

Estimation of Adsorption Efficiency of Nanoparticle Doped Litter Activated Carbon for The Removal of Phenanthrene From Soil Solution



Basic science

KEYWORDS : PAH, Properties of PAHs, Nanometallic compound, GC-MS, Effect of PAHs

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ABSTRACT

Environmental pollution, in particular contamination by PAHs is increasingly becoming a threat to humans and animals owing to their carcinogenic and mutagenic properties. In this research an effort has been made to fabricate litter and plant debris with nanometallic oxides generating a surface that can act as a better adsorbent for the removal of Phenanthrene (PAH), a common soil pollutant. Optimization of various parameters such as temperature, dosage, pH and time of the adsorbent was done by using response surface method. The result showed a significant increase in the PAH adsorption efficiency by doped surface. The maximum percentage adsorption of phenanthrene was 83.26% at 40°C and pH 7 by 8g of adsorbent at 8 hour of adsorption. Minimum % adsorption was 32.8% and average % adsorption was found to be 58.03%. The result presented in this study may aid in removal of phenanthrene and direct the bioremediation of environment in particular soil and sediments.

1. Introduction

Environmental protection agency, USA has identified 16 PAHs as most toxic of all and phenanthrene stands one among those deadly PAHs (agency of toxic substances, 1990). PAHs generation in environment is attributed to incomplete combustion of substances containing carbon and hydrogen that produce free radicals, a precursor of PAHs (Barry et al, 2007). Major anthropogenic factors contributing to PAHs generation are power plants and house heating, transport emissions and industries. However PAHs emission by natural factors such as forest fires, volcano eruptions and humus conversion cannot be overlooked. In all, major site of accumulation of these hydrophobic pollutant is soil accounting for > 80% followed by sediments (10% of total accumulation) (Zhou, 2005). Bioavailability of PAHs in soil is influenced by factors like organic matter content, texture and aggregation of soil (Abbey F, 2011) as reported by Hundal et al. (2001), on the retention of large amounts of phenanthrene by steatite clays.

Extensive literature analysis has shown that an effective way to perform the conversion and mineralization of this type of substances is the application of advanced oxidation processes (AOPs). Furthermore, combined processes, particularly AOPs coupled with biological treatments, seem to be one of the best solutions for the treatment of effluents containing PAHs (Liada et al, 2013). In particular activated carbon is mostly used due to its highly porous structure and large absorptive area. Difficulty in regeneration makes a disadvantage for using it as an adsorbent (Tan et al, 2012). When compared to commercial activated carbons and adsorbents, prepared from plastic wastes, the samples obtained from bean-pods activation presented larger adsorption capacities for naphthalene uptake (Cuyppers, 2001). Soil organic carbon comes mainly from active biomass carbon. For above-ground and belowground processes, most of the active organs and small individuals complete their physiological functions in a few years, fall into the soil as fine litter, and activate complex belowground processes (Zhou et al, 2007).

In today's world, overcoming the challenges of environmental threat is the main motive of humankind incorporating all possible processes thereafter; it is highly desirable to develop nano technology that harvests energy from the environment to fabricate self-power and low-carbon nano devices that can be a potent source of removal of deadly pollutants like PAHs.

2. Materials and Methods

2.1 Sample preparation: The coarse (wood shavings) and fine (leaf and root debris) litter was collected from fields and farmland of Bangalore and Chennai from area rich in vegetation. The

collected samples had moisture of 20-25%. Coarse and fine litter were dried naturally under atmosphere and then grounded separately to less than 2 mm and pyrolyzed in bench furnace in a low oxygen environment for respectively 5-10 min for wood shavings at 500 °C, and fine litter at 380°C.

Chemical activation of wood char and litter was done by impregnation of activating agent followed by thermal degradation. In this study, biochars were soaked overnight in 30% 0.5 N HCl, activated 1 h at 450 °C under and allowed to cool to room temperature overnight. Excess of acid was removed by rinsing with boiling DDW. Dried particles were subjected to mechanical sieving and 2 gm dosage of prepared biochar/ LAC (Litter activated carbon) was taken for X-Ray diffraction analysis to find the presence of carbon in it. The peak of XRD analysis gives an idea of presence of carbon content in the LAC.

2.2 Preparation of nanometallic particle. Ferric benzoate was chosen metallic nanoparticle used in this study. Preparation was done by mixing ferric nitrate and benzoic acid (Sigma Aldrich, USA) in a ratio of 1:1 v/v and stirred for 20 min on a magnetic stirrer. The product was filtered using hot distilled water and kept in an oven to remove the water and moisture content from it.

2.3 Process of Impregnation

The composite was prepared by soaking LAC (10 gm) to an aqueous solution of Iron (III) benzoate dihydrate or Ferric benzoate (8.14 g). The solution was stirred in a magnetic stirrer for about 6 hrs. Fabricated LAC (litter activated carbon) with adsorbed ferric benzoate was filtered using filter paper and oven dried for an hour. The LAC was further pyrolysed at 600°C for 10 min in the muffle furnace.

2.3 Phenanthrene adsorption and optimization of Influencing Parameters.

Preparation of Phenanthrene solutions.

Soil samples from pollution sites of North Bangalore and Chennai were collected and sieved for removal of visible impurities. The samples were air dried to eliminate the influence of moisture on the PAH extraction efficiency. All the samples were subjected to physical and chemical analysis. 5g of each sample were dissolved in 100 ml of cyclohexane to form a stock solution which were diluted further and amount of phenanthrene was obtained by GC-MS. Binding assays were carried out by adding 4 g of impregnated LAC to 100 ml of phenanthrene containing soil solution at concentrations of 50-200 ppm (prepared by dissolving varied conc. of stock solution to water and cyclohexane) for 10 h

and optical density at 260nm was recorded each hr. . The adsorption capacities were calculated based on the differences between the concentrations of solutes before and after adsorption. The percentage of adsorption is calculated by $\% \text{ ADS} = (C_0 - C_e) / C_0 * 100$

Where % ADS is the rate of adsorption in percentage

C_0 is the initial concentration

C_e is the final concentration.

Aliquots of the suspension were filtered using disposable syringe containing 0.22 μm millipore filters (Millipore Corp., Bedford, MA, USA) to remove suspended material. Analysis is done with the help of Gas Chromatography Mass Spectroscopy (Thermo fisher, USA) equipped with a flame ionization detector with a capillary DB-5 column. PAHs were quantified using calibration curves by direct injection of standard mixtures with known concentration. Effect of influencing parameters such as temperature, time, concentration of LAC, was done by Design Expert-9 software using Response Surface Methodology (RSM).

2.4.3 Scanning electron microscopy

Surface characterization on activated biochars before and after application of different concentrations of phenanthrene was done by viewing samples under scanning Electron Microscope (Gemini SEM 300, India). Samples were mounted on standard 1/2 inch SEM stubs using double-stick adhesive tabs and coated with 11-15 nm of 60/40 gold-palladium in a Technics Hummer II sputter coater. Samples were viewed in the SEM operating at a working distance of 11 mm with a magnification of 600-15,000 \times . The acceleration voltage of the electron beam was 20-30 kV.

2.5 Experimental Design and Statistical Analysis

The experimental design was a completely randomized design with a two way factorial treatment structure of PAH conc \times 3 processing conditions \times 5 dosage of LAC. Three samples were taken for each treatment, but these were subsamples of the treatments not replications. Therefore analysis of variance for main effect and 2-way interactions used a model with the 3-way interaction as error and variability among samples as sub-sampling error. All statistical significant differences inferred in this study were determined at the 1 degree of freedom and 5% confidence level.

3. Results and Discussion

The proportion of biochar produced from fine and coarse litter is found to be dependent on pyrolysis conditions such as temperature and time (Downie et al 2009) hence these parameters were chosen carefully for maximum output. In this study adsorption of phenanthrene from soil aliquots on the surface of fabricated LAC with ferric benzoate is studied for obtaining adsorption max. The optical density for soil aliquots of different concentrations were calculated at 260nm and values were converted into concentration by calculating calibration curve for phenanthrene with $1.OD = 30\mu\text{g}/100\text{ml}$ of soil solution

Optimization of parameters

For evaluation of effect of adsorbent dosage, temperature, time and concentration of adsorbate a response surface methodology (RSM) with a box Behnken design was employed in this study for removal of phenanthrene. The F values of the design for phenanthrene) removal were 20.04%, respectively, and demonstrate that the models were statistically significant with almost 0.001% chance in phenanthrene removal indicating no interfering parameter. The lack of fit F value of removal is 0.48 which implies that it was not significant relative to the pure error. A non-significant lack of fit was considered good and was desired for the model to fit quadratic models were valid for the present study.

As revealed from table above, the coefficients of determination (R^2) value is found to be 0.9525, for removal of phenanthrene that clearly demonstrate the results to be promising R^2 should be between zero and 1 ($0 \leq R^2 \leq 1$) and a greater value is good. The standard deviation of a random variable, statistical population, data set, or probability distribution is the square root of its variance and the term PRESS means that the predicted residual sum of squares is used as a criterion for the model's efficiency to predict the responses of a new experiment with the lowest values of PRESS indicating the best structures (Tarpey, 2000). The Result of percent adsorption was calculated using the following regression equation (Oehlert and gray, 2000):

$$\text{Adsorption} = 21.4 + 1.32 A + 2.69 B + 2.11 C + 1.26 D + 0.420 A^2 - 1.58 B^2 - 1.53 C^2 - 0.930 D^2 + 0.750 AB + 0.300 AC + 0.175 AD + 0.600 BC + 0.475 BD - 0.075 CD$$

Where A denotes the concentration of phenanthrene in mg/l, B denotes time, C adsorbent dosage and D denotes the temperature.

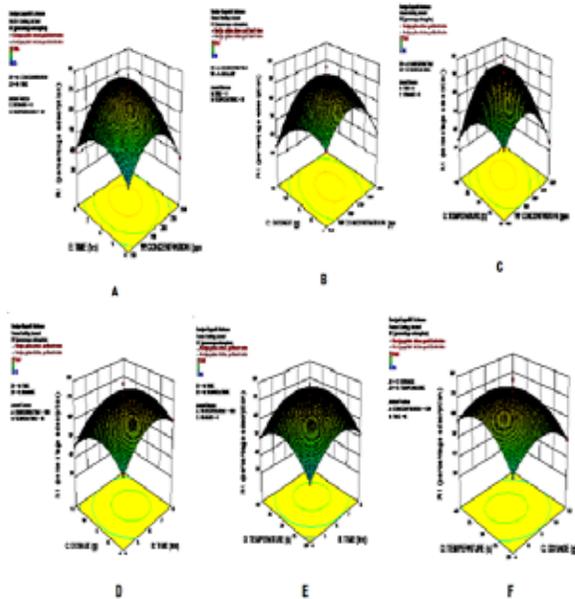
Table 1: Analysis of variance of the fitted quadratic equation and model summary statistics for removal% of phenanthrene; A, Initial ion concentration (mg/L); B, Removal time (s); C, Adsorbent dosage (g) & D, Temperature ($^{\circ}\text{C}$); PRESS, Predicted residual sum of squares

Source	Sum of Squares	Df	Mean Square	F	p-value	
				Value	Prob > F	
Model	3779.932	14	269.9952	20.03972	7.29E-07	Significant
A	467.7109	1	467.7109	34.71468	3.92E-05	
B	198.97	1	198.97	14.76806	0.001792	
C	42.82421	1	42.82421	3.178521	0.096301	
D	96.70282	1	96.70282	7.177527	0.017977	
AB	90.25	1	90.25	6.698582	0.021466	
AC	144	1	144	10.68804	0.005594	
AD	361	1	361	26.79433	0.000141	
BC	1	1	1	0.074223	0.789262	
BD	0	1	0	0	1	
CD	16	1	16	1.18756	0.294225	
A ²	1925.662	1	1925.662	142.9275	9.81E-09	
B ²	746.808	1	746.808	55.42997	3.13E-06	
C ²	662.3418	1	662.3418	49.16068	6.14E-06	
D ²	799.9202	1	799.9202	59.37209	2.11E-06	
Residual	188.622	14	13.473			
Lack of Fit	4.75	10	0.475	0.010333	1	not significant
Standard deviation	3.670559					
PRESS	314.66					
R ²	0.952471					
Adjusted R ²	0.904942					
Predicted R ²	0.920712					
Adequate precision	14.61638					

Using the above equation, the maximum percentage adsorption

of phenanthrene was 83.26% at 40°C and pH 7 by 8g of adsorbent at 8 hour of adsorption. Minimum % adsorption was 32.8% and average % adsorption was found to be 58.03%. The analysis is a second-order model. The analysis of variance for fitting the data to the second-order and contour plots help characterize the response surface. The graphical visualization of such model is very helpful in understanding the second-order response surface. Specifically, contour plots can help characterize the shape of the surface and locate the optimum response approximately.

Figure 2: Response surface 3D plots indicating the effect of interaction between (A) % adsorption w.r.t time and concentration of phenanthrene. (B) % adsorption w.r.t dosage and concentration of phenanthrene (C) % adsorption w.r.t temperature and concentration of phenanthrene (D) % adsorption w.r.t time and dosage of adsorbent (E) % adsorption w.r.t time and temperature (F) % adsorption w.r.t dosage and temperature.



The graphs clearly indicates increase in phenanthrene adsorption with increase in the parameters like time, dosage of adsorbent, conc. of adsorbate and temperature and tends to decrease after attaining a maximum point owing to the saturation in adsorption efficiency.

As mentioned in Figure 2 (A,B,C,D,E,F), all the factors taken into account had a direct effect in improving the sorption capacity of fabricated LAC, while the concentration of the phenanthrene confirmed a stronger effect on the adsorption efficiency than dosage of adsorbent. It is realized that the interaction effect of time and temperature had the non significant influences on the removal efficiency of phenanthrene however the most significant influence is brought about by interaction of initial concentration with temperature and dosage. It is also analyzed that after attainment of optimum maximum the adsorption values start decreasing in all the cases. This optimum max. can be defined as saturation level after which the removal efficiency decreased since the sites are covered with phenanthrene. The adsorbent dosage plays an important role in the removal efficiency and clearly demonstrates that with increasing the adsorbent dosage, removal efficiency

improves (Luengo et al, 2010). This could be explained due to the presence of ferric benzoate nanoparticles attributing to the exterior surface adsorption.

As all the adsorption sites of these nanoparticles can be found

on the exterior of the adsorbent; it is possible for the adsorbate (ion) to get into these active sites, thus causing a rapid approach to equilibrium (Hu et al, 2004). The results for optimum maximum is presented for all the parameters in table 2 and these experiments demonstrate that all the results were in good agreement.

Surface characterization

The SEM images of impregnated LAC with ferric benzoate indicated that the samples consisted of both large 50-100µm and small 5-10µm pores or voids that gave an appearance of honeycomb. These pores act as active sites of adsorption. Surface area of adsorption increases by the addition of nanometallic particles. SEM photograph after adsorption indicate the decrease in porosity and free active sites due to adsorption of phenanthrene into pores or voids.

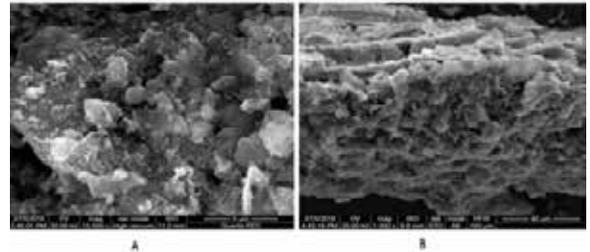


Figure 3 (A,B): Scanning electron microscopic images of impregnated LAC before and after adsorption of phenanthrene

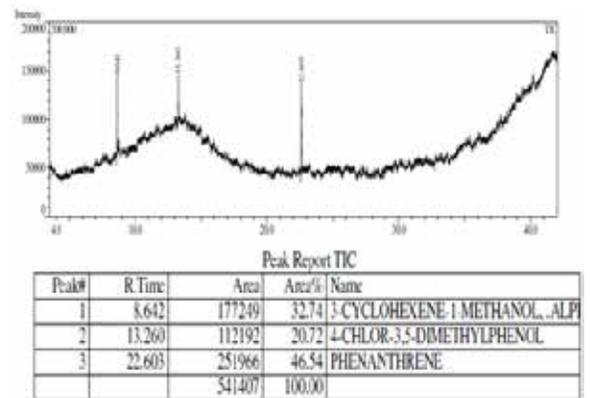


Figure 4A GC-MS report of soil samples before adding adsorbent.

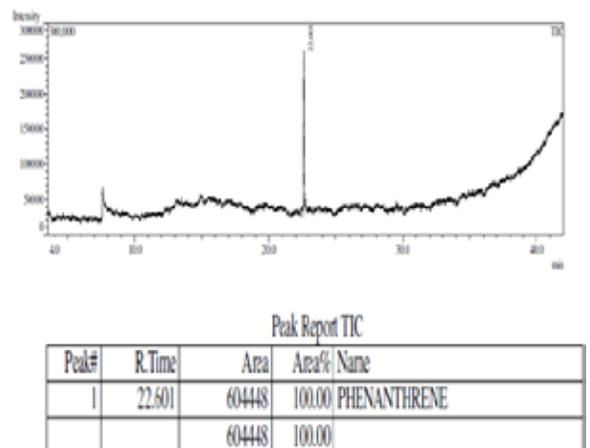


Figure 4B: GC-MS report after adding adsorbent.

As indicated by gas chromatography and mass spectrophotometry experiment (Figure 4A, 4B) the removal efficiency of phenanthrene from soil samples is increased by 2.5 fold after adding adsorbent, attributing to the good adsorption property of the adsorbent, therefore litter activated carbon doped with ferric benzoate provide a better surface for the removal of PAH from soil samples.

Conclusion

In this study, the effective removal by entrapped palm shells and nano metallic oxides of phenanthrene was studied. Activated carbon obtained from palm shells and iron (III) benzoate have resulted to be very good adsorbent for phenanthrene removal from diluted aqueous solution. The optimum conditions for the removal of phenanthrene using entrapped PAC and iron (III) benzoate adsorbent is at a dose of 8g and at a temperature of 40°C which showed a removal efficiency of 83.3%. The experiment showed that the adsorption of phenanthrene by entrapped PAC and iron (III) benzoate adsorbent was rapid and maximum adsorption capacity were achieved in approximately 8 hour. Similarly, maximum adsorption achieved at a 7 pH and at the 200mg/l concentration. The SEM analysis showed that the porosity of the entrapped PAC and iron (III) benzoate decreased after adsorption due to the adsorption of phenanthrene. The GC-MS showed that the phenanthrene presence in soil solution after adsorption was negligible. Response surface methodology (RSM) gave the best design of the experiment effectively at different parameters. Use of $C_{21}H_{15}FeO_6$ nanoparticle for removal of harmful effluents is environmental friendly particularly impregnation of low cost litter nanoparticle is economically attractive and achievable.

The work can serve as a method for removal of harmful particles directly from soil samples.

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