Removal of Polycyclic Aromatic Hydrocarbons Present in Tyre Pyrolytic Oil Using Low Cost Natural Adsorbents

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Abstract—Polycyclic aromatic hydrocarbons (PAHs) are formed during the pyrolysis of scrap tyres to produce tyre pyrolytic oil (TPO). Due to carcinogenic, mutagenic, and toxic properties PAHs are priority pollutants. Hence it is essential to remove PAHs from TPO before utilising TPO as a petroleum fuel alternative (to run the engine). Agricultural wastes have promising future to be utilized as biosorbent due to their cost effectiveness, abundant availability, high biosorption capacity and renewability. Various low cost adsorbents were prepared from natural sources. Uptake of PAHs present in tyre pyrolytic oil was investigated using various low-cost adsorbents of natural origin including sawdust (shisham), coconut fiber, neem bark, chitin, activated charcoal. Adsorption experiments of different PAHs viz. naphthalene, acenaphthalene, biphenyl and anthracene have been carried out at ambient temperature (25°C) and at pH 7. It was observed that for any given PAH, the adsorption capacity increases with the lignin content. Freundlich constant K_f and 1/n have been evaluated and it was found that the adsorption isotherms of PAHs were in agreement with a Freundlich model, while the uptake capacity of PAHs followed the order: activated charcoal> saw dust (shisham) > coconut fiber > chitin. The partition coefficients in acetone-water, and the adsorption constants at equilibrium, could be linearly correlated with octanol–water partition coefficients. It is observed that natural adsorbents are good alternative for PAHs removal. Sawdust of *Dalbergia sissoo*, a by-product of sawmills was found to be a promising adsorbent for the removal of PAHs present in TPO. It is observed that adsorbents studied were comparable to those of some conventional adsorbents.

Keywords—Acenaphthene, anthracene, biphenyl, Coconut fiber, naphthalene, natural adsorbent, PAHs, TPO and wood powder (shisham).

I. INTRODUCTION

POLYCYCLIC Aromatic Hydrocarbons (PAHs) is also called as polynuclear hydrocarbons, produced as gases or particles and are created from incomplete combustion when organic matter is burnt so these are considered as persistent environmental contaminants and many of them are suspected of being carcinogenic [1], [2]. Due to their carcinogenic, mutagenic and toxic properties they are priority pollutants [3]. Anthropogenic sources [4], [5] of PAHs as combustion of coal and oil [6], exhaust from motor vehicles [7] and water effluents from petrochemical plants [8] are significant compared to natural sources. Bioremediation [9], [10], ozonation [11], [12], adsorption and photo degradation [13] are the techniques have been applied successfully for the minimization of PAHs in domestic and/or industrial

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wastewater. The adsorption of PAHs onto activated carbon from various media such as oil [15], [16] gaseous [17], [18] and water [19], [20] has been reported.

It was reported that pyrolysis of scrap tyres produced oil similar in properties to a light fuel oil, with similar calorific value, sulphur and nitrogen contents. The oil was found to contain 1.4 % sulphur and 0.45 % nitrogen on mass basis and have similar fuel properties to those of diesel fuel. The oils contained significant concentration of polycyclic aromatic hydrocarbons, the concern over PAH is centred on the associated health hazard, some of which have been shown to be either carcinogenic and/or mutagenic [21]-[23] and may therefore restrict their handling.

Due to often resistant to biological degradation, PAHs are not efficiently removed by conventional physiochemical methods such as coagulation, flocculation, sedimentation, filtration or ozonation [24]. However, adsorption processes are effective in removal of persistent organic pollutant. Activated carbon is widely used [25], but high cost and difficult regeneration are clearly disadvantages [26]. Interesting alternatives for removal of organic pollutant [27], [28] from wastewaters are presented by using low cost natural adsorbents [31], [32]. In India, huge amounts of waste are produced by large scale agriculture, mainly saw dust (Shisham), which contains lignin 14-34%, neem bark contains 14.63% lignin, 3.43% protein, 0.68% alkaloids and 4.16% minerals and coconut fiber contains lignin 32% for which applications are only sparingly available.

TABLE I
AVERAGE CHEMICAL COMPOSITION OF SOME OF THE AGRICULTURAL WASTES

Agricultural Wastes	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Sources
Coconut shell	37-40	33	08	[22], [23]
Sugar cane bagasse	22	44	27	[20], [21], [29], [30]
Wood Sawdust	25-30	40-55	24-37	[14]
Rice husk	20	37	24	[24], [25], [33], [34]

The purpose of this study was to investigate the adsorption features of adsorbents from agricultural waste materials with respect to removal of PAHs from TPO. Results were compared with performances of some commercial adsorbents used in practice.

II. MATERIALS AND METHODS

A. PAHs

PAHs: naphthalene (Nap), acenaphthene (Acen), biphenyl

(Biph) and anthracene (Anthr) (>98% purity) were obtained from Loba Chemie (Mumbai, India).

B. Adsorbents

The adsorbents used in the present work are mainly of low cost agro residue/ agricultural wastes of natural origin. Agricultural waste viz. wood fiber/ saw dust (shisham), coconut fiber, Neem bark were collected from nearby places. These waste materials were washed with water and dried. These dried materials were then crushed and grinded into small pieces and converted into powder form. Then adsorbent powder was dried to remove moisture in sunlight and stored in airtight flasks. The resulting product is used as adsorbent without any pretreatment.

C. Instrumental Analysis

A gas chromatograph supplied by Thermo Fisher equipped with a flame ionization detector (FID) and with a capillary DB-5 column was used for qualitative and quantitative analysis of PAHs. The volume for injection was 1 µL. The analysis started at 120°C and the temperature was increased to 250°C at a rate of 10°C/min. Nitrogen was used as a carrier gas at a flow rate of 1mL/min. PAHs were quantified using calibration curves by direct injection of standard mixtures with known concentrations.

D. Adsorption Studies

PAHs were diluted by dissolving in acetone (0.2 g/50 mL). Then 0.50 g dry adsorbent was added in flasks containing PAH in acetone and samples containing different adsorbents were prepared and for pure analysis of TPO, in a closed flask 50ml of TPO diluted in 50ml of acetone, to reduce the viscosity, in different closed conical flasks and four different dry adsorbents of weight 0.50gm the sample was shaken for 12 h at ambient temperature ($25\pm~2^{\circ}$C) (pH 7.5). After filtration, PAHs were quantified by GC-FID. The same procedure was repeated for all the PAHs and adsorbent studied.

The adsorption capacities were calculated based on the differences of the concentrations of solutes before and after the experiment (1):

$$q_e = (C_o - C_e)\,V/W \qquad (1)$$

where, q_e is the concentration of the adsorbed solute (mg/g); C_o and C_e are the initial and final concentration of the solute in solution (mg/L); V is the volume of the solution (mL) and W is the mass of the adsorbent (g). Adsorption isotherms (relationship between the adsorption capacities and the concentrations of PAHs) were investigated using the linearized form of the Freundlich sorption isotherm equation as reported by [16].

III. RESULTS AND DISCUSSION

A. Optimization of pH

The dependence of bisorption capacities of PAHs on various pH are shown in Fig. 1, The bisorption capacity increased with increasing pH of PAHs solution. As the pH of the solution increases from 2.0 to 7.0, PAHs show an increase in binding to the adsorbent with optimum binding reaches at pH 7.0. This gives us an insight into the mechanism of the binding involved within the adsorbent. Previous studies have reported the binding of PAHs to some agricultural wastes with optimum pH lying between 6 and 7.
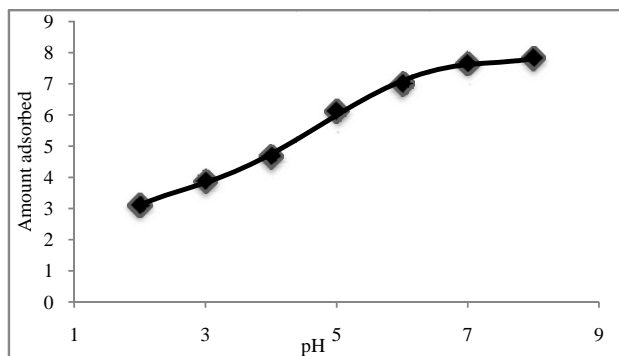

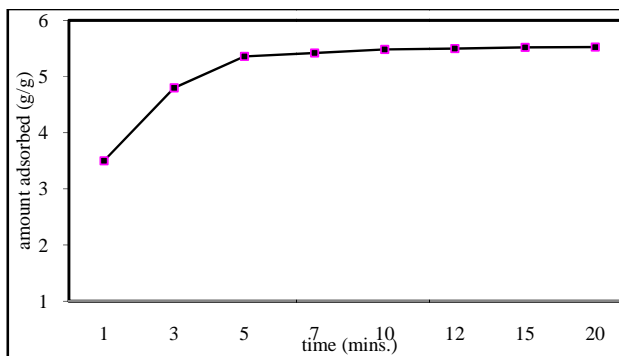Fig. 1 Effect of pH on adsorption of naphthalene on saw dust

Fig. 2 Effect of time on adsorption of naphthalene on saw dust

B. Optimization of Equilibrium Adsorption Time

Effect of contact time on adsorption is shown in Fig. 2. It is evident from figure that with increase in contact time adsorption of PAH increases. Initially rate of adsorption is high and after 10hr to 14hr there is slight increase in adsorption rate and after 12hr adsorption is almost constant.

C. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The nature of solvent evidently influences the adsorption of solutes. It remains true that interactions between an adsorbent and an organic adsorbate can be governed by Langmuir and Freundlich isotherms [25], [35], [36]. The Langmuir model is based on monolayer adsorption on equi-energetic active surface sites, while the Freundlich model relies on heterogeneous adsorption. However, to evaluate the linearity, the experimental data were only fitted to the linearized form of the Freundlich sorption isotherms equation (2);

$$log\ q_e = log\ K_f + \frac{1}{n} log\ C_e \qquad (2)$$

where, q_e is the concentration of the adsorbed solute (mg/g); C_e is the concentration of the solute in solution (mg/L); K_f (mg $g^{1-(1/n)} l^{1/n}\ g^{-1}$) is related to the adsorption capacity of adsorbent and $1/n$ is related to the surface heterogeneity. Straight lines were obtained by plotting log q_e against log C_e, for multi solute adsorption as shown in Figs. 3-5, Freundlich parameters $(1/n$ and $K_f)$ were obtained slopes and intercepts.
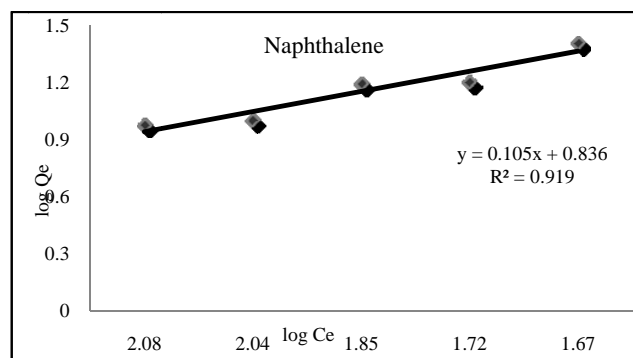

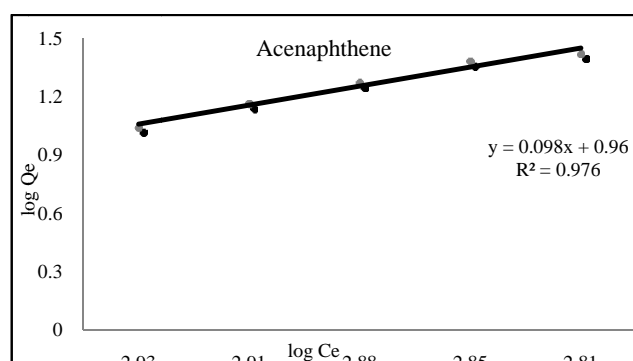Fig. 3 Freundlich adsorption isotherm of naphthalene using shisham as adsorbent

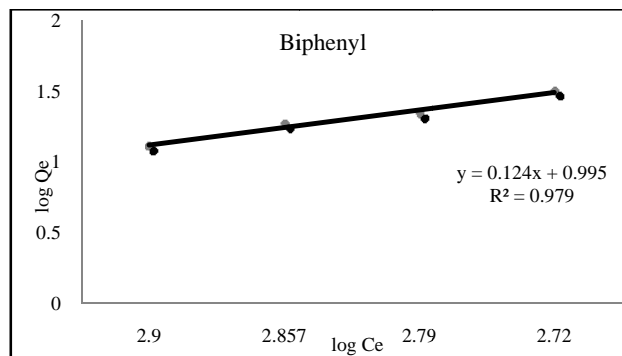Fig. 4 Freundlich adsorption isotherm of acenaphthene using shisham as adsorbent

Fig. 5 Freundlich adsorption isotherm of biphenyl using shisham as adsorbent

The adsorption process of organic solutes is determined by various interactions that govern the association between solute and adsorbent, such as Van der Waals and dipole-dipole interactions, electrostatic forces, and weak intermolecular associations [37], [25]. Since PAHs are non-polar compounds, adsorption must be governed mainly by hydrophobic interactions [38], [27]. In order to reveal a potential relationship between adsorption efficiency and lignin content, experimental partition coefficients, K_{ads}, were correlated to the published n-octanol-water partition coefficients, K_{ow} [38].

TABLE II
SELECTED PROPERTIES OF PAHs STUDIED

Name	Structure	Formula	Molecular weight (g/mol)	Log K_{ow}
Anthracene		$C_{14}H_{10}$	178.2	4.6
Biphenyl		$C_{12}H_{10}$	154.21	4.09
Acenaphthene		$C_{12}H_8$	152.19	3.98
Naphthalene		$C_{10}H_8$	128.17	3.30

TABLE III
PARAMETERS DERIVED FROM FREUNDLICH ISOTHERM EQUATION FOR THE ADSORPTION OF PAHs ON DIFFERENT NATURAL ADSORBENTS (25°C, PH 7.5)

	Naphthalene			Acenaphthene			Biphenly			Anthracene		
	Freundlich parameters			Freundlich parameters			Freundlich parameters			Freundlich parameters		
	K_f	$1/n$	R^2	K_f	$1/n$	R^2	K_f	$1/n$	R^2	K_f	$1/n$	R^2
Shisham	0.030	0.89	0.92	0.011	0.96	0.95	0.015	1.01	0.98	0.027	0.82	0.97
Coconut Fiber	0.060	1.56	0.90	0.020	1.22	0.92	0.015	1.98	0.95	0.048	0.89	0.91
Chitin	0.135	0.08	0.88	0.33	1.99	0.94	0.127	0.15	0.94	0.015	0.26	0.93

Partition coefficients (K_{ads}) defined (3), were calculated from the linear variation of the sorbed PAHs concentrations, q_e, with aqueous naphthalene solution, C_e [27], [28]. For each sample event, K_{ads} was determined from the regression q_e versus C_e. The slope of the graph yields the partition coefficient (3):

$$K_{ads} = q_e / C_e \qquad (3)$$

where (K_{ads}), (mg $Kg^{-1}_{adsorbent}$/ mg L^{-1}) is the partition coefficients, C_e is the dissolved PAHs concentration (mg L^{-1}) and q_e is the mass of sorbed PAHs per dry unit weight of adsorbent (mg g). The natural polymers lignin fraction has

been identified as the principal factor determining the degree of sorption of nonpolar compounds [28]. Thus, the lignin-water partition coefficients (K_{lignin}) for PAHs interacting with intact adsorbent (i.e. Shisham, Coconut fiber, Chitin) were calculated (4) from adsorbent partition coefficients (K_{ads}) and lignin mass (f_{lignin}):

$$K_{lignin} = K_{ads}/f_{lignin} \qquad (4)$$

where K_{lignin} (mg kg^{-1}_{lignin}/mg L^{-1}) is the partition coefficient between lignin and the solution; f_{lignin} (f_{lignin} $g^{-1}_{adsorbent}$): the amount of lignin present. For this study, f_{lignin} was considered to be equivalent to 34% (f_{lignin} = 0.34) for shisham, to 32% (f_{lignin}= 0.32) for coconut fiber and 20% (f_{lignin}=0.20) for chitin. The parameter K_{ow} is the n-octanol-water partition coefficient and is a measure of a compound's hydrophobicity. The equilibrium K_{ads} was calculated while published K_{ow} values [38] for PAHs was used. The parameter K_{ow} is the n-octanol-water partition coefficient and is measure of compound's hydrophobicity. Thus, the partition coefficients of PAHs by shisham and coconut fiber based on the lignin content can be estimated from the known values of K_{ow}. These results confirm previous observations on adsorption of aromatic hydrocarbons to agricultural wastes which appear to be controlled mainly by the lignin content [27], [28]. The higher lignin content in sawdust (shisham) 34% compared to coconut fiber 32% and 20% in chitin, agrees with the extent of adsorption of PAHs followed the order: activated charcoal> shisham> coconut fiber> chitin the adsorption features of agricultural wastes proved well comparable to those of conventional adsorbents such as activated charcoal for removing PAHs from organic solvents.

IV. CONCLUSIONS

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants due to their carcinogenic, mutagenic and toxic properties. When tyre pyrolytic oil (TPO) is utilized as fuel alternative, PAHs present in TPO are generally released with exhaust during automobile combustion and enter into environment. Hence it is necessary to reduce the concentration of PAHs up to the acceptable levels before utilizing TPO as a fuel alternative.

This study showed that adsorption of polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, anthracene and biphenyl) from tyre pyrolytic oil can be affected using low-cost adsorbents of natural origin. Widely available agricultural residues such as shisham saw dust and coconut fiber could be useful for the purpose. From the analysis of results obtained it may be concluded that, the contact time is an important factor in the adsorption of PAHs. The equilibrium time was reached at 12 hr. A correlation could be found with the lignin contents of agricultural residue used to prepare adsorbents and it is observed that PAHs adsorption is directly proportional to lignin content. The adsorption efficiencies followed the order activated charcoal> shisham> coconut fiber> chitin.

The adsorption features of agricultural wastes proved well comparable to those of conventional adsorbents such as activated charcoal for removing PAHs from organic solvents. The adsorption isotherms are in good agreement with Freundlich model.

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