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Development of Adsorbent from Solid Waste of Potato Peel for Decontamination of Wastewater Containing 4-Nitrophenol

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Abstract: Discarded potato peels were charred at 500^0C and utilized as adsorbents for the reclamation of wastewater contaminated with 4-nitrophenol. Batch studies investigating the effects of several parameters like pH, contact time, temperatures were carried out to determine the optimum adsorption condition using synthetic wastewater. Adsorption was found to be more favorable under acidic medium. Column studies, kinetic studies and thermodynamic studies were also performed to understand the applicability and feasibility of the adsorbent for industrial usage. The thermodynamic parameters like ΔG^0, ΔH^0 and ΔS^0 were evaluated by using the van't Hoff plot. The adsorption process was found to be spontaneous and endothermic in nature as evident from ΔG^0 and ΔH^0 values of -3.985 kJ/mol and 62.512 kJ/mol respectively. Several isotherm models were applied and Freundlich isotherm model with coefficient of determination value (R^2 = 0.998) was found as the best fit isotherm model to describe the equilibrium adsorption data. Certain physico-chemical and spectroscopic characterization of potato peels char (PPC) were analyzed in an attempt to better understand the adsorption process.
Keywords: Potato peels char (PPC), 4-nitrophenol, adsorption, isotherm, kinetic, thermodynamic.

1. Introduction

Environmental pollution of water discharged from several industries is of great concern. The need for the reuse/reclamation of wastewater in industrial and agricultural sectors is rising due to scarcity of freshwater availability. 4-Nitrophenol has been taken up as a candidate adsorbate in the present study as it is the most prevalent form of mononitrophenol discharged from industrial effluents like leather, paint, pharmaceutical, pesticide etc[1]. The Environmental Protection Agency (EPA) sets the standards for disposal of toxic chemicals form industrial organization into waterways. The maximum discharged limit for 4-nitrophenol has been set to 0.162 mg/L for industrial effluents.

Adsorption is one such treatment technology that can be devised for reuse and recycling of Industrial wastewater in a cost effective manner. This reclamation itself will reduce the demand of water. In the search for newer and better adsorbents, activated carbons have always proved to be a versatile adsorbent in the field of wastewater treatment. Many researchers are digging out the potential of several agro/industrial based activated carbons. The aim of the present work is to explore the potential of biochar obtained from potato peel without any chemical activation for the abatement of 4-nitrophenol (4-NP, denoted hereafter) through various batch and column studies.

2. Materials and Method

2.1 Preparation of the adsorbent

The mode of the preparation of the adsorbent was quite simple which includes washing to remove the impurities, drying at 80^0C and charring in well-capped silica crucibles at 500^0C in a furnace for 2 h. The product was then powdered and stored in a desiccator until use.

2.2 Characterization methods

FT-IR spectra (4000–400 cm^{-1}) in KBr were collected on a Spectrum BX Series FT-IR spectrometer having a resolution of 4 cm^{-1}. The samples were pressed to a thin disc with KBr before measurements. The nitrogen adsorption and desorption isotherms were measured at 77.74 K using an ASAP 2010 V 5.02 analyzer (Micromeritics Co., Ltd.).Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distributions were calculated using the Barret–Joyner–Halenda (BJH) model. SEM images were taken with a Scanning Electron Microscope **(SEM)**, Leo 1430vp field emission scanning electron microscope (EHT, 20 kV).

2.3 Experimental method

The effect of parameters like adsorbent dosages, solution pH on the adsorption behavior of 4-NP over the prepared biochar of potato peel (PPC) were investigated in batch and fixed mode by diluting the stock solution of

1000 mg/L. In the adsorption procedure, 0.1-1.5 g of adsorbent material was added to aliquots of 20 mL solutions. The pH of the solution was adjusted with 0.1 M HCl or NaOH to the pH range of 1–14. The suspension was shaken for a preselected period of time (1 h) at a constant temperature, and then filtered. The residual solution concentration was analyzed by Cary Bio 100 UV–visible spectrophotometer at $\lambda_{\max}$ value of 315 nm.

The equilibrium adsorption capacity of the 4-NP was calculated using the equation below:

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{m \times 1000}, \tag{2.1}$$

where q_e is the equilibrium adsorption capacity of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium concentrations of solute (mg/L), m is the mass of adsorbent (g), and V is the volume of the solution (mL). The UV adsorption reading was taken as the average of the triplicate reading in order to reduce the measurement errors. The effect of contact time study was taken up to determine the kinetics of the adsorption process and the optimum time necessary for equilibrium uptake of 4-NP by PPC. For the fixed bed study, glass column with cotton plug support at both ends were used in wet packing of the adsorbent. The flow rate was maintained at 2mL/min.

2.4 Adsorption isotherm modeling

The use of the adsorbent for the removal of 4-NP was optimized using several adsorption isotherms. The adsorption equilibrium data was applied to various two parameter models viz. Langmuir, Freundlich, Temkin, Dubunin-Radushkevich and three parameter Redlich Peterson isotherm. The linearized mathematical expressions for the isotherms are given as under:

1. Langmuir adsorption isotherm[2]

$$\frac{C_e}{q_e} = \frac{1}{a_L b_L} + \frac{C_e}{a_L}. \tag{2.2}$$

Here, a_L($mg.g^{-1}$) = monolayer adsorption capacity and b_L($L.g^{-1}$) = Langmuir isotherm constant. Langmuir parameter, b_L, can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor, R_L, and defined by

(2.3) $$R_L = \frac{1}{1+b_L C_0}.$$

If the value of R_L is equal to zero or one, the adsorption is either linear or irreversible, and if the value is in between zero and one, adsorption is favorable to chemisorption. The value of R_L as determined from the Langmuir parameter was found to be 0.614, showing the adsorption process is a favorable one.

1. Freundlich isotherm[3]

(2.4) $$\log q_e = \frac{1}{n_F}\log C_e + \log K_F,$$

where K_F(mg.g-[1])(L.mg^{-1}) and 1n_F are the Freundlich adsorption coefficients.

2. Temkin isotherm[4]

(2.5) $$q_e = B\ln C_e + B\ln K_{Tem}.$$

B = (RT/b_T), Temkin isotherm constant corresponding to the heat of adsorption, with the symbols carrying their conventional respective meanings and K_{Tem}(L.mol^{-1}) = the equilibrium binding constant.

3. <u>Dubunin-Radushkevich isotherm</u>[5]

(2.6) $$\ln q_e = \ln\phi - \psi_D\left\{\ln\left[1+\frac{1}{C_e}\right]\right\}.$$

Φ_D (mg.g^{-1}) and ψ_D = adjustable parameter in the Dubunin-Radushkevich equation.

4. Redlich-Peterson isotherm[6]

$$\ln\left[K_R.\frac{C_e}{q_e}-1\right]=\beta\ln C_e+\ln a_R, \tag{2.7}$$

where a_R(L.mg^{-1}) and K_R(L.mg^{-1}) = Redlich-Peterson isotherm constant, β = constant of the Redlich-Peterson isotherm whose value lies between $0 < \beta < 1$.

2. Results and Discussion

3.1 Characterization of the PPC biochar

SEM image of PPC (Figure 1) revealed the surface morphological structure which is highly heterogeneous with prominent and well developed pores.

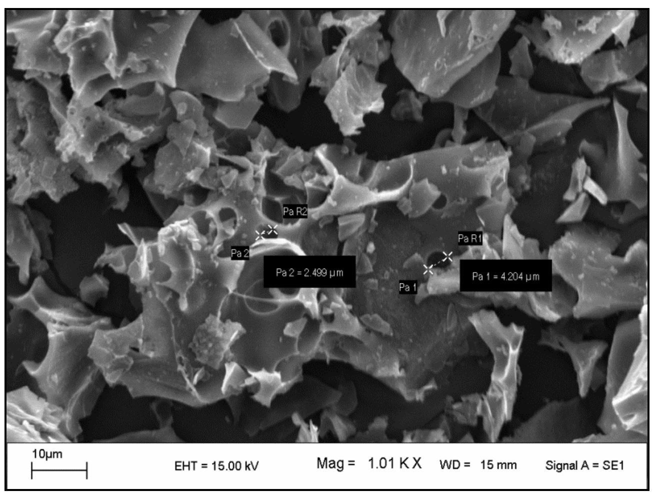

Fig. 1 SEM image of PPC

Surface area and porosity analysis forms an important part of adsorbent characterization. The surface area report is given in Table 1. As expected for a biochar derived from plant residue, the reported BET surface area was relatively low as compared to those of activated carbons. The nitrogen adsorption isotherm (Figure: 2) reveals a Type II adsorption isotherm according to IUPAC classification which is frequently found for surfaces with high mesopore and macropore distribution.

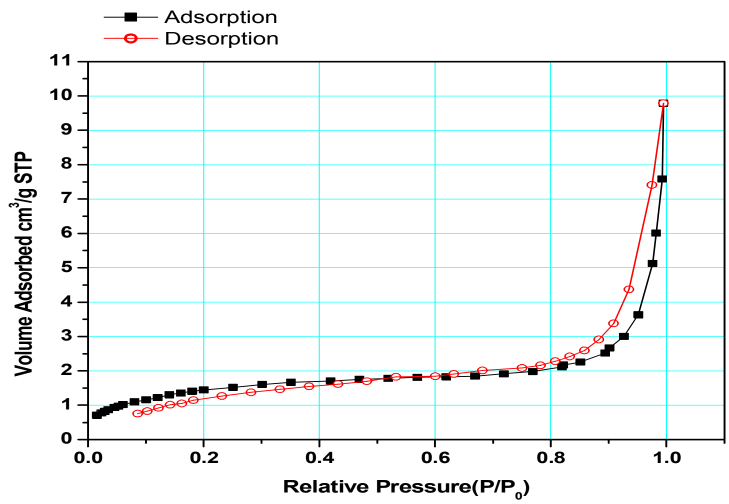

Fig. 2 Nitrogen adsorption-desorption isotherm plot for PPC

Table 1: Summary report for BET analysis of PPC

Area(m^2/g)	
1.Single point surface area at P/P_0 0.20062	5.038
2.BET surface area	5.498
3.BJH adsorption cumulative surface area of pores[a]	3.448
4.BJH desorption cumulative surface area of pores[a]	3.741
Volume(cm^3/g)	
1.Single point adsorption Total pore volume[b]	0.0079
Pore size (nm)	
1. Adsorption Average Pore Diameter(4V/A by BET)	5.76
2.BJH adsorption average pore Diameter(4V/A)	16.863
3.BJH desorption average pore Diameter(4V/A)	15.383

Process parameters: [a] pores between 1.7 and 300 nm diameter; [b] Pores less than 82.577 nm diameter at P/P_0=0.975.

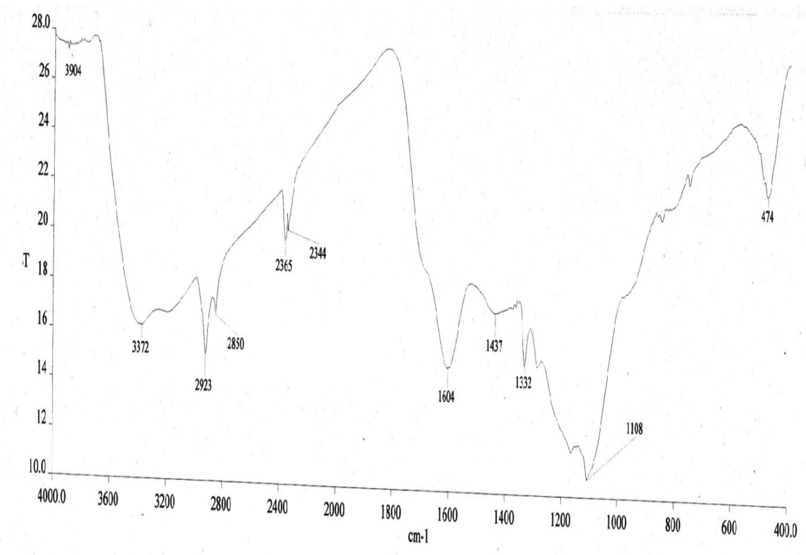

Fig. 3 FTIR spectra of PPC.

The adsorbent was characterized by FTIR spectra for determination of functional groups responsible for adsorption. Some of the prominent peaks include a broad peak at 3372 cm^{-1} due to the –OH stretching of the hydrogen bonded carboxylic group, -C=O stretching of amides at 1604 cm^{-1} and a very intense and prominent peak at 1108 cm^{-1} due to -C-O stretching of the amide group. Another sharp and intense peak at 2923 cm^{-1} is due to H-C-H asymmetric and symmetric stretching of alkanes while the peak at 1604 cm^{-1} is due to the N=O bending of nitro groups.

3.2 Isotherm modeling

Figure (4-8) shows the linear fitting of the different isotherms at 275, 308 and 318 K. For the equilibrium isotherm data, the experimental studies were conducted in the natural pH condition of the adsorbent without any pH alteration. The effect of pH study however proved that PPC is more efficient in acidic pH range between 2-5 pH. A quick analysis of these adsorption isotherms at various temperatures based on coefficient of determination value suggest that Freundlich isotherm is the best fit isotherm to explain the experimental data. Table 2 gives the isotherm constant for Freundlich isotherm at different temperatures. It can be observed that the values of K_F are increases with increasing the temperature of solution from 298 to 318K. The increase in these values with temperature confirms also that the adsorption process is endothermic. More heterogeneous surfaces will show $1/n_F$ value closer to zero[7]

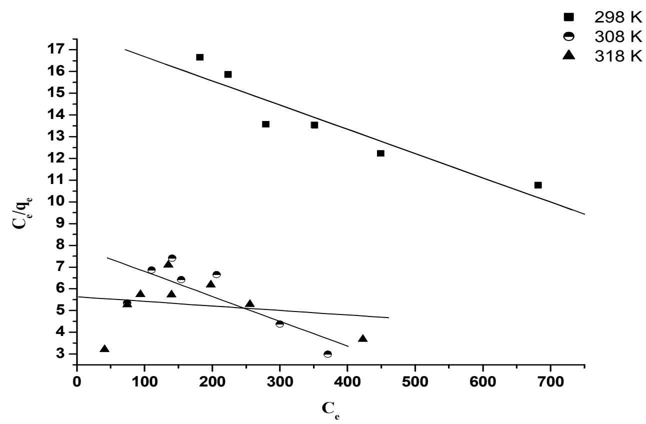

Fig. 4 Langmuir isotherm fitting of 4-NP adsorption by PPC at different temperatures

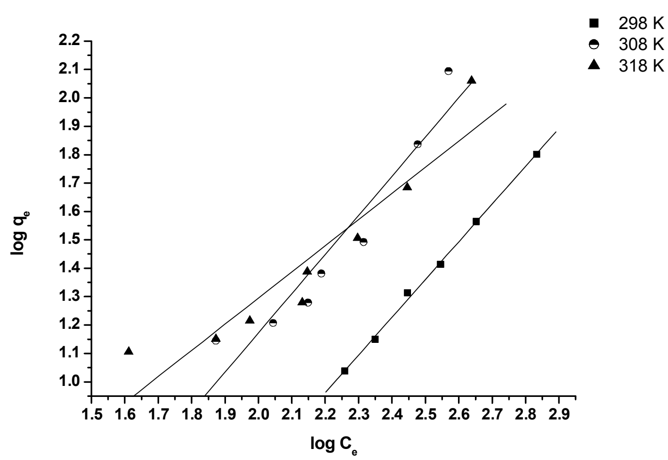

Fig. 5 Freundlich isotherm fitting of 4-NP adsorption by PPC at different temperatures

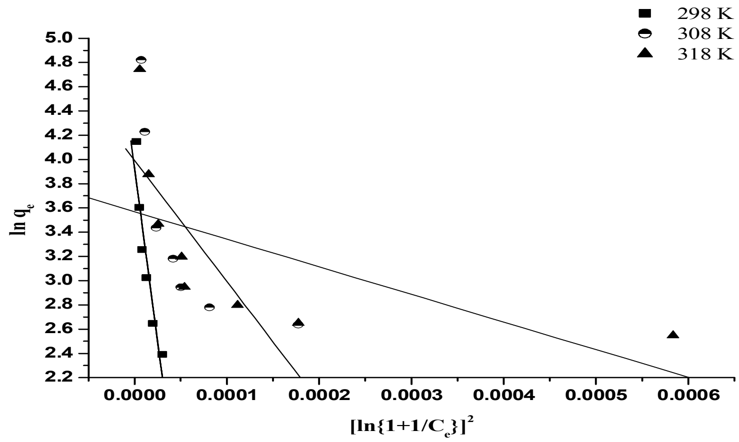

Fig. 6 Dubunin-Radushkevich isotherm fitting of 4-NP adsorption by PPC at different temperatures

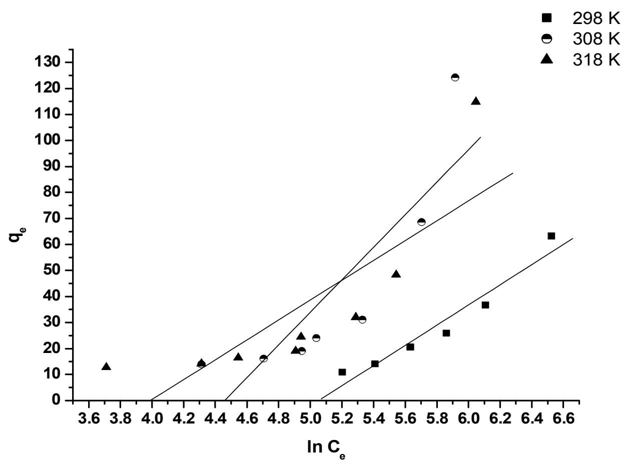

Fig. 7 Temkin isotherm fitting of 4-NP adsorption by PPC at different temperatures

Table 2. Freundlich parameters for 4-NP adsorption at different temperatures

Operating temperature(K)	n_F	K_F (mg.g-^{1})(L.mg^{-1})	R^2
298 K	0.752	0.0109	0.998
308 K	0.7251	0.0259	0.9097
318 K	1.085	0.2836	0.8776

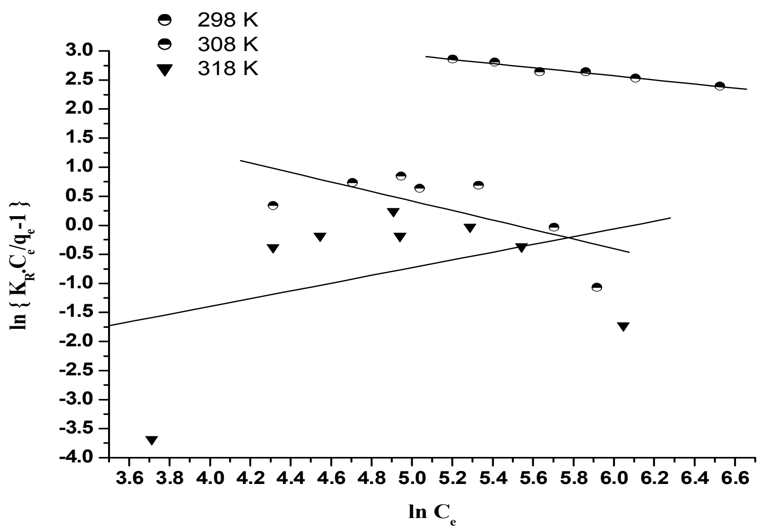

Fig. 8 Redlich-Peterson isotherm fitting of 4-NP adsorption by PPC at different temperatures

The Freundlich maximum adsorption capacity may be calculated using Halsey equation[8] where $q_m = K_F.C_0^{1/n}$. For the present study the calculated Freundlich maximum adsorption capacity was 106.36 mg/g.

3.3 Kinetic study

The contact time study showed that the optimum time necessary for equilibrium adsorption of 4-NP by PPC was determined to be 5h.The Langergren pseudo-first order kinetic model was employed to understand the rate of adsorption uptake whose linearized form is given by equation

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t,$$

where k_1 stands for the first order rate constant in h^{-1} which can be calculated from the plot of $\log\left(q_e - q_t\right)$ vs t (min). q_e and q_t are the amount of 4-NP at equilibrium and time (t).

The adsorption data was also studied by the second-ordered kinetics whose linearized form is given as

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{t}{q_e},$$

where k_2 is the second order rate constant in g.mg^{-1}.h^{-1}

Elovich equation is a useful model for describing chemisorption.

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

where a and b are the Elovich constant which are indicative of initial adsorption rate (mg.g^{-1}.h^{-1}) and desorption constant (g.mg^{-1}) during an adsorption process. The value of $1/b$ as determine from the slope of the plot of q_t versus $\ln t$ relates to the number of sites available for adsorption.

Table 3: Kinetic constants for the uptake of 4-NP by PPC.

	Pseudo-first order	
k_1(h^{-1})	q_e(mg.g^{-1})	R^2
1.378	45.86	0.6309
	Pseudo-second-order	
k_2(g.mg^{-1}. h^{-1})	q_e(mg.g^{-1})	R^2
0.0505	20.36	0.968
	Elovich equation	
a	b	R^2
7.44	3.757	0.943

The degree of goodness of linear plot of these kinetic models was judged from the value of the determination coefficient of the plot. The parameters of the kinetics models (pseudo-first, pseudo-second) with their correspondent coefficients of determination are calculated from the slopes and intercepts of the linear plot of these models and they are summarized in Table 3.It follows that the adsorption of 4-NP by PPC follows pseudo-second order kinetics.

3.4 Fixed bed study

The results of dynamic flow experiments were used to obtain the breakthrough curves for adsorption of 4-NP from aqueous solutions by plotting C_t/C_0 versus time (t). It shows that the column gets saturated after 180 min.

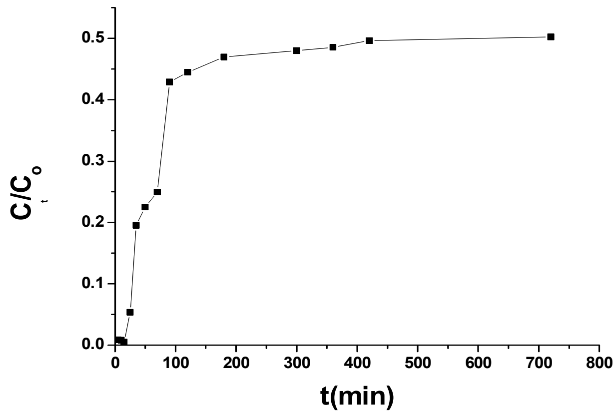

Fig. 9 Breakthrough curve from dynamic fixed bed study for 4-NP adsorption by PPC.

Breakthrough capacities, the amount adsorbed until the effluent concentration of the adsorbate is equal to the influent solution concentration, are computed from the breakthrough curves. The total amount of 4-NP adsorbed through the column can be calculated from the area under the breakthrough curve. The total amount of 4-NP adsorbed through the column was thus calculated using some simple mathematical expressions and was found to be 6.44×10^{-4} mg for 720 min of continuous inflow of the phenol solution for the feed amount of 1.44 mg. The shape of the breakthrough curve can be used to interpret the nature of the adsorption. A steep rise in the curve was detected in the present study which may be attributed to the low residence time of the solute in the column. This observation has also been reported for other aromatic pollutants[9] and is also a common occurrence for organic pollutants adsorbing over activated carbon[10].

3.5 Thermodynamic studies

The thermodynamic parameters like Gibbs free energy change, ΔG^0, enthalpy change, ΔH^0 and entropy change, ΔS^0 are calculated from the usual thermodynamic relations as described by the equations below:

(3.4) $$\Delta G^o = \Delta H^o - T\Delta S^o$$

(3.5) $$\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^0}{R}$$

Table 4 Thermodynamic parameters for adsorption of 4-NP on PPC (pH= natural, C_0= 1000 mg.L^{-1})

Temperature (K)	ΔG^0 (kJ.mol^{-1})	ΔH^0 (kJ.mol^{-1})	ΔS^0 (J.K^{-1}.mol^{-1})
298	-3.985	62.513	223.15
308	-6.216		
318	-8.4478		

As shown in the table, the negative value of ΔG^o confirms the feasibility of the process and the spontaneous nature of adsorption. It was also seen that ΔG° values decreases with increasing temperatures, which itself is a revelation of higher adsorption at higher temperatures. The ΔH^0 value suggested endothermic nature of adsorption taking place at the solute sorbent interface. The positive value of ΔS^0 indicate the increase randomness at the solid/solution interface during the adsorption process. The high value of ΔS^0 indicates irreversible nature of adsorption.

3.6 Economic analysis of PPC

In order to determine the economic feasibility of the application of PPC adsorbent, cost analysis for preparation of 1 Kg of the adsorbent was conducted using break up cost analysis method which include per unit electrical energy consumption for drying, heating and everything else. Overhead cost was calculated at 10 % of the net cost and the total cost was thus estimated to be around 1.22 US $ as compared to 34.50 US $ for 1 Kg of activated Charcoal, Himedia, A.R. Grade (www.himedialabs.com). It may be inferred that the low adsorption capacity is compensated by the low cost nature of the biochar developed from potato peel char (PPC).

Conclusion

The Freundlich isotherm explains the adsorption data adequately compared to the other models studied herein and the maximum adsorption capacity determined from Freundlich constant was 106.36 mg/g at 298 K with the adsorption process following pseudo second order kinetic model. The removal of 4-NP by PPC is purely endothermic process as revealed by the change in enthalpy value. The present work elucidates PPC as a potential adsorbent for the removal of 4-NP from aqueous solutions. One of the striking feature of the biochar lies in of preparation as compared to that of activated carbon. It compensates the comparative low adsorption capacity on an overall basis. The adsorption potential of PPC may further be enhanced by chemical activation process for more efficient removal of 4-NP from aqueous streams.

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