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Determination of polycyclic aromatic hydrocarbons adsorption on Tehran oil refinery contaminated soil and its modeling

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Abstract

Polycyclic aromatic hydrocarbons are widely distributed contaminants which have drawn increasing public health concern because of their mutagenic and carcinogenic. This study was carried out to investigate the potential of Polycyclic Aromatic Hydrocarbons adsorption on Tehran oil refinery soil. Also, the modeling of the petroleum adsorption process in soil column is among the crucial objectives of this study. So, we prepared a pilot plant, and after packing it with Tehran oil refinery contaminated soil in specific weight and 25 cm height, oily wastewater containing polycyclic aromatic hydrocarbons influence on it. The column pressure head and its conditions have been stable during experiment. The adsorption of PAHs on soil was estimated by measuring the concentration of PAHs in effluences of the drainage every 15 min intervals up to 4 h, and the bed soil column at the end of experiment. The maximum adsorption capacity of Tehran oil refinery soil was 90.8%. Then, it has been compared the suitability of two predictive models Freundlich isotherm and Langmuir isotherm in analyzing the adsorption of PAHs on soil. The result showed that empirical Langmuir equation wasbetter than the Freundlich equation in describing the behavior of Polycyclic Aromatic Hydrocarbons adsorption onto Tehran oil refinery soiland the adsorption coefficient was calculated as 0.184. Finally, HYDRUS -1Dsoftware was used to model the changing of Polycyclic Aromatic Hydrocarbons adsorption in soil column and the results showed that the experimental data were well fitted by HYDRUS model.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds found as major contaminations in air, soil, and aquatic systems. PAHs are characterized by two or more fused aromatic rings, which undergo transformation in the environment, and are known to be toxic to humans (Diana and Frank, 1990; Christopher *et al.*, 1996; Ke*et al.*, 2005; Edward *et al.*, 2008; Arodi*et al.*, 2009). Many of PAHs are known to be carcinogenic and mutagenic. Environmental protection agency included 16 of them in the list of priority pollutants (naphthalene, anthracene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indo(1,2,2-cd)pyrene, dibenzo(a,h) anthracene,benzo(g,h,i)perylene(Arodi*et al.*, 2009). Human beings are exposed to PAHs via air and drinking water, but mostlyby intake of food. Accumulation of PAHs in agricultural soils may increase uptake of them by crops, and threat the quality and safety of food (Hao*et al.*, 2007). In addition to their natural occurrence, anthropogenic inputs from accidental oil spills as well as leaks and spills have resulted in a significant accumulation of PAHs in the soil (Hao*et al.*, 2007). Petroleum pollutants tend to adsorb, desorb, biodegrade and photolyze and so on in the soil, but adsorption / desorption is a pair of extremely important environmental geochemistry behavior. Sorption will be a factor in determining the movement of contaminants with the groundwater flow. Sorption is defined either as the attachment of the Petroleum pollutants to the soil surface or as the intake of them into the soil matrix. The rate of the influence of oil pollution in soil column depends on a number of factors which include; the permeability of the soil, adsorption properties of the soil, the partition coefficient and water content in soil (Xiaoyan*etal.*, 2006). Nevertheless, several studies have demonstrated migration of PAHs at depth of soil column and have reported the groundwater contamination by these pollutants (Diana and Frank, 1990; Christopher *et al.*, 1996; Ke*et al.*, 2005; Edward *et al.*, 2008; Arodi*et al.*, 2009;Hao*et al.*, 2007; Xiaoyan*et al.*, 2006). The adsorption kinetics can be described byvarious models depending upon the mechanism oftransport (pore diffusion, solid diffusion, and bothmechanisms in parallel) assumed inside the particles (Suresh and B.V,2010).Adsorption isotherms describe qualitative information onthe nature of the solute-surface interaction as well as thespecific relation between the concentration of adsorbateand its degree of accumulation onto adsorbent surface atconstant temperature.In this case, (Hao*et al.*, 2007) investigated the state of the contamination and distribution of PAHs in agricultural soils in the subtropical regions of China. The results of them indicated that pyrolytic origins were the dominant sources of PAH in the southern subtropical areas of China. Other researches (Chiedu*et al.*, 2013) studied the sorption behavior of benzene, toluene, ethyl benzene, xylene and naphthalene using clay and sand sediments and their results showed that clay has a better capacity to retain naphthalene and BTEX than sand and this may not be unrelated to its large surface area, high porosity and higher hydraulic conductivity for the solutes arising from its good binding sites (small pore sizes) that tend to hold the adsorbates to its particles.(Tracy and Donald, 2005) evaluated the effect of soil moisture and soil pH levels on adsorption, Desorption, and Degradation of three herbicides in soil and revealed that the percentage of applied herbicide found in soil solution was greater at pH 7 than at pH 5 for all three herbicides. Over time, less herbicide was in the soil solution and less was desorbed. (Raoul, 1989) reviewed on adsorption of organic chemicals on soils sediments and mentioned that no general rules can be proposed to describe univocally the relation between the shape of isotherms and the nature of adsorbate-adsorbent system. Furthermore, theoretical developments exist both for the thermodynamics and the kinetics of adsorption, but evaluation of adsorption can be obtained through either laboratory measurements or use of several correlations.As mentioned above, there have been a large number of investigations studied on adsorption of PAHs Contamination on soils, and adsorption process is descripted through the various models. However, several factors effect on adsorption process and it is so necessary, experimental results for discussing the kinetics of adsorption. Also, PAHs could be adsorbed to soil particles, accumulated on soil column and conduced groundwater contamination. So, there is a strong need for measuring of these high risk contaminants in all sensitive areas such as oil refineries and petrol stations and studding of adsorption behavior to predict soil column and groundwater contamination.Thus, present study was carried out to investigate the potential of Polycyclic Aromatic Hydrocarbons adsorption on Tehran oil refinery soil.This study also compares the suitability of two predictive models Freundlich isotherm and Langmuir isotherm in analyzing the adsorption of PAHs on to Tehran oil refinery contaminated soil. Finally, HYDRUS -1Dsoftware was used to model the changing of Polycyclic Aromatic Hydrocarbons adsorption in soil column.HYDRUS computer model solves Richards's equation for variably-saturated water flow and advection dispersion type equations for heat and solute transport. The program may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. The flow region may be composed of no uniform soils. Flow and transport can occur in the vertical, horizontal, or a generally inclined direction.

Materials and metods

Soil samples

Soil samples were collected from four different geographical direction of a land next to the active units of Tehran oil refinery in Iran. The samples were transported to the laboratory on ice and stored at 4°C until they were analyzed. The soil properties of samples are provided in Table.1.The presence of PAHs contamination in the soil of this land was confirmed by solvent extraction (Dichloro methane) in an ultrasonic water bath, and high performance liquid chromatography (HPLC) analysis using a Waters Binary 2 all pump model 510 liquid chromatography with a fluorescence detector. The column used was Waters PAH C18 S-5 μmpacking materials at 30 °C.A mixture of 65% Acetonitrile and 35% water was used as the mobile phase A, and pure Acetonitrile used as the mobile phase B at a flow rate of 1 ml / min (Maryam *et al.*,2010).

Preparation of wastewater

A substrate of petroleum containing 5%of vacuum bottom in gasoline of Tehran oil refinery prepared and used as a source of the PAHs. 1 liter of the substrate added to 50 liter of water and used as the synthetic wastewater. The wastewater was mixed in the inlet tank to obtain monotonous drop. The concentrations of PAHs in the synthetic wastewater were determined by solvent extraction (Dichloro methane) in an extractor, and high performance liquid chromatography (HPLC) analysis as mentioned above(Maryam *et al.*,2010). The concentration of total PAHs in the synthetic wastewater was 155.7 (μg/l).

Pilot experiments

A rectangular pilot plant of stainless steel with a glass window was prepared. Dimensions of the pilot were 70×40×100 cm and an interlaced plate was at the end of it as a drainage that equipped with a valve for sampling of effluences. Before packing the pilot with Tehran oil refinery contaminated soil, it has been layered with various sizes of sands from coarse to fine up to 25 cm. Then, it was packed with specific measured weight of soil sample in 25 cm height, and the synthetic wastewater influenced on it. In all experiments, the steady-state regime was achieved by a constant pressure drop. The column pressure head and its conditions have been stable during experiments. Tests were run for 4 h at room temperature, 30 C° and were sampled from outlet of unit 15 min intervals, and the bed of soil column at the end of experiments. PAHs were extracted from solid and aqueous samples and then their concentrations weremeasured by high HPLC as mentioned above (Maryam *et al.*, 2010).

PAHs adsorption modeling

HYDRUS -1Dsoftware was used to model the changing of Polycyclic Aromatic Hydrocarbons adsorption in soil column. HYDRUS computer model solves Richards's equation for variably-saturated water flow and advection dispersion type equations for heat and solute transport (Jirka*et al.*, 2005). The modeling was based on the present pilot experiment and the physico-chemical characteristics of the soil sample.

Results and discussions

The native soil approximately had a neutral pH (7.41) and the Saturated soil moisture was 29.9%.The mean of the initial amount of the total PAHs in soil samples was 406.5 (μg/Kg)and it has been considered in calculations. Removals were defined as the difference between inlet and outlet concentrations divided by the inlet concentration. They were calculated after reactor stabilization. Fig.1 shows the effect of contact time on the adsorbed amount of PAHs by the soil. Adsorption increased sharply with contact time in the first 1 hr and attained maximum (90.8%) within 180 min.So, sorption happened in two steps: a high rate steps and low rate steps. The results of previous researchers confirm this behavior (Reuben NO and Miebaka JA, 2008).Thus, the soils of studied area have high efficiency of PAHs adsorption. The adsorbent phase concentrations of PAHs (q_e) were calculated according to following equation (1):

$q_e = v (C_o - C_e) / m$ (1).

Where C_o and C_e are the initial and equilibrium concentrations of PAHs (mg/l), respectively, v is volume of liquid in the reactor (l), and m is the mass of adsorbent (g) (Kunquan and Xiaohua, 2009). Adsorption isotherms are critical in optimizing the use of adsorbents, and the analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (Tan*et al.*, 2008). Equations that were used to describe the experimental isotherm data were Freundlich isotherm and Langmuir isotherm. The Freundlich and Langmuir isotherms are empirical models which are defined as follows, respectively:

$x/m = K_f c_e^{1/n}$(2)

$x/m = abC_e/(1+bC_e)$ (3).

Table 1. The physico-chemical characteristics of the soil samples.

Soil sample	pH (1:1)	CEC meq/L	Organic Carbon%	Total N %	Total P mg/L	Soil texture	Saturated soil moisture %
1	7.22	52.3	0.61	1.4	20.3	Clay	27.7
2	7.25	51.5	1.12	1.3	19.3	Clay	30.5
2	7.42	51.1	0.81	1.1	18.1	Clay	30.7
4	7.49	52.1	0.84	0.8	15.6	Clay	30.8
pilot	7.41	52.10	0.73	1.2	19.1	Clay	29.9

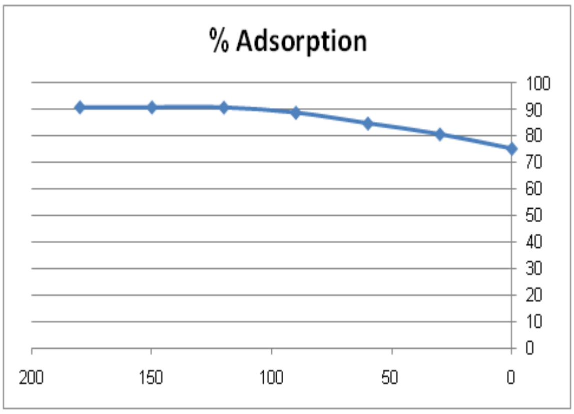

Fig. 1. Changing of PAHs adsorption capacity on soil column.

Where x/m is mass of adsorbate adsorbed per unit mass ofadsorbent (mg/g), K_f, a and b are empirical constants,and C_e is equilibrium concentrations of adsorbate(Kunquan and Xiaohua, 2008).The fig.2 and fig.3 show the suitability of two predictivemodels Freundlich isotherm and Langmuir isotherm inanalyzing the adsorption of PAHs on the soil sample,respectively. In order to compare the validity of eachisotherm model, the values of correlation coefficients(R^2) were calculated. These results showed that theadsorption data were well fitted by both the two isothermmodels, but the Langmuir equation gave the higher valuesof correlation coefficients (0.998) than Freundlichequation at the temperature investigated. According to the fig.4 adsorption coefficient was calculated as 0.184.Adsorption of Petroleumhydrocarbon on organoclay was studied by (Masoomeh *et al.*, 2009) and finding showed that adsorption equilibrium was attained with 1hr.

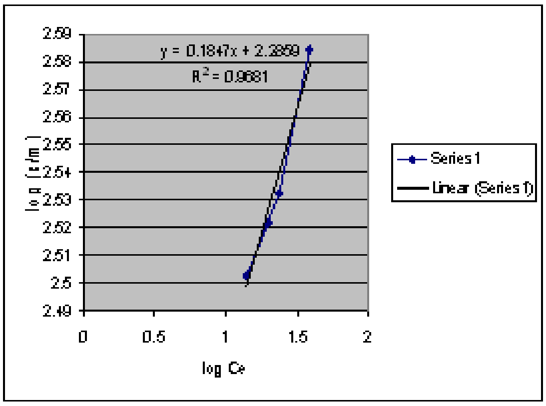

Fig. 2. Curve fitting of obtained data from soil column as adsorbent by Freundlich isotherm.

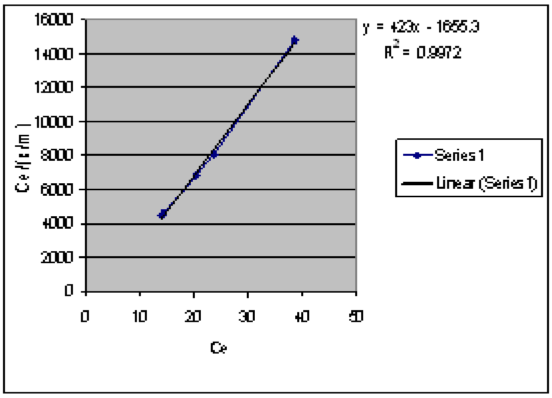

Fig. 3. Curve fitting of obtained data from soil column as adsorbent by Langmuir isotherm.

Finally, HYDRUS -1Dsoftware was used to model the changing of Polycyclic Aromatic Hydrocarbons adsorption in soil column and simulate PAHs concentration profiles with dispersivity. One-dimensional uniform (equilibrium) water movement in a partially saturated rigid porous medium is described by a modified form of the Richards equation using the assumptions that the air phase plays an insignificant role in the liquid flow process and that water flow due to thermal gradients can be neglected:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(\theta)\left(\frac{\partial h}{\partial x} + \cos\alpha\right)\right] - S$$

Where his the water pressure head,θ is the volumetric water content, tis time, xis the spatial coordinate, *S*is the sink,α is the angle between the flow direction and the vertical axis , and Kis the unsaturated hydraulic conductivity(Jirka*et al.*, 2005). The modeling was based on the present pilot experiment and the physico-chemical characteristics of the soil sample. The Soil texture was clay, the experimental time was 5 h, the saturated soil moisture was 29.9% and the inlet flow rate of PAHs was calculated as 2.5 cm hr^{-1}. Fig.5. shows the comparison of the experimental results of changing of PAHs adsorption in soil column with the simulation results and the results showed that the experimental data were well fitted by HYDRUS model. To estimate the water balance components of an oak stand (Norbert, 2010) used HYDRUS-1D model and found the Model simulation described the observed soil moisture and groundwater level relatively well. Also, HYDRUS-1D would be modified to simulate the transport of major ions such heavy metals in Soil Column (Jirka*et al.*, 2006).

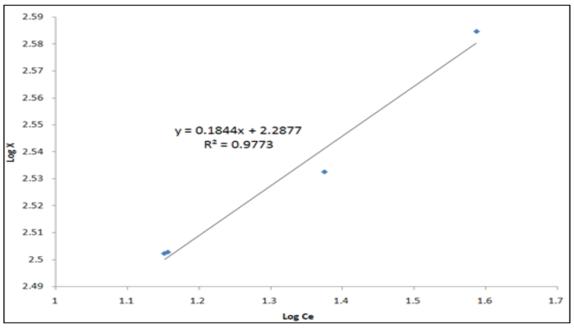

Fig. 4. Using of Freundlich isotherm to calculate the adsorption coefficient of PAHs on soil.

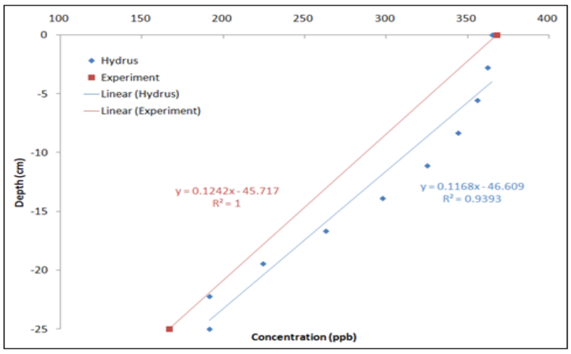

Fig. 5. Curve fitting of obtained data from soil adsorbent by drawn.

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