Adsorption of Polycyclic Aromatic Hydrocarbons using Agricultural Wastes-Effect of Lignin Content

Dharm Pal

Abstract—Due to carcinogenic, mutagenic, and toxic properties polycyclic aromatic hydrocarbons (PAHs) are priority pollutants. 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 porous adsorbent using naturally occurring agricultural wastes including sugar cane bagasse, coconut shells and rice husk were used as adsorbents for adsorbing polycyclic aromatic hydrocarbons (PAHs) (naphthalene, acenaphthene, fluorene, and pyrene). Adsorption experiments were performed at ambient temperature (25 ± 1°C) and at optimised pH 7. It was observed that for any given PAH, the adsorption capacity increases with the lignin content and for any given adsorbent, the value of $K_f$ follows the order of naphthalene > fluorene > phenanthrene > pyrene. The uptake capacity of PAHs followed the order: coconut shells > sugar cane bagasse > rice husk. The applicability of the Freundlich models was tested and data obtained were in good agreement. The partition coefficients and the adsorption constants at equilibrium, could be linearly correlated with octanol-water partition coefficients. It is observed that adsorbents studied were comparable to those of some conventional adsorbents.

Keywords—Agricultural wastes, biosorption, natural adsorbent, PAHs.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) considered as persistent environmental contaminants and many of them are suspected of being carcinogenic [1, 2]. PAHs are priority pollutants due to their carcinogenic, mutagenic, and toxic properties [3]. Natural sources of PAHs in the environment are insignificant compared to anthropogenic sources [4, 5] that originate in combustion of coal and oil [6], exhaust from motor vehicles [7], and wastewater from petrochemical plants [8]. Many techniques e.g., bioremediation [9, 10], ozonation [11, 12], photo-degradation, and adsorption [13] have been applied successfully for the minimization of PAHs in wastewater of domestic and/or industrial plants and soils. PAHs are often resistant to biological degradation and are not efficiently removed by conventional physicochemical methods such as coagulation, flocculation, sedimentation, filtration or ozonation [15]. However, adsorption processes are effective in removal of persistent organic pollutants and, in particular, activated carbon is widely used [16], but high costs and difficult regeneration are clearly disadvantages [17]. Interesting alternatives for removal of organic pollutants [18,19] from wastewaters are presented by the use of low-cost solid residues from agricultural activities. In India, huge amounts of waste are produced by large-scale agriculture industries for which applications are only sparingly available. The chemical composition of some of the agricultural wastes is listed in Table 1.

<table>
<thead>
<tr>
<th>Agricultural Wastes</th>
<th>Lignin (%)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>coconut shells</td>
<td>40</td>
<td>33</td>
<td>08</td>
<td>[22,23]</td>
</tr>
<tr>
<td>sugar cane bagasse</td>
<td>22</td>
<td>44</td>
<td>27</td>
<td>[20,21]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>20</td>
<td>37</td>
<td>24</td>
<td>[24-25]</td>
</tr>
</tbody>
</table>

The purpose of this study was to investigate the adsorption features of adsorbents from agricultural waste materials with respect to removal of PAHs (viz. naphthalene, fluorene, phenanthrene and pyrene).

II. MATERIALS AND METHODS

PAHs Naphthalene, fluorine, phenanthrene, pyrene (>98% purity) were obtained from Loba chemie, mumbai, India.

Adsorbents Agricultural wastes viz sugar cane bagasse, coconut shells and rice husks were collected from near by places. These waste materials were washed with water, and dried. The dried materials were crushed and grinded into small pieces and used as adsorbent without further modification.

Analyses of PAHs 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. The temperature of the injector and of the detector was set at 250 °C. Helium was used as a carrier gas at a flow rate of 1 mL/min. PAHs were quantified using calibration curves by direct injection of standard mixtures with known concentrations.
Adsorption studies 10 mL of PAHs were taken with 0.5 g of dry adsorbents and the sample was shaken for 12 h at ambient temperature (25°C) (pH 7.5). After filtration, PAHs were quantified by GC–FID. The same procedure was repeated for all the PAHs & Adsorbent studied. The adsorption capacities were calculated based on the differences of the concentrations of solutes before and after the experiment according to the following Equation (1):

\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

where \( q_e \) is the concentration of the adsorbed solute (mg/g); \( C_0 \) and \( C_e \) are the initial and final concentrations of the solute in solution (mg/L); \( V(\text{mL}) \) is the volume of the solution and \( W(\text{g}) \) is the mass of the adsorbent. 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 Cooney et al. [16].

III. RESULT AND DISCUSSIONS

Adsorption isotherms Although the nature of the 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 [16, 26, 27]. 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 isotherm equation as reported by Cooney et al. [16].

Table II

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Formula</th>
<th>Mol.Wt [g/mol]</th>
<th>Log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrene</td>
<td>C_{16}H_{10}</td>
<td>202.25</td>
<td>5.18</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>C_{14}H_{10}</td>
<td>178.22</td>
<td>4.57</td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>C_{13}H_{10}</td>
<td>166.22</td>
<td>4.18</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C_{10}H_{8}</td>
<td>128.17</td>
<td>3.30</td>
<td></td>
</tr>
</tbody>
</table>

Table III

<table>
<thead>
<tr>
<th>Name</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrene</td>
<td>( K_f ) ( 1/n ) ( R^2 )</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>0.020 1.22 0.95</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>0.011 0.96 0.92</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.020 0.81 0.94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phenanthrene</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell</td>
<td>0.015 1.98 0.98</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>0.015 1.01 0.95</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.005 1.73 0.94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluorene</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell</td>
<td>0.048 0.89 0.97</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>0.027 0.82 0.91</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.013 0.70 0.93</td>
</tr>
</tbody>
</table>
TABLE 3.4  
FREUNDLICH PARAMETERS FOR NAPHTHALENE

<table>
<thead>
<tr>
<th>Naphthalene</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>0.060</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>0.030</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Partition coefficients ($K_{ads}$), defined according to Eq. (4), were calculated from the linear variation of the sorbed PAHs concentrations, $q_e$, with aqueous naphthalene solution, $C_e$ [19,18]. 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 Equation (4):

$$K_{ads} = \frac{q_e}{C_e}$$  

(4)

Where ($K_{ads}$), (mg Kg$^{-1}$ adsorvent/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$^{-1}$). The natural polymers lignin fraction has been identified as the principal factor determining the degree of sorption of nonpolar compounds [19]. Thus, the lignin–water partition coefficients ($K_{lignin}$) for PAHs interacting with intact adsorbent (i.e., sugar cane, coconut shells & rice husk) were calculated from adsorbent partition coefficients ($K_{ads}$) and lignin mass ($f_{lignin}$) according to the following Equation (5):

$$K_{lignin} = \frac{K_{ads}}{f_{lignin}}$$  

(5)

Where $K_{lignin}$ (mg kg$^{-1}$ lignin/mg L$^{-1}$) is the partition coefficient between lignin and the solution; $f_{lignin}$ (g lignin g$^{-1}$ adsorvent) the amount of lignin present. For this study, $f_{lignin}$ was considered to be equivalent to 22% ($f_{lignin}$ = 0.22 for sugar cane bagasse [22,19], 40% ($f_{lignin}$ = 0.40) for coconut shells [22,23] and 24% ($f_{lignin}$ = 0.20) for rice husk[24-26]. The equilibrium $K_{ads}$ was calculated while published $K_{ow}$ values [29] for PAHs was used. 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 [29] for PAHs was used. The parameter $K_{ow}$ is the n-octanol–water partition coefficient and is a measure of a compound’s hydrophobicity. Thus, the partition coefficients of PAHs by sugar cane bagasse and coconut shells 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 appears to be controlled mainly by the lignin content[18,19]. The higher lignin content in coconut shells 40% compared to 20 % in rice husk, and 22% in sugarcane bagasse [22, 23], respectively, agrees with the extent of adsorption of PAHs followed the order: coconut shells > sugar cane bagasse > rice husk.

IV. CONCLUSIONS

Adsorption of PAHs such as can be effected using low-cost natural adsorbents. The adsorption capacity parameter $K_f$, increases with the lignin content and for any given adsorbent, the value of $K_f$ follows the order of naphthalene > fluorene > phenanthrene > pyrene. Uptake capacity of PAHs followed the order: coconut shells > sugar cane bagasse > rice husk. The adsorption isotherms of PAHs were in good agreement with a Freundlich model.
REFERENCES


