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ORIGINAL ARTICLE

Utilization of Pine Nut Shell derived carbon as an efficient alternate for the sequestration of phthalates from aqueous system

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Abstract This study highlights the importance of a cheap bio waste; Pine Nut Shell (PNS), from which a carbon is synthesized that can efficiently remove toxic phthalates from an aqueous system. PNS derived carbon shows high affinity toward phthalates in descending order along with adsorption capacity i.e., dibutyl phthalate (DBP) 5.65 mg/g > diallyl phthalate (DAP) 3.64 mg/g > diethyl phthalate (DEP) and 2.87 mg/g > dimethyl phthalate (DMP) 2.48 mg/g. Different characterization techniques such as FTIR, elemental analysis, point of zero electric charge (PZC), SEM, EDX and BET were employed to investigate the binding sites and surface area of the adsorbent. Adsorption experiments were performed both in batch and column modes. Equilibrium studies showed that the Langmuir isotherm fits best to experimental data. Kinetically, adsorption phenomena obeyed pseudo second order. Furthermore, thermodynamic results expressed the exothermic nature of adsorption on the basis of negative value of enthalpy change. Column sorption method

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Abbreviations: DMP, dimethyl phthalate; DEP, diethyl phthalate; DAP, diallyl phthalate; DBP, dibutyl phthalate; C_i, initial concentration; PNS, Pine Nut Shells; PNSC, Pine Nut Shell derived carbon; q_e, equilibrium concentration; Q, adsorption intensity or capacity; V, volume of solution taken; M, mass of adsorbent taken; BET, brunauer emmett teller; APE, average percent error; H_i, peak height obtained before adsorption; H_f, peak height obtained after adsorption

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was also adapted to check the feasibility of the adsorption process through the investigation of flow rate, breakthrough curve and pre-concentration factor which is found to be 13 for DMP and DEP and 16 for DAP and DBP. Methanol was found to be best solvent for the recovery of phthalates. Application in real water samples also showed good efficiency of PNS derived carbon for the removal of phthalates.

1. Introduction

Phthalates are a group of organic chemicals which can be used as plasticizers and also for improving the softness and flexibility of poly vinyl chloride (PVC), rubber, cellulose and styrene productions. Different consumer products such as cosmetics, children toys, personal care products, blood transfusion bags, paper coatings, food packaging, binders and decorating products are found to contain phthalates (ATSDR, 1995). Phthalates are only physically confined to the polymeric matrix hence are loosely held into the polymeric frame, therefore, such chemicals can easily be released into food, beverages and drinking water or blood samples, which may enter into the human body through different routes (European Union Council, 2001). These compounds are considered among the most toxic organic pollutants that may cause cancer, liver damage and genetic disorders especially damage to the male reproductive system (Hoyer, 2001; Chang et al., 2009). Research has proved that phthalates exhibit estrogenic properties as a result of which, they are categorized under the classification of endocrine disrupting compounds (Staples et al., 1997). US environmental protection agency and other authentic health care organizations list phthalates among the priority pollutants. The presence of phthalates in surface, ground and drinking waters to levels above their total daily intake values have raised serious scientific concern toward their remediation. The National Institute of Occupational Safety and Health (NIOSH, 1995) has established a recommended exposure limit of 5 ppm for diethyl phthalate (DEP). The European Food Safety Authority set a total daily intake value for diethyl hexyl phthalate (DEHP) and dibutyl phthalate (DBP) as 5 and 2 mg/kg/bw/day, respectively (EFSA, 2005). To ameliorate water quality and to decrease the level of phthalates above their toxic limit, different treatment methods such as photo catalytic degradation (Xu et al., 2007), microbial degradation (Chang et al., 2004), coagulation, flocculation (Thébault et al., 1981), membrane separation employing dense reverse osmosis and nanofiltration (Yoon et al., 2006) and adsorption (Walter et al., 2006) have been proposed for the quick and complete elimination of phthalates.

In this study the adsorption process is preferred over the aforementioned methods of removing phthalates, since it is a simple, reliable and less time consuming technique that excavates trace levels of phthalates from aqueous streams (Ekmekyapar et al., 2006). Different materials either natural or synthetic have been investigated for the removal of phthalates from aqueous solutions. Such materials may include active carbon (Mohan et al., 2007), active carbon modified with cupric nitrate or tertiary butyl ammonium iodide (Adhoum and Monser, 2004), cellulose triacetate (Kosobutskaya and Tovkalo, 1982), nitrocellulose fibers (Lewis and Roberts, 1982) biomass of activated sludge or sea weed (Fang, 2004), calcium montmorrilonite and calcite (Sullivan et al., 1982), modified chitosan beads (Murai et al., 1998), manganese oxides (Matocha and Sparks, 1997), kaolinite, boehmite, goethite, montmorillonite and calcite (Fang and Huang, 2009), surfactant coated nano/micro sized alumina (Jidong et al., 2008), some polymeric resins are also investigated including hydrophilic hyper cross linked polymeric resin NDA 702 (Zhang, 2007), aminated polystyrene resin NDA-101 (Zhang, 2008), co polymer of divinyl benzene and styrene XAD-4 (Xu et al., 2011). The use of ionic liquid coated XAD-4 has also been exploited for the sorption of phthalates from aqueous medium (Qureshi et al., 2012). The literature revealed that very little work has so far been reported on the adsorption of phthalates on natural materials.

In this work we are reporting, for the first time, Pine Nut Shell (PNS) (family *Pinaceae*, genus *Pinus*) as a cheap biosorbent and carbon (PNSC) derived from PNS carbonization for the simultaneous removal of four phthalates namely DMP, DEP, DAP and DBP. Pine nuts are very delicious and nutritious seeds. They are commonly found in Afghanistan. Two species of pines are very common namely the Korean pine (*Pinuskoraiensis*) found in north East Asia and the Chilghoza pine (*Pinusgerardiana*) in the western Himalayas. This paper presents the adsorptive performance of the Chilghoza pine (*Pinusgerardiana*) PNS derived carbon (PNSC) to eradicate a series of toxic phthalates from water systems through the optimization of different experimental parameters such as pH, time, dose of sorbent, concentration and temperature. Performance of PNSC as a sorbent in real water samples is also examined.

2. Materials and methods

2.1. Adsorbent

PNS were obtained from the local market. They were pulverized and sieved in an Ro-Tap type electrical sieve shaker, mesh size ranging between 140 and 600 μm. The material was washed thoroughly with doubly distilled de-ionized water to remove dust, followed by washing with methanol to eliminate any adhered organic impurities. After washing thoroughly, PNS were dried in an oven at 60 °C overnight and stored in a vacuum desiccator. An amount of 0.1 g of each PNS was treated with 1, 0.5, 0.1, 0.01 M HCl and NaOH to increase the number of active sites and surface area (Babu and Ramakrishna, CHM-047). In order to increase the porosity and surface area of the adsorbent, the PNS was also treated thermally and carbon was generated. 5 g of PNS was heated in a muffle furnace (Phoenix, Sheffield, England) at 500 °C for 1 h then kept in vacuum desiccators for further use as adsorbents. This resulted in carbonized material referred to as carbon (Memon et al., 2009). This carbonized PNS is signified as PNSC onward.

2.2. Reagents

All the reagents used were of analytical grade. Phthalate ester mixtures (DMP, DEP, DAP and DBP) were purchased from Merck. HPLC grade methanol and acetonitrile were purchased from Fischer Scientific (UK). All stock solutions were prepared by carefully measuring the required volume of phthalate mixtures into methanol and further dilutions were carried out in de-ionized water. The stock solutions were wrapped with aluminum foil and stored at 4 °C until next use. pH of the working solution was adjusted with 0.1 M HCl and 0.1 M NaOH. All glassware were dipped in 5 M HNO_3 and then washed with de-ionized water before use.

2.3. Instrumentation

A mixture of four phthalates was analyzed via HPLC (Hitachi model L-6200) coupled with a UV–Visible detector (Hitachi L-4200). Phthalates were eluted on reverse phase column inertsil; ODS-3 (250 mm × 4.6 mm) with acetonitrile and water in a ratio of 75:25. The selected wavelength was 226 nm with a flow rate of 1 mL/min. Adsorbent material was characterized by FTIR (using Thermo Nicolet 5700 FTIR spectrometer as KBr pellets), CHNS analyzer (PerkinElmer). BET surface area and pore size distribution were determined by N_2 adsorption using Quanta chrome NovaWin2; Quanta chrome Instrument at −196 °C. Surface morphology and textural study of PNS and PNSC was carried out through SEM images using a scanning electron microscope (Jeol model JSM6380 LV) and chemical analysis was carried out through EDX.

2.4. Sorption procedure

2.4.1. Batch sorption study

Adsorption of a mixture of phthalates was carried out in batch mode by adding 0.1 g of PNSC into an Erlenmeyer flask containing 5 ppm aqueous solution of phthalate mixtures (10 mL). The flask was shaken for 30 min. The analyte solution was filtered using whatman filter paper of 110 mm mesh size. Different adsorption parameters such as pH, dose of adsorbent, shaking time, concentration, and temperature were optimized. Adsorption experiment was performed using a pH range of 2–10, time 5–120 min, sorbent dose 20–600 mg, concentrations of phthalates 0.5–10 mg/L, and temperature 20–60 °C. The reusability test of PNSC was performed under optimized conditions by taking phthalate loaded PNSC into 5 mL methanol and then the mixture was shaken for 15 min. 5 ppm of the phthalate mixture was inoculated into the adsorption medium and the mixture was agitated for a predefined time. Real water samples were spiked with 1 ppm of phthalate mixtures and were analyzed through HPLC by directly injecting 20 μL. The removal efficiency of PNSC was investigated by the difference of peak heights obtained before and after adsorption of the corresponding phthalate mixture using the following equation:

$$\%sorption = \frac{H_i - H_f}{H_i} \times 100 \tag{1}$$

Maximum batch sorption capacity Q of PNSC was obtained through the following equation:

$$Q = \frac{V \cdot (C_o - C_f)}{M} \tag{2}$$

where C_o and C_f are the initial and equilibrium concentrations of phthalates (mg/L), V is the volume of the solution (L), M is the mass of the adsorbent (g).

Extent of adsorption may also be calculated as the amount of adsorbate adsorbed per unit area of adsorbent which is formulated below as (Ayranci and Bayram, 2005):

$$M = \frac{(C_o - C_t) \cdot V}{52.35 \cdot m} \tag{3}$$

where C_o and C_t are the initial concentrations and solution concentration at a given time, 52.35 m^2/g is the specific surface area of PNSC, V and m are the volume of solution and the mass of the adsorbent respectively.

Statistical function such as average percent error (Hamdaouia and Naffrechoux, 2007) was adopted to validate kinetic and equilibrium sorption models apart from regression analysis using the following expression:

$$\mathrm{APE}(\%) = \frac{\sum_{i=1}^{N} [(q_{e(\exp erimental)} - q_{e[predicted]})/q_{e\,[\exp erimental]}]}{N} \times 100 \tag{4}$$

where N is the number of experimental data.

2.4.2. Column sorption study

Column sorption was performed in a solid phase extraction assembly supplied by Supelco using an empty SPE cartridge onto which 0.1 g of PNSC was loaded in between glass wool to prevent any loss of adsorbent material. Upon completion of column preparation, the column was connected to a piston mini pump with poly tetrafluoro ethylene (PTFE) tubes (i.d. 0.5 mm). The entire assembly was carefully rinsed with milli Q water prior to use. PNSC packed SPE column was conditioned by passing 10 mL methanol and 10 mL milli Q water through the column. After column conditioning, 10 mL of solution containing 5 mg/L phthalate mixture was passed through the column to optimize different column operational parameters such as flow rate, breakthrough volume and recovery.

The adsorbent exhaustion rate is the mass of adsorbent per volume of liquid treated at breakthrough (Ko, 2000):

$$\text{Adsorbent exhaustion rate} = \frac{\text{Mass of the adsorbent}}{\text{Breakthrough volume}} \tag{5}$$

3. Results and discussions

3.1. Characterization

To explore the surface active sites and also to locate the presence of different functional groups present on the surface of PNS and PNSC, FTIR study of the adsorbent material is performed before and after adsorption and also for the raw surface as shown in Fig. 1. Three IR spectra's; one for raw PNS indicated as (A), phthalate loaded PNSC indicated as (B) and other for PNSC indicated as (C) are shown in Fig. 1. The broad band at 3400 cm^{-} in (A) suggests the presence of

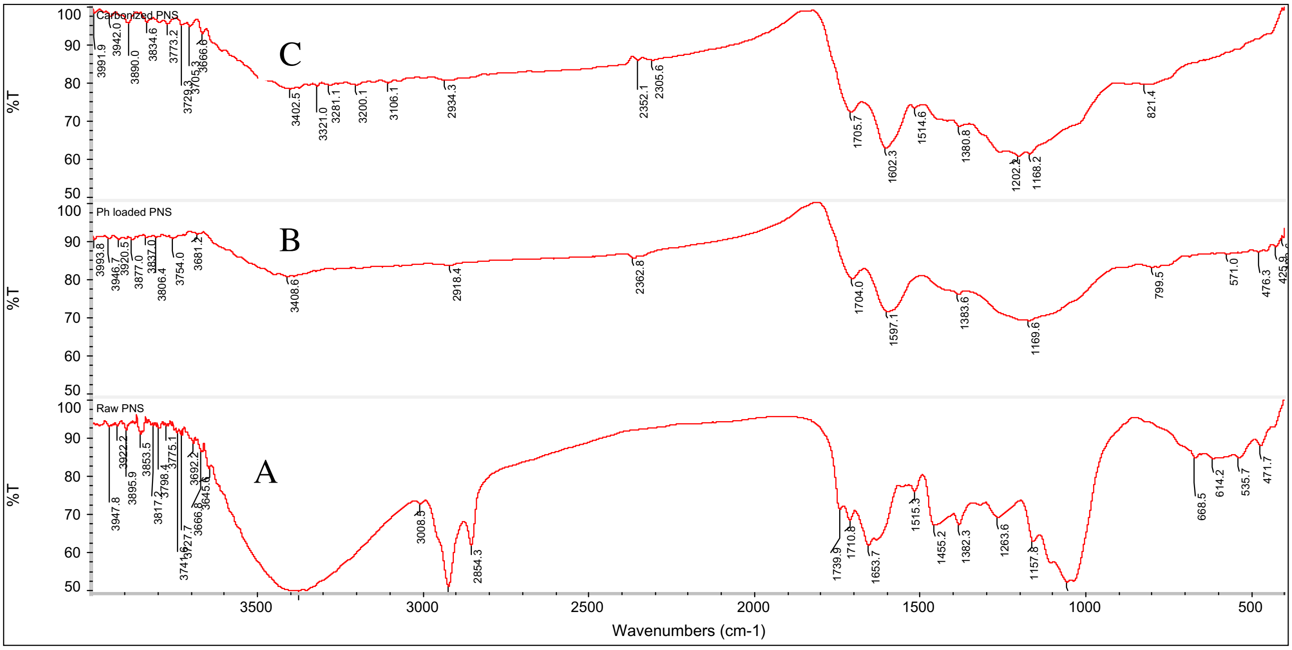

Figure 1 FTIR spectra of raw PNS (A), phthalate loaded PNS (B) and carbonized PNS (C).

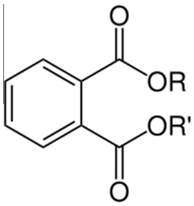

Fig. 1 (*continued*)

hydrogen bonded hydroxyl groups, two bands at 2920 and 2854 cm^{-} suggest C–H stretching of alkyl groups. The band at 1455 cm^{-} may be assigned to the C–H bending of a methylene group, the medium band at 1382 cm^{-} represents the presence of a methyl group, the broad band at 1263 cm^{-} refers to the first overtone of C–H bending vibration while a broad and strong band at 1100 cm^{-} may be due to C–O stretching. The band at 668 cm^{-} points to the rocking or in-plane bending of the methylene group. In case of (C), the intensity of hydroxyl groups has been significantly reduced. In (B), the positions of bands of, C=C at 1597 cm^{-}, methyl at 1383 cm^{-}, methylene in plane bending at 799 cm^{-} have been slightly shifted which highlight the major participation of these functional groups to the adsorption of phthalates. This investigation also reveals that major forces for holding phthalates onto the adsorbent surface are hydrophobic and pi–pi interactions.

Point of zero electric charge of both raw and PNSC was determined by a simple electrolyte addition method (Mahmood et al., 2011). Briefly, 0.1 g each of PNS and PNSC were immersed separately into 10 mL 0.05 M of different pH solutions and were shaken at constant speed for 24 h. After filtration, the final pH of the filtrate was measured and the difference between the initial and final pH was plotted against the initial pH as shown in Figs. 2 and 3.

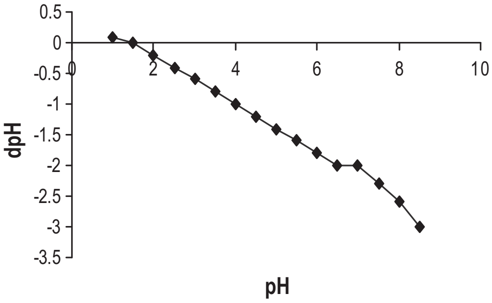

Figure 2 Showing point of zero electric charge on carbonized PNS and raw PNS.

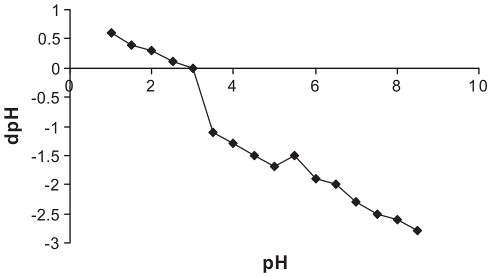

Figure 3 Showing point of zero electric charge on carbonized PNS and raw PNS.

Figs. 4 and 5 show SEM micro graphs of raw PNS and PNSC respectively. It can be noticed that the surface of raw PNS was constricted and was rough with minute amount of small pores, whereas, the surface of PNSC was also rough but pores have become enlarged and certain cracks have been developed which participates in the enhancement of specific surface area of PNSC. Furthermore, the surface adhered

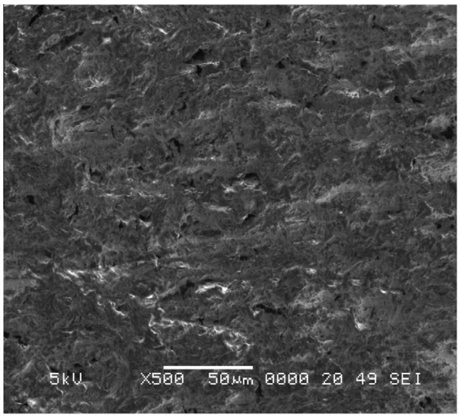

Figure 4 Showing textural characteristics of raw PNS and carbonized PNS respectively.

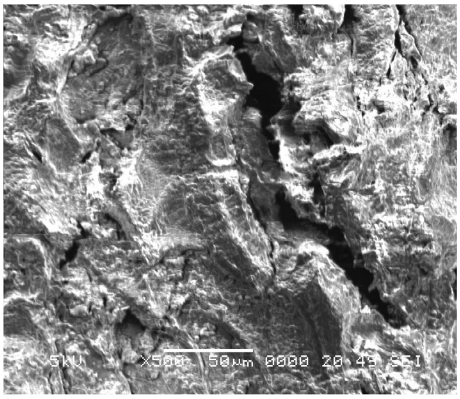

Figure 5 Showing textural characteristics of raw PNS and carbonized PNS respectively.

atoms were characterized through EDX to understand the role of adhered atoms toward phthalate uptake.

From Fig. 6 it was observed that the surface of the PNSC was rich in aluminum and silicon minerals.

Elemental analysis of PNS and PNSC compares the presence of carbon contents in both samples. It was found that the percent of carbon increased in PNSC and the proportion of oxygen and hydrogen decreased with respect to the PNS as shown in Table 1.

Table 1 Textural characteristics of raw PNS and carbonized PNS.

Properties	Raw PNS	Carbonized PNS
BET surface area	24.84 m^2/g	52.35 m^2/g
% *C*	48.63	56.36
% *H*	6.072	3.31
BJH surface area	29.16 m^2/g	43.01 m^2/g
Pore diameter	35.23 Å	35.23 Å
Point of zero electric charge	3	1.5

Multipoint BET plot and the Barret Joyner Halenda (BJH) method was adapted to measure the specific surface area and pore size distribution of the both PNS and PNSC adsorbents given in Table 1. It was observed that PNSC resulted in a two fold increase of specific surface area as compared to PNS. Pore size distribution was found to be 35.23 Å for both PNS and PNSC showing that a vast majority of pores fall within the range of mesopore structure. Detailed characteristics of both PNS and PNSC are summarized below in Table 1.

3.2. Effect of pH

Influence of pH on sorption studies was examined within the range of 2–10, by preparing 5 mg/L of phthalate mixture in double distilled deionized water followed by pH adjustment using 0.1 M HCl and NaOH, respectively. An amount of PNSC (0.1 g) was added to the phthalate solutions of different pH and shaken for 1 h. After filtration, the residual concentration of each phthalate was analyzed. It was found that the percent removal of phthalate mixture decreased with rise in pH of the solution. Maximum phthalate uptake was found to be at pH 2 as shown in Fig. 7.

This can be explained on the basis of point of zero electric charge of the adsorbent, since the PZC of the carbonized adsorbent is pH 1.5. The surface of PNSC generates a negative charge at pH > 1.5 and the Phthalate molecule (Fig. 1b) exists in protonated form at pH 2 owing to the presence of oxygen atoms attached to the phthalate molecule which enhances electrostatic attraction between a positively charged phthalate molecule and a negatively charged PNSC. Furthermore, pKa values of two carboxylic acid groups of phthalates are 3 and 5.4 (Adhoum and Monser, 2004), respectively. Above these

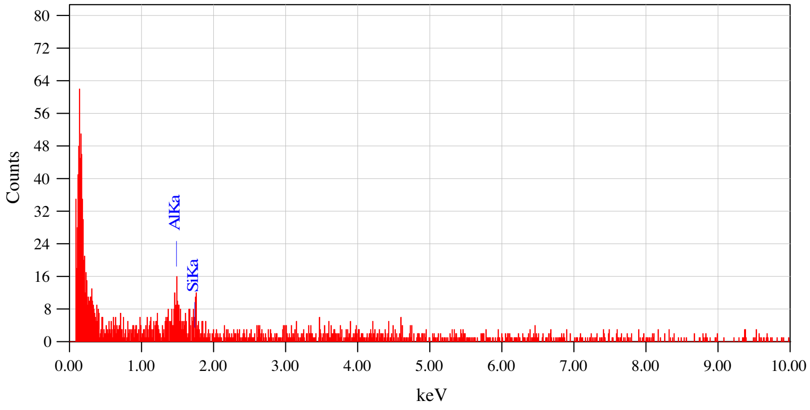

Figure 6 EDX spectra of carbonized PNS.

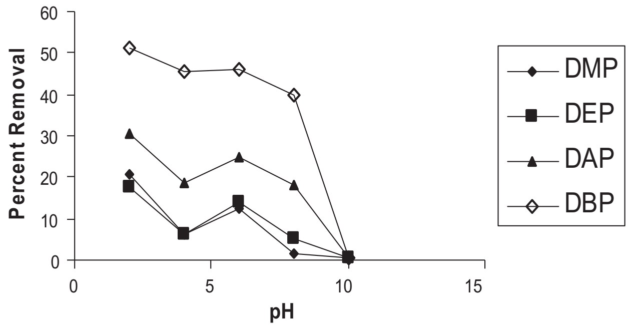

Figure 7 Effect of pH on percent removal of phthalates.

pH values phthalates will get hydrolyzed to generate the carboxylate anion which results in repulsive forces between the negatively charged adsorbate and negatively charged adsorbent. The sorption inhibition observed throughout the basic pH range might also be attributed to an increase in hydroxyl ion concentration leading to the formation of aqua complexes which thereby retard sorption. Sorption among phthalates rises with increasing alkyl chain which may be due to strong hydrophobic interactions and dispersive forces playing between longer alkyl chains in phthalates and hydrophobic sites on PNSC. This result is in close agreement with the reported literature (Mohan et al., 2007).

3.3. Effect of dose

Fig. 8 shows the effect of the amount of adsorbent studied by taking different amounts of PNSC (0.02–0.6 g) keeping other parameters constant. Percent uptake of all the phthalates increases rapidly from 0.02 to 0.4 g but after that, a very small rise in percent removal of all phthalates is noticed. To carry out further studies 0.4 g of PNSC was selected as an optimum dose for phthalate removal. It may also be explained on the basis of the maximum coverage of active sites by phthalate on or before 0.4 g sorbent and a state of equilibrium is nearly achieved on the surface of PNSC.

3.4. Effect of time and kinetics of adsorption

Adsorption kinetic results are useful to predict the uptake rates as well as to possibly suggest the nature of adsorption. The experimental adsorption kinetic results were obtained for PNSC at an initial concentration of a mixture of phthalates as 5 mg/L, pH 2, dose 0.4 g and temperature 25 °C as shown in Fig. 9. It can be found that the adsorption uptake of phthalates on PNSC was fast and after 120 min, adsorption performance ceased due to the complete dissemination of phthalate molecules onto the adsorbent surface. Further understanding of adsorption behavior and rate limiting step was gained by applying different kinetic models.

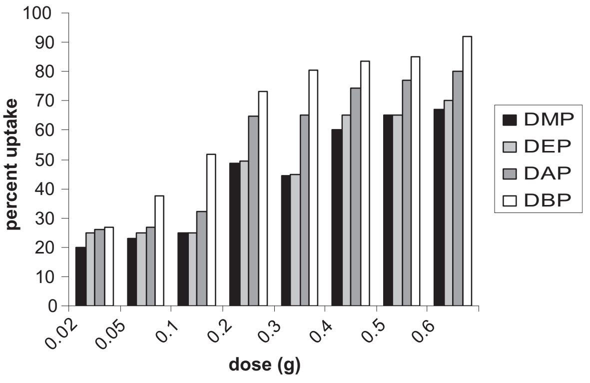

Figure 8 Effect of carbonized PNS dose on phthalate removal.

3.4.1. Lagergren pseudo first order model

The Lagergren equation is the earliest example describing the rate of adsorption in the liquid phase system. This equation has been one of the most used equations particularly for pseudo first order equations (Lagergren, 1898):

$$\ln(q_e - q_t) = \ln q_e - k_1.t \tag{6}$$

where k_1 (min^{-}) is the adsorption rate constant, q_e and q_t are the values of amounts adsorbed per unit mass at equilibrium and at time t respectively. The values of k_1 and q_e can be obtained from slope and intercept respectively. The experimentally calculated q_e and adsorption constant k_1 are given in Table 2.

3.4.2. Pseudo second order model

Pseudo second order kinetics may be tested on the basis of equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{7}$$

where k_2 is the second order rate coefficient, q_e and q_t are the concentrations of adsorbate at equilibrium and at time t. Linear plot of t versus t/q_t gives a straight line from which the value of k_2 and q_e can be determined from their intercept and slope respectively. The pseudo-second order equation has also been interpreted as a special kind of Langmuir kinetics. This line of interpretation assumes that (i) the adsorbate concentration is constant in time and (ii) the total number of binding sites depends on the amount of adsorbate adsorbed at equilibrium. One of the advantages of the pseudo-second order equation for estimating the q_e values is its small sensitivity for the influence of the random experimental errors. The correlation coefficient for the second order kinetics is found to be 0.999 for all phthalates which confirms the validity of pseudo second order rate kinetics for the sorption of phthalates. Furthermore, calculated APE% also supports pseudo second order kinetics. The calculated parameters are given in Table 2. The obtained

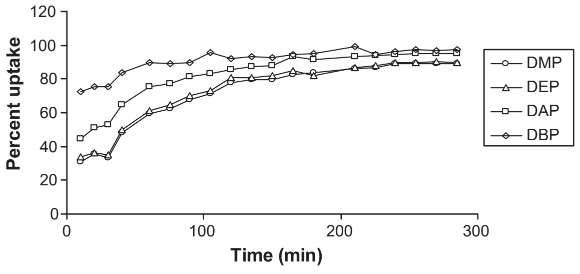

Figure 9 Kinetic study on phthalate removal over carbonized PNS.

Table 2 Kinetic parameters for different models obtained for different phthalates.

Pseudo first order $\ln(q_e - q_t) = \ln q_e - k_1 t$	q_e (mg/g)	K_1 (min$^-$)10^{-3}	R^2	% APE
DMP	3.89	5.5	0.988	2.31
DEP	3.69	6.5	0.971	1.67
DAP	3.76	6.6	0.955	1.69
DBP	1.44	8.2	0.865	2.56
Pseudo second order $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) \cdot t$	K_2 (g mg$^-$ min$^-$)10^{-3}	q_e (mg/g)	R^2	% APE
DMP	4.38	5.18	0.993	1.23
DEP	4.81	5.17	0.993	1.45
DAP	8.62	5.15	0.998	1.02
DBP	26.1	4.98	0.999	2.01
Morris Weber equation $q_t = k_i.t^{0.5} + C_i$	K_i (mg/g min$^{-0.5}$)	C_i	R^2	
DMP	0.0103	2.0908	0.829	2.87
DEP	0.01	2.202	0.813	2.67
DAP	0.0081	2.932	0.778	3.21
DBP	0.0038	3.994	0.711	2.54

rate constant value for DBP was extremely high for DBP which suggests high affinity of the surface toward the latter molecule.

3.4.3. *Morris Weber equation*

Sorption kinetics are controlled by different steps including solute transfer to the adsorbent particle surface, transfer from adsorbent particle to intra particle active sites and retention of sorbate on those sites via complexation, adsorption and intra particle diffusion phenomena. Contribution of intra particle diffusion mechanism can be tested by applying the Weber Morris equation (Weber and Moris, 1963) which is:

$$q_t = k_i.t^{0.5} + C_i \tag{8}$$

The significant feature of this model is that the linear plot of q_t vs $t^{0.5}$ should pass through the origin (zero intercept), which indicates that intra particle diffusion is the actual rate limiting step. Since the plot revealed that the line did not pass through its origin (results not shown), therefore, intraparticle diffusion is not a rate limiting step. Where q_t is the fraction of the solute adsorbed on the adsorbent at time t and K_i (mg/g min$^{-0.5}$) is the diffusion coefficient C_i is the intra particle diffusion constant obtained from the intercept of the line. It is directly proportional to the boundary layer thickness (Table 2). As the value of intraparticle diffusion constant rises from DMP to DBP, the external mass transfer increases which means phthalates with a small alkyl chain such as DMP are accessible to inner pores of the adsorbent while phthalates with larger alkyl chains such as DBP are only accessible to the surface of the adsorbent. Hence, DMP greatly favors bulk sorption whereas, DBP favors surface sorption. The trend of adsorption mechanism varies with variation in alkyl chain length, i.e. from bulk to surface with a rise in alkyl chain. The diffusion rate of DMP was higher than DEP, DAP and DBP due to its higher concentration, remained in the solution phase after surface adsorption, results in an increase of the driving force, which increases the diffusion rate.

3.5. *Adsorption isotherms and adsorption affinity*

An adsorption isotherm describes the relation between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid medium at equilibrium. Effect of concentration on the adsorption performance of PNSC was examined by varying the concentrations of phthalates from 0.5 to 10 ppm, other parameters were kept constant. It was observed that percent uptake decreases with a rise in concentration of phthalates which may be explained due to weaker interactions of phthalates or may be due to intermolecular attraction of phthalates together in a solution which may exceed the pore diameter and hence resistance to adsorption could be achieved as shown in Fig. 10. The given data were applied to validate sorption isotherms. Adsorption affinity of selected phthalates was calculated in terms of its distribution coefficient K_d (Bonnesen et al., 2000):

$$K_d = \frac{\text{mg of phthalate adsorbed/g adsorbent}}{\text{mg of phthalate present/L of solution}} \tag{9}$$

The calculated distribution coefficient for the four phthalates is shown in Table 3. With rise in concentration, distribution coefficient of phthalates decreases supporting that adsorption decreases with rise in initial concentration.

The sorption experimental data were evaluated to use in sorption isotherms. Freundlich isotherm was tested in the following form (Freundlich, 1906):

$$\ln C_{ads} = \ln A + \frac{1}{n} \ln C_e \tag{10}$$

where C_{ads} (mg/g) is a concentration sorbed on a sorbent, A is a sorption capacity constant in the same unit. $1/n$ is another constant related to energy or intensity of sorption. It is a measure of deviation from linearity. The value ranges from 0 to 1. The obtained value of n was greater than 1 which suggests favorable adsorption of studied phthalates (Hameed, 2009). Freundlich isotherm describes the heterogeneity of surface and exponential dispersion of active sites and energies. The plot of ln C_{ads} versus ln C_e gives a straight line from which ln A and $1/n$ can be determined through intercept and slope and calculated parameters are listed in Table 4.

Langmuir isotherm (Langmuir, 1918) was tested to evaluate the sorption of phthalates onto PNSs in the following form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Q.b} + \frac{C_e}{Q} \tag{11}$$

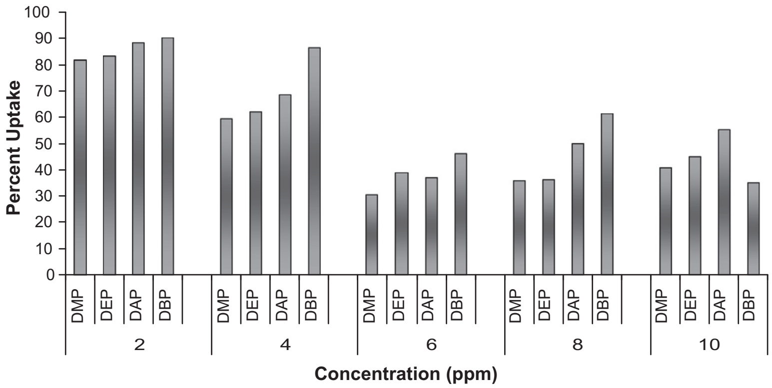

Figure 10 Effect of concentration of phthalates on their percent removal over carbonized PNS.

Table 3 Distribution coefficients for four different phthalates on carbonized PNS.

Initial concentration (mg/L)	K_d (L/g)			
	DMP	DEP	DAP	DBP
2	4.45	4.92	7.51	9.00
4	1.46	1.63	2.17	6.27
6	0.55	0.63	0.57	0.851
8	0.48	0.56	0.98	1.57
10	0.66	0.81	1.22	0.541

Table 4 Parametres of different adsorption isotherms for four phthalates.

Langmuir isotherm $\frac{C_e}{C_{ads}} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}}$	Freundlich isotherm $\ln C_{ads} = \ln A + \frac{1}{n} \ln C_e$	D-R isotherm $\ln q_e = \ln X_m - \beta\, \varepsilon^2$
DMP		
$Q_{max} = 2.48$ mg/g,	$\frac{1}{n} = 0.21$	$X_m = 3.156$ mg/g
$b = 3.48$ (L mg^{-})		$\beta = -0.0643$
$R^2 = 0.853$	$A = 1.99$ (mg/g) (L mg)$^{1/n}$	$E = 6.91$ kJmol^{-}
% APE = 2.41	$R^2 = 0.451$	$R^2 = 0.41$
$M = 0.054$ mg m^{-2}	% APE = 5.45	% APE = 3.44
DEP		
$Q_{max} = 2.87$ mg/g	$\frac{1}{n} = 0.25$	$X_m = 4.14$ mg/g
$b = 2.98$ (L mg^{-})		$\beta = -0.0526$
$R^2 = 0.971$	$A = 2.14$ (mg/g)(L mg)$^{1/n}$	$E = 7.64$ kJmol^{-}
% APE = 1.98	$R^2 = 0.560$	$R^2 = 0.746$
$M = 0.055$ mg m^{-2}	% APE = 5.78	% APE = 3.56
DAP		
$Q_{max} = 5.65$ mg/g	$\frac{1}{n} = 0.26$	$X_m = 4.143$ mg/g
$b = 1.083$ (L mg^{-})		$\beta = -0.0526$
$R^2 = 0.891$	$A = 2.53$ (mg/g)(L mg)$^{1/n}$	$E = 6.91$ kJmol^{-}
% APE = 2.03	$R^2 = 0.523$	$R^2 = 0.746$
$M = 0.075$ mg m^{-2}	% APE = 6.02	% APE = 2.99
DBP		
$Q_{max} = 3.64$ mg g^{-}	$\frac{1}{n} = 0.16$	$X_m = 4.28$ mg/g
$b = 12.9$(L mg^{-})		$\beta = -0.0428$
$R^2 = 0.972$	$A = 2.91$ (mg/g)(L mg)$^{1/n}$	$E = 8.46$ kJmol^{-}
% APE = 1.54	$R^2 = 0.441$	$R^2 = 0.874$
$M = 0.093$ mg m^{-2}	% APE = 5.67	% APE = 3.02

The Langmuir isotherm is explicit about well defined homogenized functionalities possessing equal sorption energy, independent surface coverage and no interaction between the sorbed molecule. The plot of $\frac{C_e}{C_{ads}}$ vs C_e gives $\frac{1}{Q}$ and b as a slope and intercept from which the value of Q can be determined. In the equation b is a constant related to free energy of sorption and rises from DMP to DBP suggesting maximum affinity of surface atoms of PNSC toward DBP and favors encapsulation of DBP over its surface while for other members the value is small which further encourages the surface sorption of DBP on PNSC. The regression coefficient for all phthalates examined were higher indicating good fit of the langmuir isotherm to our experimental data which is also proved from calculated values of average percent error (APE%).

D-R isotherm (Ahmed and Mohammed, 2008) is used to estimate the characteristic porosity of the adsorbent and the apparent energy of adsorption. The model is represented by the equation:

$$\ln q_e = \ln X_m - \beta\, \varepsilon^2 \tag{12}$$

where q_e is the amount sorbed in mg/g, X_m is the sorption capacity (mg/g), β is a constant related to free energy and ε is a Polanyi potential which is related as

$$\varepsilon = R\, T \ln\left(1 + \frac{1}{C_e}\right) \tag{13}$$

where R is a gas constant in kJ/mol, T is the temperature in K and C_e is the equilibrium concentration. Polanyi potential is defined as the work done in removing the molecule to infinity from its location. The linear plot of ε^2 vs $\ln q_e$ gives β as a slope and $\ln X_m$ as intercept. Knowing the value of slope, the energy E can be calculated from the following equation:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{14}$$

All the characteristic parameters for the aforementioned isotherms along with the adsorption capacity per unit area of adsorbent are summarized in Table 4.

On the basis of the calculated adsorption capacity of phthalates, a comparative study was carried out from the reported work of different researchers and the results are summarized in Table 5.

3.6. Effect of temperature

Effect of temperature on the percent uptake of phthalates was monitored to understand the nature of sorption. It was ob-

Table 5 Comparitive study of adsorption capacities of different adsorbents versus arbonized adsorbent.

Phthalates	Adsorbents reported	Adsorption capacities (mg/g)		Refs.
DMP	Chitosan beads	0.009		Catherine et al. (2010)
DEP				
DAP				
DBP		0.022		
DMP	Nano/Micro sized alumina	Nano	Micro	Jidong et al. (2008)
DEP		0.289	0.136	
DAP				
DBP				
DMP	SBA-15, C_8 SBA-15, C_{18}SBA-15	0.00178, 0.0031, 0.00374		Huang et al. (2008)
DEP				
DAP	SBA-15, C_8 SBA-15, C_{18}SBA-15	0.00245, 0.00965, 0.001052		
DBP				
DMP	α-Cyclodextrin linked chitosan beads	2.76		Chen et al. (2007)
DEP		2.82		
DAP				
DBP		3.16		
DMP	RTIL-XAD-4			Qureshi et al. (2012)
DEP				
DAP				
DBP		4.75		
DMP	β-Cyclodextrin	0.075		Murai et al. (1998)
DEP		0.109		
DAP				
DBP		0.683		
DMP	Multi walled carbon nanotubes (10–20 nm)	10–20 nm diameter	40–60 nm diameter	Walter et al. (2006
DEP	(40–60 nm)	0.05	0.031	
DAP		0.216	0.158	
DBP				
DMP	Pine Nut Shells (PNS)	2.48		Present study
DEP		2.87		
DAP		3.64		
DBP		5.65		

served that percent uptake decreases with increase in temperature as shown in Fig. 11 suggesting that adsorption is an exothermic process.

Thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were calculated from the following equations (Liu and Liu, 2008):

$$\Delta G = -R\,T \ln K \tag{15}$$

where R is a gas constant (0.008314 kJ/mol) and T is a temperature in Kelvin and K is calculated from the following formula. According to the 9th comment by reviewer 2).

$$K = \frac{F_e}{1 - F_e} \tag{16}$$

where Fe is the fraction of solute adsorbed at equilibrium.

Effect of temperature on equilibrium is determined as:

$$\ln\ K = -\frac{\Delta H^o}{R.\,T} + \frac{\Delta S^o}{R} \tag{17}$$

ΔH and ΔS can be determined from the slope and intercept respectively. Table 6 shows the calculated thermodynamic parameters for the mixture of phthalates.

Table 6 shows that all the thermodynamic parameters are found with a negative sign reflecting exothermic, highly spontaneous adsorption phenomena. This type of adsorption is energetically more favored at ambient temperature. From the work reported by Liu and Liu (2008), the heat evolved during adsorption within the range 2–20 kJ/mol infers physical adsorption while the range between 80–200 kJ/mol infers chemical adsorption. From the above tabulated data it can be considered that the range of heat of adsorption falls between the boundaries of both physical and chemical adsorption hence adsorption can be inferred as physico-chemical in nature.

3.7. Regeneration of adsorbent

Regeneration of adsorbent is a very important parameter in the field of adsorption science. It is very necessary that the material of interest should be very cheap and economical and may offer better recyclability to save cost and prevent biomass disposal. In order to check the reusability of PNSC, 0.4 g of phthalate loaded PNSC was put into 3 and 5 mL of each of different solvents namely, methanol, ethanol, acetonitrile and ethyl acetate and sequentially agitated in respective solvents for 30 min to check the desorption of phthalates from carbonized PNS. It was found that 3 mL methanol can be a good stripping solvent as it was of low cost and showed good recovery. PNSC were dried in an oven and again added to the aqueous solution of phthalate mixture and their adsorption performance was checked five times. It was observed that reusability experiments gave excellent results as shown in Fig. 12. PNSC proved to be a good sorbent up to three times of its application in the aqueous environment.

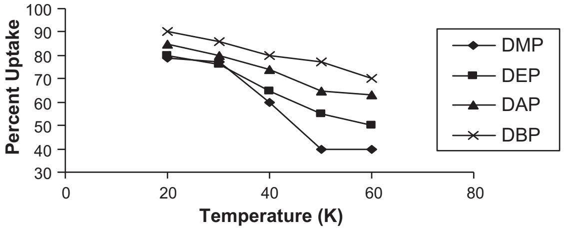

Figure 11 Effect of temperature of solution of phthalates on removal efficiency of phthalates.

Table 6 Thermodynamic parameters of adsorption of phthalates on carbonized PNS.

Phthalate	ΔH (kJmol^{-})	ΔS (JK^{-}mol^{-})	ΔG (kJmol^{-})
			293 K
DMP	−41.1	−0.12	−3.22
DEP	−30.2	−0.09	−3.37
DAP	−25.8	−0.07	−4.22
DBP	−26.8	−0.07	−5.35

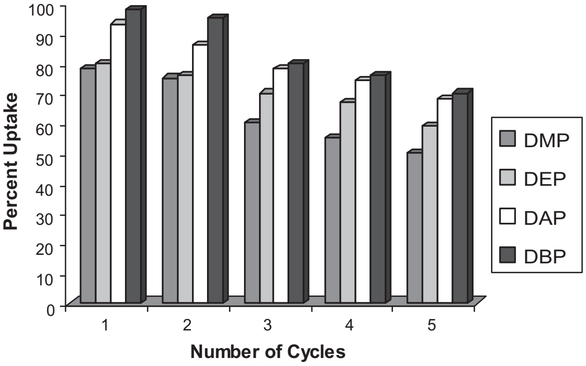

Figure 12 Reusability of carbonized PNS against phthalate removal.

3.8. Columns sorption studies

3.8.1. Effect of flow rate

Flow rate was optimized using solid phase extraction cartridges. Each cartridge was loaded with 0.1 g PNSC. 10 mL of feed concentration (5 mg/L) of phthalates was passed through the SPE cartridge with different flow rates ranging from 0.5–5 mL/min. It was observed that removal efficiency increases at low flow rate and goes on decreasing with increasing flow rate. The maximum removal efficiency up to 95% was observed at 2 mL/min for each phthalate. When the flow rate is increased up to 5 mL/min, the removal efficiency decreases up to 80% for all phthalates but for dimethyl phthalate removal efficiency significantly drops off to 55.04%. This may be due to the fact that the slower the flow rate, greater will be the equilibrium contact between the phthalate and PNSC surface and hence greater will be the removal efficiency. The total rate of adsorbent exhaustion was found to be 0.198 min.

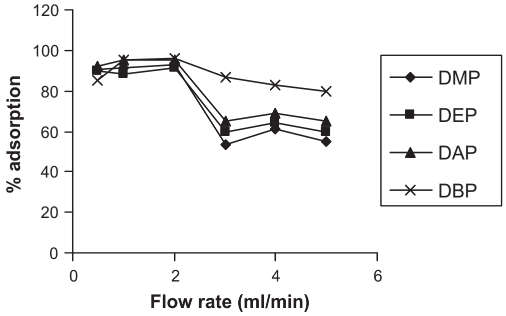

Figure 13 Effect of solution flow rate on percent removal of phthalates on carbonized adsorbents.

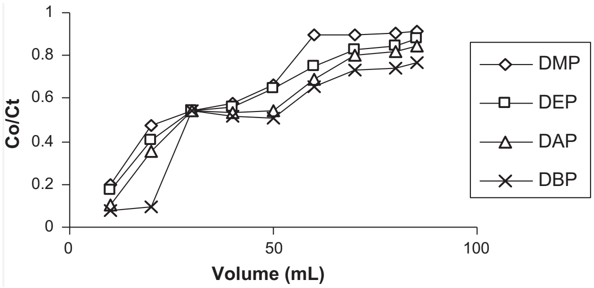

Figure 14 Breakthrough curve indicating breakthrough volume of carbonized PNS adsorbent.

Table 7 Analytical applications of four phthalates in three water samples.

Samples	Added	Found	Percent removal onto PNS
Kotri industrial samples	DMP 5 mg/l	ND	57.5
	DEP 5 mg/l	ND	56.1
	DAP 5 mg/l	ND	80.42
	DBP 5 mg/l	ND	98.18
Phulely canal samples	DMP 5 mg/l	ND	43.52
	DEP 5 mg/l	ND	51.5
	DAP 5 mg/l	ND	73.45
	DBP 5 mg/l	4 mg/l	91.83
Tap water samples	DMP 5 mg/l	ND	40.3
	DEP 5 mg/l	ND	48.3
	DAP 5 mg/l	ND	63.07
	DBP 5 mg/l	ND	76.117

3.8.2. Breakthrough curve study (influence of volume)

Breakthrough volume refers to the volume of solution at which effluent concentration becomes 5–6% of influent concentration (Mondal, 2009). 0.1 g of PNSC was loaded onto a solid phase extraction cartridge and the solution of phthalate mixture continuously flowed through at a fixed flow rate of 2 mL/min. After passing every 10 mL of phthalate solution, effluent concentration was analyzed via HPLC for the determination of breakthrough volume. The curve obtained was S-shaped. For all analytes breakthrough occurred at around 20 mL, hence the breakthrough capacity calculated was 2 mg/g for all studied phthalates. See Fig. 13.

3.8.3. Limit of preconcentration and preconcentration factor

The limit of preconcentration was determined by increasing the dilution of the phthalates in solution keeping the total amount of loaded phthalates at 10 μg. Adsorbed phthalates were recovered (desorbed) with 3 mL of methanol (as optimized). All four phthalates can be removed quantitatively from solutions of concentration up to 0.25–0.2 μg/mL with recovery of around 80% yielding preconcentration factors of 13 for DMP and DEP and 16 for DAP and DBP. See Fig. 14.

3.9. Analytical application

In order to validate our developed method and to check the performance of our newly explored adsorbent, PNSC was applied to real water and wastewater samples that were obtained from three different areas namely Kotri industrial wastewater, the Phulely Canal and laboratory tap water. Water samples were filtered using nylon membrane filter paper of 0.45 μm. They were then spiked with 5 mg/L phthalate mixtures. Two sets of samples; one spiked set and the other a non-spiked set of samples were analyzed via HPLC and an adsorption experiment was performed, quantification was performed by the external standard addition method. It was observed that among three non-spiked samples only the sample obtained from the Phulely Canal contained an amount of DBP greater than maximum contamination limit (MCL), the amount present was 4 mg/L. The adsorption experiment was performed in a solid phase extraction assembly through optimized concentrations and almost good removal efficiency of PNSC was observed as shown in Table 7.

4. Conclusion

The study was useful in exploring the applicability of PNS derived carbon as a valuable adsorbent with highly porous structure and excellent performance toward phthalate uptake. This new material is easy to synthesize as compared to expensive activated carbon which requires a special experimental set up. The adsorption was found to be feasible at room temperature and shows an exothermic nature. The trial to examine the application of PNS derived carbon in real water samples showed a remarkable performance of this new bio waste toward water purification. This cheap adsorbent can be used in water filtration plants for making water drinkable since it exhibits a unique performance and requires ambient conditions for operation.

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