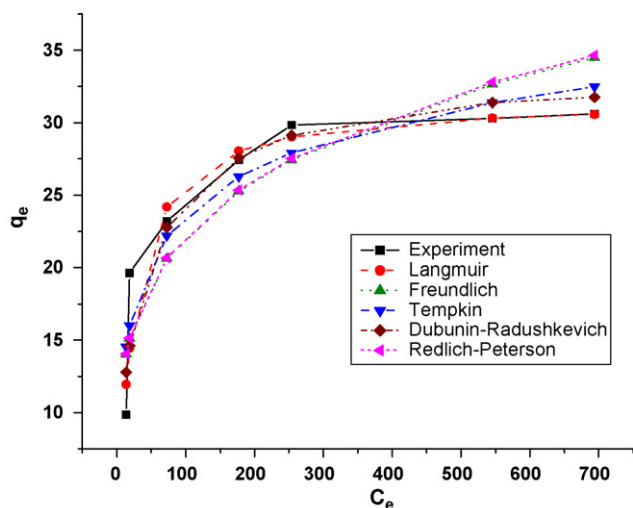


Fig. 3. Validity of adsorption isotherm with experimental data at 298 K.

giving R^2 value closest to unity, the fitting is Langmuir > Redlich-Peterson > Dubunin-Radushkevich > Temkin > Freundlich (Table 2). A comparison of the experimental adsorption data with the linearized plot of Langmuir, Freundlich, Temkin, Dubunin-Radushkevich and Redlich-Peterson model is shown in Fig. 3 which showed a greater scattering from the experimental values in Freundlich and Redlich-Peterson model while Langmuir isotherm curve was almost superposed by the experimental data. Temkin and Dubunin-Radushkevich showed moderate fitting. Thus the examination of the linear isotherm plots suggested that the Langmuir isotherm model yielded a much better fit than other models. It is further confirmed from the shape of the isotherm curve showing sharp curvature near the saturation point with short equilibrium time that the isotherm is characteristic of Langmuir equilibrium with good adsorption capacity. The theoretical q_{\max} values calculated were 31.55, 32.79 and 28.57 mg/g at 298, 308 and 318 K respectively. There is a decrease in q_{\max} value at 318 K showing that higher temperature is not favourable for 4-NP adsorption onto AAJSC. The highest R^2 value (closest to unity) of the Langmuir isotherm suggested that a single surface reaction describes the adsorption mechanism.

3.3. Effect of contact time

The experiments were carried out with adsorbent dosage of 0.2 g/20 mL of different 4-NP concentrations (200, 400, 800 and 1000 ppm) at 298 K for different periods of contact time with maximum reaching up to 24 h. Fig. 4 shows the uptake of 4-NP versus contact time at different initial concentrations of 4-NP. It indicated that the equilibrium contact time needed for 4-NP adsorption was 4 h and independent of initial concentration. It was also evident from Fig. 4 that the adsorption density increased with increased adsorbate concentration. Adsorption was rapid within the first 1 h and became almost asymptotic after 12 h. This was because of the fact that a large number of vacant surface sites were available for adsorption in the initial stage. The amount of adsorbate is rapidly accumulated on the adsorbent surface mainly within the first 4 h after which the remaining vacant sites are difficult to be occupied due to the formation of repulsive forces between 4-NP on adsorbent surface and in solution phase owing to decrease in concentration gradient [37]. The decrease of adsorption rates is well illustrated by the plateau line after 4 h of adsorption.

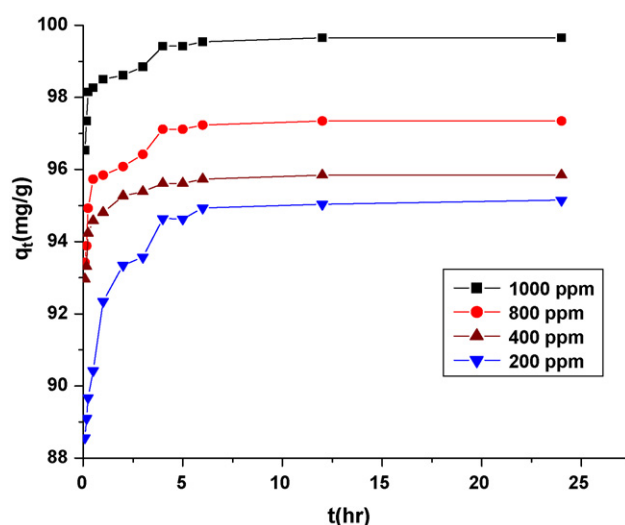


Fig. 4. Effect of contact time and initial concentration on adsorption of 4-NP onto AAJSC ($C_0 = 200, 400, 800, 1000$ ppm, $m = 0.20$ g, $V = 20$ mL, temperature = 298 ± 2 K).

3.4. Adsorption kinetic studies

The kinetic study is helpful in the prediction of the adsorption rate and provides important information for designing and modeling the processes. The kinetic data obtained from the batch adsorption at 298 K using 0.2 g of AAJSC in 20 mL of 1000 mg/L of 4-NP were analyzed using three different kinetic models: pseudo-first-order, pseudo-second-order and Elovich equations. Intraparticle diffusion was also applied to investigate whether the adsorption process was controlled by diffusion in the adsorbent particles and consecutive diffusion in the bulk of the solution [38].

3.4.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model was given by Lagergren and Svenska [39] and has been widely used to predict the adsorption kinetics.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

The plot of $\log(q_e - q_t)$ versus t gave the slope of k_1 and the intercept $\log q_e$. The value of k_1 and correlation coefficient R^2 obtained from the plot are given in Table 3. The correlation coefficient value obtained was relatively small and the experimental q_e value did not agree well with the calculated value. This shows that the adsorption of 4-NP on AAJSC is not a first-order reaction.

3.4.2. Pseudo-second-order kinetic model

The pseudo-second-order equation [40] based on the equilibrium adsorption is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

The linear plot of t/q_t versus t can be used to determine q_e and k_2 from slope and intercept of the plot. Table 3 shows a good agreement between the experimental and calculated q_e values. The correlation coefficient for the second-order-kinetic model approaches 1, indicating the applicability of second-order kinetic model to describe the adsorption of 4-NP on AAJSC.

3.4.3. Elovich equation

The Elovich equation is a useful model for describing activated chemisorption. The simplified equation can be expressed as

Table 2
Isotherm parameters and their respective error functions for adsorption of 4-NP.

Isotherm	Solution temperature (K)	Parameters			R ²	ERRSQ	HYBRID	MPSD	ARE	EABS
Langmuir		<i>a</i> (mg/g)	<i>b</i> (L/g)							
	298	31.55	0.05		0.99	33.16	37.70	15.32	8.16	9.77
	308	32.79	4.01 × 10 ⁻³		0.97	8.31	8.29	6.53	4.61	6.55
	318	28.57	4 × 10 ⁻³		0.87	38.44	41.89	19.17	12.24	15.55
Freundlich		<i>K_F</i> (mg/g)	1/ <i>n</i>							
	298	7.75	0.23		0.76	75.40	82.45	23.60	16.10	22.06
	308	2.18	0.37		0.86	11.71	10.13	7.78	5.15	7.21
	318	4.66	0.44		0.67	50.11	40.08	20.66	13.58	17.62
Tempkin		<i>K_{Tem}</i> (L/g)	<i>B</i> (J/mol)							
	298	1.81	4.55		0.87	45.52	64.92	23.29	12.90	15.30
	308	0.037	7.43		0.89	9.36	9.52	7.07	4.87	6.79
	318	7.48 × 10 ⁻¹⁰	6.43		0.74	40.30	46.47	20.76	13.11	16.19
Dubunin-Radushkevich		<i>q_{DR}</i>	<i>E</i> (kJ/mol)							
	298	31.97	11.15		0.84	36.81	45.06	17.71	9.61	11.46
	308	25.33	5.17		0.93	7.05	6.45	5.48	3.88	5.86
	318	21.82	5.66		0.75	37.42	38.37	17.68	2.12	15.72
Redlich-Peterson		<i>n</i>	<i>β</i>	<i>q_m</i> (mg/g)						
	298	0.23	1.33	7.74	0.97	76.13	103.74	26.47	2.13	0.66
	308	0.982	0.15	0.12	0.99	11160.36	275289.5	221.84	151.4	240.19
	318	0.42	2.87	1.23	0.77	50.21	60.63	22.50	1.95	0.81

Table 3
Pseudo-first-order- and pseudo-second-order kinetic model parameters for adsorption of 4-NP (298 K).

Initial 4-NP (mg/L)	<i>q_{e(exp)}</i> (mg/g)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model				Elovich equation				
		<i>q_{e,cal}</i> (mg/g)	<i>k₁</i> (h ⁻¹)	R ²	Δ <i>q</i> %	<i>q_{e,cal}</i> (mg/g)	<i>k₂</i> (g/mg h)	R ²	Δ <i>q</i> %	<i>q_{e,cal}</i> (mg/g)	<i>a</i>	<i>b</i>	R ²	Δ <i>q</i> %
1000	39.38	3.22	0.28	0.98	34.71	40	0.63	1.0	0.59	39.75	5.51	1.17	0.97	0.35

follows [41]:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \quad (10)$$

where *a* and *b* are the constants for this model obtained from the slope and intercept of the linear plot of *q_t* versus *ln t*. The R² value obtained from Elovich equation is 0.967 which is lower than that of pseudo-second-order value. The *q_e* value calculated from the Elovich equation agreed well with the experimental data (Table 3).

3.4.4. Validity of kinetic model

The applicability of the kinetic model to describe the adsorption process was further validated by the normalized standard deviation, Δ*q*(%), which is defined as:

$$\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}]^2}{N - 1}} \quad (11)$$

where *N* is the number of data points, *q_{exp}* and *q_{cal}* (mg/g) are the experimental and the calculated adsorption capacity, respectively. Table 3 lists the Δ*q* values obtained for the three models tested.

3.5. Effect of pH on adsorption and pH_{ZPC}

The initial pH of the adsorption medium and pH_{ZPC} of the prepared adsorbent are important parameters affecting the adsorption process. The pH_{ZPC} value was determined to be approximately 2.90 for AAJSC (Fig. 5). It was found that during the course of the adsorption, pH change was almost negligible. After addition of 0.2 g of the adsorbent to 20 mL of 1000 ppm 4-NP solution, the pH was recorded as 3.19. The change of pH of the solution was monitored after every 1 h interval and was recorded as 3.30, 3.30, 3.26, and 3.29 during the first 4 h of adsorption respectively. The study of initial pH effect on adsorption will help in determination of equilibrium pH of adsorption as the pH change during the course of

adsorption is negligible. The uptake of 4-NP by AAJSC was studied in the pH range of 2–12. A fixed amount of AAJSC (0.2 g) was added in 20 mL of the aqueous 4-NP solution and shaken continuously at 298 K and pH was measured after equilibrium adsorption was attained. The maximum uptake was achieved at a pH around 9.05. It can be correlated with the pH at which 4-NP is highly soluble. At pH lower than the pH_{ZPC}, the surface of AAJSC is positively charged while at pH greater than pH_{ZPC}(2.90), the surface of the adsorbent becomes negatively charged and 4-NP adsorption is facilitated due to electrostatic interaction of 4-NP with the negatively charged surface of the adsorbent. Hence there is an increase in adsorption after pH greater than 2 and remains nearly constant up to pH 7. There is again a sudden rise in adsorption capacity after pH 7. It can be correlated with the p*K_a* value of 4-NP (7.18).

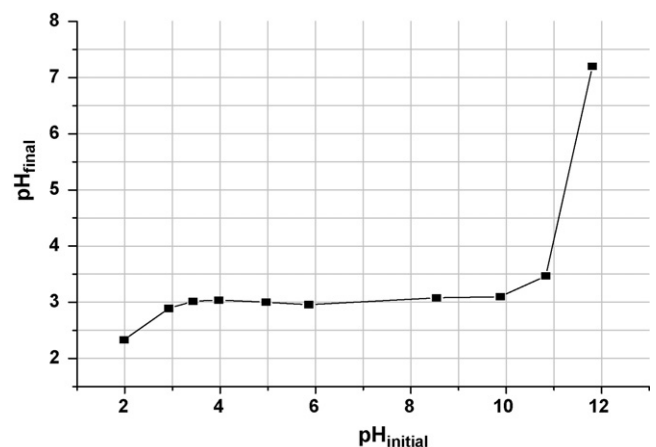


Fig. 5. Plot for the determination of pH_{ZPC}.

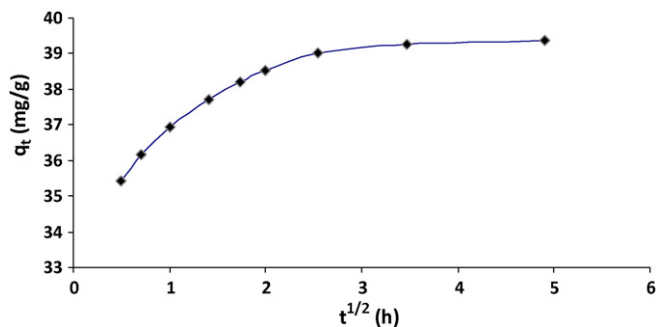


Fig. 6. Plot of Weber-Morris equation for 4-NP onto AAJSC.

3.6. Adsorption mechanism

The intraparticle diffusion model [42] was also used to analyze and elucidate the diffusion mechanism. The intraparticle model is expressed as

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

where, q_t is the amount of 4-NP adsorbed at equilibrium (mg/g) at time t , C is the intercept and k_p is the intraparticle diffusion rate constant (g/g h^{-1}). According to Eq. (12), a plot of q_t versus $t^{1/2}$ should be straight line with a slope k_p and intercept C ; when adsorption mechanism follows the intraparticle diffusion process. The value of C gives an idea about the thickness of boundary layer i.e. the larger the intercept the greater is the boundary layer effect. Fig. 6 shows the plot of q_t versus $t^{1/2}$ for 4-NP onto AAJSC. The deviation of straight line from the origin may be because of the difference in the rate of mass transfer in the initial and final stages of adsorption. This also indicates that the pore diffusion is not the rate controlling step. It was found from Fig. 6 that there are two separate regions—the first straight line is attributed to the macro-pore diffusion (phase-I) and the second linear portion to micro-pore diffusion (phase-II). The maximum adsorption of 4-NP was obtained within the $t^{1/2}$ of 0.5 h. The phase-I may be explained because of the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The phase-II may be attributed to a very slow diffusion of the adsorbents from the surface film to micro-pores, which are the least accessible sites of adsorption. This also stimulates a very slow rate of migration of adsorbates from the liquid phase on to the adsorbent surface.

3.7. Thermodynamics of adsorption

The effect of temperature on the adsorption of 4-NP by AAJSC was studied in the temperature range of 298–318 K. The thermodynamic parameters, such as enthalpy (ΔH°), entropy (ΔS°) and Gibb's free energy (ΔG°) were estimated using the following relation [43]:

$$K_c = \frac{C_a}{C_e} \quad (13)$$

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

where K_c is the equilibrium constant, C_e the equilibrium concentration in the solution (mg/L) and C_a is the solid phase concentration at equilibrium (mg/L), standard enthalpy (ΔH°) and entropy (ΔS°) were determined from Van't Hoff equation.

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{2.303RT} \quad (15)$$

ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ as shown in Fig. 7 and presented in Table 4. Values of free energy changes are negative; confirming that the

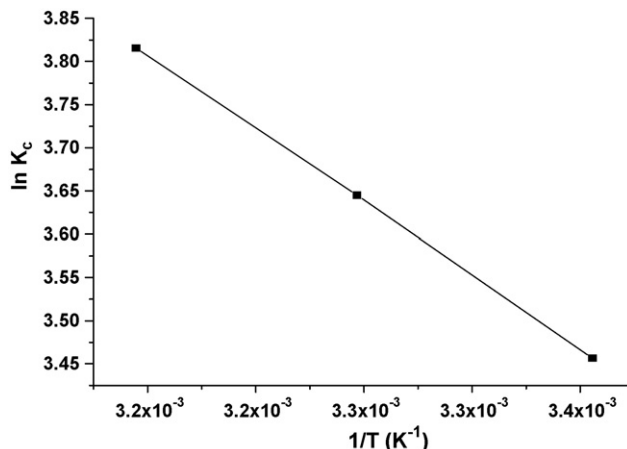


Fig. 7. Plot of $\ln K$ versus $1/T$ for the adsorption of 4-NP.

Table 4

Thermodynamic parameters for the adsorption of 4-NP onto AAJSC.

Temperature (K)	ΔH° (J/mol)	ΔG° (kJ/mol)	ΔS° (J/mol K)
298	3917.40	-18.79	76.21
308		-19.55	
318		-20.32	

adsorption of 4-NP on AAJSC is spontaneous and thermodynamically favourable. The more negative values of ΔG° implied that a greater driving force is required for the adsorption process. The ΔG° value decreases as the temperature increases, indicating a less driving force resulting in lesser adsorption capacity at higher temperatures. The positive value of ΔS° indicated a greater stability of adsorption process with no structural changes at the solid-liquid interface. The positive value of ΔH° indicated that the adsorption process is endothermic in nature.

3.8. Desorption and regeneration studies

Desorption efficiency was found to be highest (36%) in case of 0.1 M NaOH (Fig. 8) and hence 0.1 M NaOH was used as regenerating agent. The regenerated adsorbent was repeatedly tested for its adsorption efficiency two times and the decrease in adsorption efficiency per cycle was found to be negligible (1.01% and 1.23% in the first and second cycle, respectively). 4-NP loaded adsorbent may also be utilized as replacement of cement proportions in the

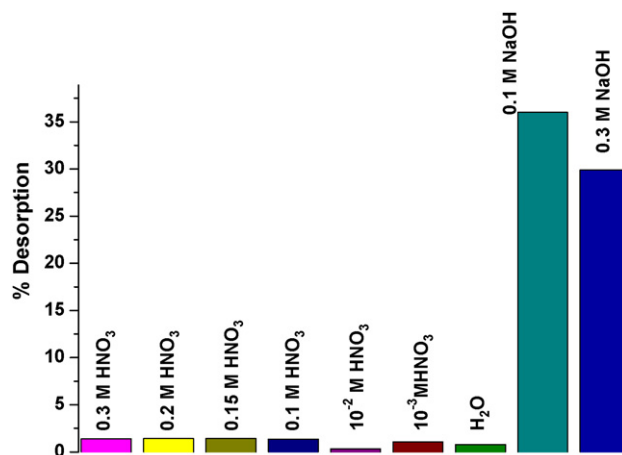


Fig. 8. Desorption of 4-NP with different concentrations of solvent ($C_0 = 1000$ mg/L, $w = 0.2$ g, $V = 20$ mL, temperature = 298 ± 2 K).

Table 5
Comparison of 4-NP adsorption on various low-cost adsorbents with AAJSC.

Adsorbent	Capacity	Refs.
Activated jute stick char	39.38	[Present study]
Sugar fly ash	0.76–1.15	[44]
Wood fly ash	134.9	[45]
Fly ash	7.80–9.68	[46]
Samla coal	51.54	[47]
Rice husk	15.31	[48]
Rice husk char	39.21	[49]
Petroleum coke	11.06	[49]
Coke breeze	4.64	[49]
Bagasse fly ash	8.3	[44]
Zeolite	1.02	[50]
Pyrolysed oil shale	4.895	[51]
ZnCl ₂ pyrolysed oil shale	6.026	[51]
KOH pyrolysed oil shale	0.895	[51]

preparation of cement blocks, thereby eliminating the problem of sludge disposal. Another way of disposal of 4-NP laden jute stick char may be incineration.

3.9. Comparison of AAJSC with other adsorbents and cost analysis

The adsorption capacity of 4-NP onto activated jute stick char was compared with other adsorbents reported in literature [44–51] and is shown in Table 5. It can be seen from the table that AAJSC compares well with the other adsorbents reported. AAJSC is suitable for 4-NP removal from aqueous solution since it has relatively high adsorption capacity and the cost of the adsorbent is also low as the precursor and as char itself is easily available as solid waste. The comparison of adsorption capacities of various low-cost adsorbents with AAJSC shows that it is effective for the removal of 4-NP.

Cost analysis is an important criterion in the selection of an adsorbent for a particular treatment process. The efficiency of commercial activated carbon (CAC) in the treatment of water contaminated with phenolic compounds is well known but the expensive nature of CAC demand the need of developing activated carbons that are prepared from low cost materials giving reasonable adsorption capacity over and above its economic feasibility. The cost of CAC is nearly 11\$ per kg, which is quite high for developing nations to afford. The economical application of AAJSC lies on its efficient means of regeneration and reactivation without much effort after its adsorption capacity has been reached. The cost of using (1) expensive chemicals to oxidize the adsorbed material, (2) steam to drive off the adsorbent material, (3) solvents and (4) biological conversion process was eliminated as the adsorbent is easily recovered using 0.1N NaOH.

4. Conclusion

This work clearly indicated the potential of AAJSC as an adsorbent for the removal of 4-NP from aqueous solutions. The maximum adsorption capacity of the adsorbent was found to be about 39.38 mg/g. Adsorption process follows Langmuir isotherm with pseudo-second-order kinetic model and an equilibrium time of 4 h and an equilibrium pH of 9.05. The positive value of ΔS° showed the stability of the adsorption process, whereas the results of ΔH° and ΔC° indicated the endothermic and spontaneous nature of adsorption process on the surface of AAJSC. Further investigations are needed for economically feasible regeneration of the adsorbent and application of the adsorbent for real industrial wastewater. However, in many parts of the world where jute stick is available at low or no cost, regeneration is not required and the 4-NP laden jute stick char can be disposed of by incineration.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.12.027.

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