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Removal of Phenanthrene from Water Using Activated Carbon Developed from Orange Rind

Himanshu Gupta

Department of Chemistry Indian Institute of Technology Roorkee, Roorkee -247667(U.K.), India

Email: hims.research@gmail.com; Phone: +91-8791481480; Fax: +91-1332-273560

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Abstract. Water contamination due to polycyclic aromatic hydrocarbons is a matter of environmental concern in the recent years. Therefore, the adsorption of polycyclic aromatic hydrocarbon (PAH), phenanthrene, was investigated on laboratory synthesized activated carbon prepared from orange rind. The prepared adsorbent has surface area of 352.14 m$^2$/g. The effects of various experimental parameters such as adsorbent dose, initial concentration, pH, shaking time and temperature on the removal of the PAH have been investigated. The adsorption of PAH rises with the increase in shaking time and achieves equilibrium after 90 min. With the increase in the initial concentration of phenanthrene and adsorbent dose, enhancement of the adsorption rate was observed. Increase in pH of the solution has an adverse effect on the adsorption capacity of the adsorbent. The adsorption data were described by traditional Langmuir and Freundlich adsorption isotherms. Adsorption capacity evaluated using Langmuir adsorption isotherm was found to be 70.92 mg/g. The work demonstrates an effective method for the treatment of industrial wastewaters.

Keywords: Adsorption, PAH, phenanthrene, orange rind, adsorption isotherm

1. INTRODUCTION

Polycyclic aromatic hydrocarbons are the organic compounds with two or more fused rings. Various natural to anthropogenic activities are responsible for their release into the environment. Natural activities responsible for PAH pollution are forest fires, volcanoes etc., whereas anthropogenic activities are man-made such as burning of fuels, smoking cigarette, industrial releases. These environmental pollutants are released in the wastewaters of various industries such as petroleum industries, coking industry (Zhang et al., 2012; Janosz-Rajczyk et al., 2014).

United States Environment Protection Agency (USEPA) has listed them as priority pollutants. Based on the toxicity to humans, these are categorised as prominent mutagens or carcinogens (Paschin and Bakhitova, 1979). Due to their continuous release of wastewaters containing pollutants, the available freshwater is reducing continuously, leading to the water crisis throughout the world. Therefore, water purification or recycling of wastewater is the most challenging task of the today’s world. Several water remediation methods have been utilized by various authors, but adsorption is the most widely used technique for the removal of pollutants from aqueous systems (Mojiri et al., 2013). Different research groups have used various raw materials for the preparation of cheap and effective adsorbents or activated carbon (Fierro et al., 2010; Baseri et al., 2012; Deb et al., 2013; Cui et al., 2007; Memon et al., 2008; Ismail et al., 2013; Ghaemi and Tavakkoli, 2013; Kamaruddin et al., 2013; Bashir et al., 2014; Amenaghawon et al., 2013; Al-aibi et al., 2014).

Orange peel has also been used previously for the removal of naphthalene but the adsorption capacity was quiet low (Owabor et al., 2012). Hashemian et al. (2013) reported adsorption of azo dyes from aqueous solution using activated carbon derived from orange peel. Therefore, it was planned to prepare activated carbon from the adequately available raw material orange rind. The prepared activated carbon from orange rind (ORAC) is used for the removal of three ringed PAH, phenanthrene from aqueous systems. The prepared activated carbon has high efficiency towards PAH adsorption from aqueous systems. Phenanthrene, a three ringed PAH, is chosen for the adsorption analysis as representative of both high molecular weight and low molecular weight PAHs due to its moderate solubility in water. The effect of various parameters such as adsorbent dose, initial concentration, pH, shaking time and temperature on
the removal of the PAH have been investigated. The data were described by traditional Langmuir and Freundlich adsorption isotherms and various parameters were evaluated. The present work will provide a highly efficient adsorbent for the removal of PAH from various water and wastewater systems.

2. MATERIALS AND METHODS

Phenanthrene (>99%, MERCK) was first dissolved in methanol (supplied by RANKEM) and diluted using double distilled water to prepare 25 mg L⁻¹ solution in 50% methanol. Sodium hydroxide and hydrochloric acid used for pH maintenance was supplied by RANKEM.

Fig. 1: Effect of contact time on the adsorption of phenanthrene on ORAC

Fig. 2: Effect of amount of adsorbent on adsorption of phenanthrene on ORAC

2.1. Adsorbent

Orange rinds have been used as a raw material to prepare activated carbon using the method described elsewhere (Srinivasakannan and Bakar, 2004). The waste orange rinds were collected, dried and soaked with ortho-phosphoric acid for 12 h. The soaked sample was placed at 200°C in muffle furnace for 4 h. The material obtained was cooled and again placed at 400°C in muffle furnace for 2 h. The obtained material was washed 7-8 times with double distilled water until the wash liquor becomes neutral. The orange rind activated carbon (ORAC) thus, obtained
was dried and powdered. The BET surface area of the prepared adsorbent was found to be 352.14 m$^2$/g.

2.2. Adsorption of phenanthrene

Adsorption of phenanthrene was investigated in batch mode at room temperature. Forty millilitre of 25 mg L$^{-1}$ phenanthrene solution and 10 mg of the adsorbent were taken at pH 7 for the analysis, unless otherwise mentioned. The samples were shaken for 90 min to attain equilibrium on a mechanical shaker and filtered using whatmann filter paper. The analysis of the samples was accomplished in triplicate using UV spectrophotometer at 250 nm wavelength.

3. RESULT AND DISCUSSIONS

3.1. Effect of contact time

The effect of contact time was investigated on the adsorption of phenanthrene on ORAC for a time interval of 0-150 min. The adsorption of phenanthrene on ORAC increases with the increase in the contact time till 75 min and attains equilibrium till 150 min. (Fig. 1). Therefore, 90 min was chosen as shaking time for all the other studies.

| Table 1: Langmuir and Freundlich parameters for phenanthrene adsorption on ORAC |
|--------------------------|------------------|
| **Langmuir Parameters**  |                 |
| $q_0$                    | 70.9219          |
| b                        | 0.4017           |
| $r^2$                    | 0.9942           |
| **Freundlich Parameters**|                 |
| $K_f$                    | 19.6245          |
| $1/n$                    | 0.4505           |
| $r^2$                    | 0.961            |

3.2. Effect of adsorbent dosage

The influence of the dosage on the adsorption of phenanthrene onto ORAC was observed with 2-20 mg of the adsorbent. Fig. 2 shows the adsorption of phenanthrene in presence of varying amounts of the activated carbon. The adsorption of phenanthrene increases with the increase in the adsorbent dose due to higher availability of active sites for the adsorption. The adsorption of phenanthrene was almost complete with an adsorbent dose of 18 mg. The adsorption dose of 10 mg was used for the further studies to evaluate the effect of various parameters.

3.3. Effect of pH variation

The effect of pH variation on the removal of phenanthrene was studied in the pH range 2-12. Fig. 3 shows the influence of pH on the adsorption of phenanthrene from aqueous solution. The phenanthrene adsorption was maximum at low pH and minimum at high pH. In the pH range 6-8 (neutral pH), the adsorption was almost constant. At low pH, the positive charge on the adsorbent surface was high, which leads to higher interaction between the adsorbent surface and the π-electron cloud of the phenanthrene molecule. At higher pH, the positive charge on the adsorbent surface is decreased and OH$^-$ ions also competes with the phenanthrene molecules for the adsorption on the active sites, leading to the reduction in the adsorption efficiency of the adsorbent. At neutral pH, only a little influence of H$^+$ or OH$^-$ ions was present on the adsorbent surface, therefore almost constant adsorption of phenanthrene was observed.

3.4. Effect of adsorbate concentration

To investigate the effect of initial concentration, sorbate concentrations were varied in the range 10-50 mg L$^{-1}$ in the presence of 10 mg of the adsorbent. It was observed that with the increase in the sorbate concentration, the adsorption capacity of phenanthrene increases (Fig. 4). This observation is reasonable due to availability of larger number of phenanthrene molecules to interact with active sites of the activated carbon, leading to the higher adsorption capacity of phenanthrene. At the same time the remaining concentration of phenanthrene also increases due to increase in the initial concentration. Therefore, percentage adsorption of phenanthrene decreases. This observation is in accordance with (Hall et al., 2009) for the removal of acenaphthene using silica gel.

3.5. Effect of temperature

To determine the effect of temperature on the adsorption of phenanthrene onto ORAC, the samples were agitated at 20, 30, 40 and 50°C. The results indicated that the adsorption of phenanthrene increase with the rise in temperature (Fig. 5). The results suggest that the adsorption of phenanthrene on ORAC is a process of decalescence. Kobya, (2004) and Basar (2006) also observed the endothermic nature of the adsorption process during adsorption on hazelnut shell activated carbon and waste apricot activated carbon.
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4. MODELLING OF ADSORPTION ISOTHERMS

Several adsorption isotherm models were developed by various researchers, but Langmuir and Freundlich adsorption isotherm models are most widely accepted. Langmuir adsorption model is based on the assumption that adsorption occurs at localised sites and there is no interaction between adsorbate molecules. Adsorption is maximum when the adsorbent surface is covered by the adsorbate monolayer (Amarasinghe and Williams, 2007). The linear form of Langmuir adsorption isotherm for solid-liquid system is given as follows:

\[
\frac{1}{q_e} = \frac{1}{bq_o C_o} + \frac{1}{q_o}
\]

where \( C_o \) is the initial concentration, \( C_e \) is the equilibrium concentration, \( q_e \) is the amount of adsorbate per gram of adsorbent, \( q_o \) is the adsorption capacity and \( b \) is the Langmuir constant.

Freundlich isotherm is concerned with multilayer adsorption (Shaikh et al., 2011). The linear form of Freundlich adsorption isotherm for heterogeneous surfaces is given below:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \( K_f \) and \( n \) are adsorption capacity and intensity of adsorption, respectively.

The Langmuir and Freundlich adsorption isotherms are shown in Fig. 6 and 7, respectively. The isotherms obtained were used to calculate the Langmuir and Freundlich adsorption parameters given...
in Table 1. The data was found to be feasible with both Langmuir and Freundlich adsorption isotherms but on the basis of $r^2$ values, it can be concluded that Langmuir model fitted better for the adsorption of phenanthrene. The adsorption capacity ($q_e$) calculated on the basis of Langmuir adsorption isotherm was found to be 70.92 mg/g. The values of $1/n$ lie between 0 and 1 which indicates favourable adsorption (Amarasinghe and Williams, 2007).

**Fig. 5:** Effect of temperature on adsorption of phenanthrene onto ORAC

**Fig. 6:** Langmuir adsorption isotherm for the adsorption of phenanthrene on ORAC
5. CONCLUSION

The adsorbent prepared from orange rinds (ORAC) was found to be highly efficient for the removal of phenanthrene from aqueous solutions. The adsorption data were fitted to Langmuir and Freundlich adsorption isotherms. On the basis of $r^2$ values it can be concluded that the data is better fitted to Langmuir adsorption isotherm. Adsorption capacity evaluated using Langmuir adsorption isotherm was found to be 70.92 mg/g. The adsorption of phenanthrene is almost complete with 18 mg of the adsorbent. The adsorption of phenanthrene was higher at low pH and lower at high pH. The adsorption capacity of ORAC enhances with increase in concentration, whereas percent adsorption decreases. The results of effect of temperature on the adsorption studies indicated endothermic nature of the adsorption process. The adsorption of phenanthrene on ORAC will serve as representative study for the adsorption of both low molecular weight as well as high molecular weight PAHs.

REFERENCES


Himanshu Gupta is a researcher in department of chemistry at Indian Institute of Technology Roorkee, since July, 2010. His work is in the field of photocatalytic degradation and removal of organic pollutants from aqueous and solid environmental matrices. He completed his Bachelor of Science from Rohilkhand University in 2008 and Master of Science in organic chemistry from Aligarh Muslim University, India in 2010. Several national and international conferences are attended by him to present his scientific results and his work is published in various reputed journals such as chemosphere, desalination and water treatment.