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Using natural adsorbents to reduce polycyclic aromatic hydrocarbons contamination of oily wastewater

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Key words: Polycyclic aromatic hydrocarbons, Adsorption, Oily wastewater, Rice bran, sawdust.

Abstract

In recent years, an intensive research was conducted focusing on the selection of low-cost adsorbents which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment activated carbon. This study was carried out to compare the adsorption of PAHs on rice bran, sawdust and activated carbon, and investigate the adsorption properties of them. We prepared a rectangular pilot plant with an interlaced plate as drainage at the end of it, and after packing it with each of the adsorbents in specific weight and height, oily wastewater containing polycyclic aromatic hydrocarbons (PAHs) influence on it. The column pressure head and its conditions have been stable during experiments. The adsorption of PAHs on these adsorbents was estimated by measuring the concentration of PAHs in effluences of the drainage every 15 min intervals up to 4 h, and the bed of adsorbents at the end of experiments. The results showed, Activated carbon and Rice bran attained the maximum of the adsorption (92.1%) and (91.5%) within 60 min, respectively. Also, the maximum PAHs adsorption on sawdust (88.5%) observed, after 30 min. Then, the mean concentration of PAHs was calculated per unit of the mass of adsorbents at the end of experiments and revealed; time is the effective factor on adsorption values. The adsorption coefficient was calculated as 0.187, 0.131and 0.114 on rice bran, sawdust and activated carbon, respectively.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed contaminants which have drawn increasing public health concern because of their mutagenic and carcinogenic properties. In addition to their natural occurrence, anthropogenic inputs from fuel combustion, pyrolytic processes, waste incinerators, domestic heaters and spillage of petroleum products have resulted in a significant accumulation of PAHs in the environment (Freeman and Cattell, 1990; Simpson *et al*, 1996; Ke *et al*, 2005; Hilyard *et al*, 2008; Bernal-Martinez *et al*, 2009; farahani *et al*, 2010). 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 (Bernal-Martinez *et al*, 2009). A range of cleaning techniques have been successfully developed to limit the environmental impact caused by oil pollution, but timely and effective remediation is necessary to mitigate the detrimental effect of petroleum hydrocarbons on the environment.The Use of adsorption contacting system for industrial and municipal wastewater treatment has become more prevalent during recent years. Adsorption process is a proven technology for the elimination of low concentration organic compounds from contaminated water and aqueous solutions. An adsorption process is often used at the end of a treatment sequence for pollution control due to the high degree of purification that can be achieved. Moreover, adsorption processes have the advantage of ease in use and are easy to combine with other treatment technologies (Yan *et al*, 2009). Adsorption is the adhesion of a chemical substance (adsorbate) on to the surface of a solid (adsorbent) .The most widely used adsorbent is activated carbon (Okparanma and Ayotamuno, 2008) due its effectiveness, versatility and good capacity for the adsorption of heavy metals and organic molecules. However, it suffers from a number of disadvantages, mainly its high cost with large –scale use (Xiaoyan *et al*, 2006). In recent years, an intensive research was conducted focusing on the selection of low-cost adsorbents which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment activated carbon (Nameni *et al*, 2008; Wang *et al*, 2008; Shah *et al,* 2009; Zvinowanda *et al,* 2009; Ageena, 2010; Vinodhini and Das, 2010). Natural materials of both organic and inorganic nature (such as chitosan, zeolites, clay and clay minerals, etc) and certain waste products from industrial operations (such as fly ash, coal and oxides) are classified as low-cost adsorbents because they are economical and locally available (Sljivic *et al*, 2009). Cost is an important parameter for comparing the sorbent materials. However, the usage of indigenous biodegradable resources as adsorbents for treating wastewater would be less expensive. Rice bran contains functional groups associated with proteins, polysaccharides and cellulose as major constituents. Our previous studies have shown that sawdust and rice bran are a potentially useful biosorbents for treating wastewaters contaminated with heavy metals (Nameni *et al*, 2008; Wang *et al*, 2008; Shah *et al,* 2009; Zvinowanda *et al,* 2009; Ageena, 2010; Vinodhini and Das, 2010).The cost of these biomaterials are negligible compared with the cost of activated carbon or ion-exchange resins. Although, several researches have published on the removal of heavy metals, from wastewater using inexpensive bio-waste materials, new economical, easily available and highly effective adsorbents for treating oily wastewater are still needed. So, we decided to investigate and compare the adsorption potential of PAHs on rice bran, sawdust and activated carbon. At industrial scale, the time of stopping the operation must be determined after an economic and, eventually, environmental evaluation of the process. Because not only the amount of solute adsorbed but also the operating time has an important impact on the effective use of the adsorption column and on the final through put of the process, too. The optimization of this and other operating condition can be accomplished with the help of reliable mathematical models. The adsorption kinetics can be described by various models depending upon the mechanism of transport (pore diffusion, solid diffusion, and both mechanisms in parallel) assumed inside the particles (Gupta and Babu, 2010). Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. The aim of this study was to investigate and to compare the adsorption properties of activated carbon, rice bran, and sawdust for polycyclic aromatic hydrocarbons adsorption. This study also compares the suitability of two predictive models Freundlich isotherm and Langmuir isotherm in analyzing the adsorption of PAHs on to three type adsorbents that mentioned above.

Materials and metods

Preparation of adsorbents

The three adsorbents, activated carbon, rice bran, and sawdust were washed three times in de-ionised water and dried. Then the adsorbents were screened to obtain a particle size range of 0.05- 0.5 cm.

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 a extractor, and high performance liquid chromatography (HPLC) analysis using a Waters Binary 2 all pump model 510 liquid chromatograph with a fluorescence detector. The column used was Waters PAH C18 S-5 µm packing 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). The concentration of total PAHs in the synthetic wastewater was 155.7 (µg /L) (Samimi *et al*, 2009; Farahani *et al*, 2010).

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 each of the adsorbents, 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 each of the adsorbents in 15 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.

For each adsorbents test were run for 4 h at room temperature, 30 °C and were sampled from outlet of unit 15 min intervals, and the bed of adsorbents column at the end of experiments. PAHs were extracted from solid and aqueous samples by solvent extraction (Dichloro methane) in soxhlet extractor and an extractor, respectively, and then their concentrations were measured by high HPLC as mentioned above (Samimi *et al*, 2009; Farahani *et al*, 2010).

Results and discussions

The concentration of total PAHs in the synthetic wastewater was 155.7 (µg /L). 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 results of Comparison the concentration of the total PAHs in effluences of the pilot between different adsorbents that represents the relation between the concentration of PAHs in the liquid phase at equilibrium and in the solid adsorbent phase for a constant temperature. Fig.2 shows the effect of contact time on the sorption capacity of PAHs on the different adsorbents in percentage. Based on fig.2 , in case of Activated carbon and Rice bran adsorption increased sharply with contact time in the first 1 h and attained maximum (92.1%) and (91.5%) within

60 min, respectively. The maximum of the adsorption for Sawdust (88.5%) observed, after 30 min. So, sorption happened in two steps: a high rate steps and low rate steps. The results of previous researchers confirm this behavior (Okparanma and Ayotamuno, 2008). It is clear that the value of adsorption of PAHs on, Activated carbon just was a little more than the others supplied adsorbents, which was perhaps due to participation of specific functional groups on the adsorbent surface and its physicochemical properties. The results of previous researchers confirm this behavior (Qiu *et al*, 2008). The results above suggested that Although, Activated carbon was an effective adsorbent for the purification of wastewater polluted with PAHs, Rice bran and Sawdust with high efficiency of PAHs adsorption could be utilized as an alternative to the Activated carbon in oily wastewater treatment. Further, these adsorbent are cheaper than activated carbon, also sawdust and Rice bran are economical and locally available from Waste of industrial and agricultural operations. As mentioned previous, for each adsorbents test were run for 4 h and, the concentration of PAHs were measured in the bed of adsorbents column at the end of experiments. Then, the mean concentration of PAHs was calculated per unit of the mass of adsorbents (µg/Kg) and fig.3 shows these results. Based on fig. 3 revealed; time is the effective factor on adsorption values and, all of three types of used adsorbents have great potential to remove PAHs from oily wastewater. The maximum adsorption of PAHs on the adsorbents were investigated in the order, activated carbon (70.6)> rice bran (67.7)>sawdust (63.3) (µg/Kg), while contacting time was constant. Consequently, there is no significant different between these data. In this case, the results of previous researchers (Adachi *et al*, 2001; Idris *et al*, 2012) have shown that sawdust and rice bran are a potentially useful biosorbents for treating wastewaters contaminated with organic compounds such as pesticides and methylene blue.

Also, the adsorbent phase concentrations of PAHs (q_e) were calculated according to following equation (1):

$$q_e = v\,(C_o - C_e) / m \quad (1)$$

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). 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 Langmuir and Freundlich isotherm model were used to describe the biosorption equilibrium of biomass. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate (Vinodhini and Das, 2010). The Freundlich and Langmuir isotherms are empirical models which are defined as follows, respectively:

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

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

where x/m is mass of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f, a and b are empirical constants, and C_e is equilibrium concentrations of adsorbate (Li and Wang, 2009). The fig.4 until 9 show the suitability of two predictive models Freundlich isotherm and Langmuir isotherm in analyzing the adsorption of PAHs on three type adsorbents that mentioned above. In order to compare the validity of each isotherm model, the values of correlation coefficients (R^2) were calculated, that are listed in table 1.

Table 1. Isoterm correlation coefficients (R^2) for PAHs adsorption onto different adsorbents.

R^2	Model	
	Freundlich	**Langmuir**
Activated carbon	0.995	0.999
Rice bran	0.992	0.985
Sawdust	0.994	0.999

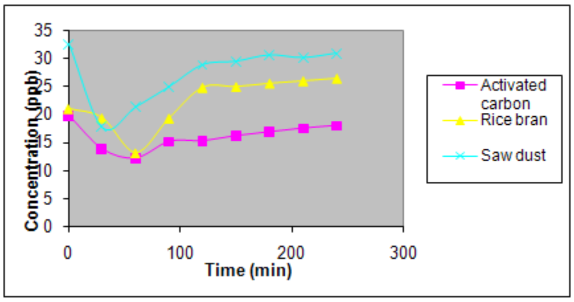

Fig.1. Comparison the concentration of the total PAHs in effluences of the pilot between different adsorbents.

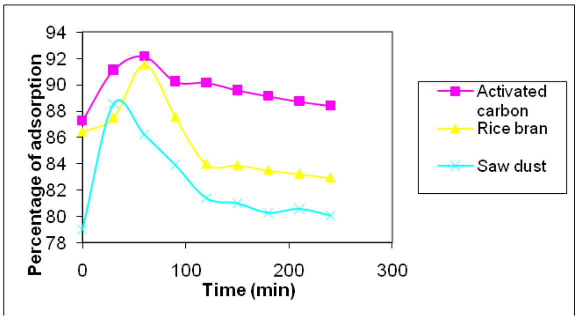

Fig.2. Comparison of sorption capacity of PAHs on different adsorbents.

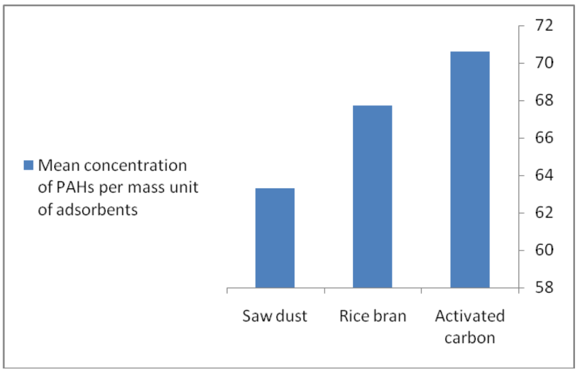

Fig.3. Comparison of the mean concentration of PAHs per unit of the mass of different adsorbents.

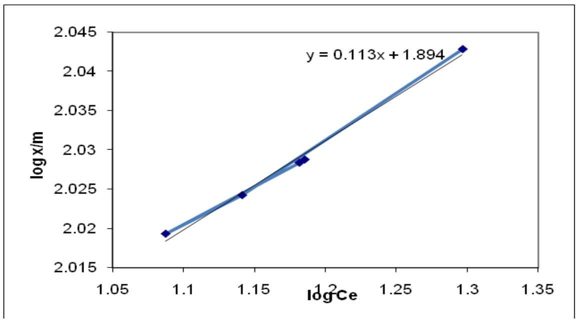

Fig.4. Curve fitting of obtained data forms Activated Carbon as adsorbent by Freundlich isotherms.

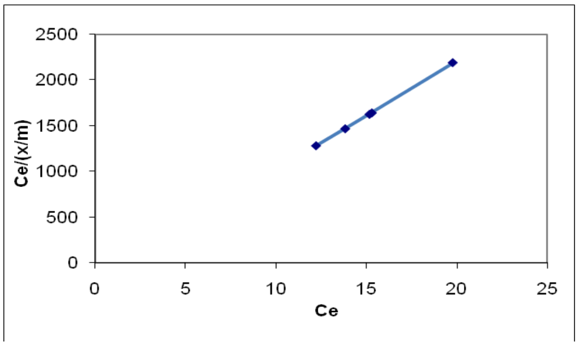

Fig.5. Curve fitting of obtained data forms Activated Carbon as adsorbent by Langmuir isotherms.

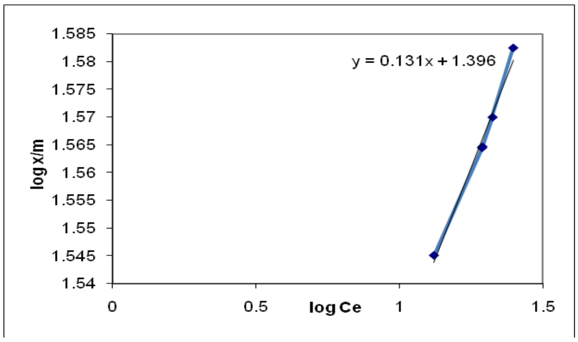

Fig.6. Curve fitting of obtained data forms sawdust as adsorbent by Freundlich isotherms.

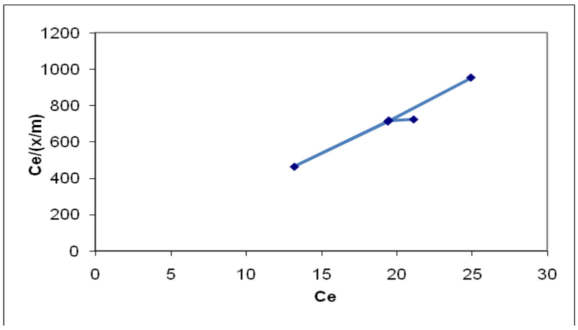

Fig.7. Curve fitting of obtained data forms sawdust as adsorbent by Langmuir isotherms.

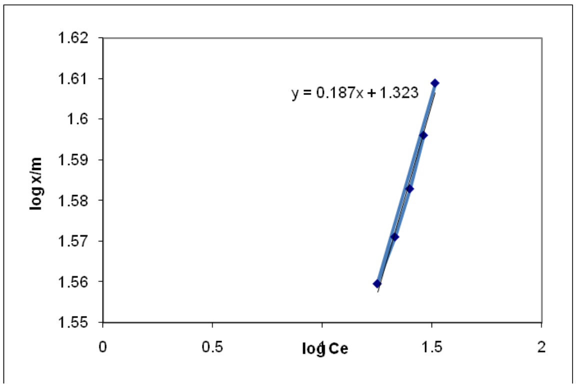

Fig.8. Curve fitting of obtained data forms Rice bran as adsorbent by Freundlich isotherms.

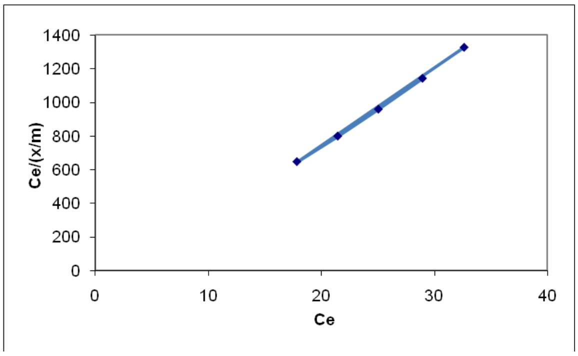

Fig.9. Curve fitting of obtained data form Rice bran as adsorbent by Langmuir isotherms.

Based on table.1, fig.8 and fig.9, it was found that the fitting to the Freundlich equation gave the higher values of correlation coefficients than those for Langmuir equation at the temperature investigated for Rice bran. It showed that the empirical Freundlich equation was better than the Langmuir equation in describing the behavior of PAHs adsorption onto Rice bran, implying that the adsorption process involved multimolecular layers of coverage. According the results of Table 1, fig.4 until fig.7, indicated that the adsorption data were well fitted by both the two isotherm models with the correlation coefficients more than 0.99 for Activated carbon and Sawdust. Thus, the adsorption process in all investigated systems was favorable.

The equilibrium isotherms represent the equilibrium curve that represents the relation between the concentration of the chemical species in the liquid phase at equilibrium and in the solid adsorbent phase for a constant temperature. The breakthrough curve is obtained through a graph of the concentration of the chemical species under study obtained at the outlet of the adsorption column as a function of operation time. After some time the bed becomes saturated and the output concentration approaches the input concentration. Finally, the adsorption coefficient was calculated as 0.187, 0.131and 0.114 on rice bran, sawdust and activated carbon, respectively. Thus, the adsorption process in all investigated systems was favorable, and rice bran and sawdust are suitable alternatives in comparison with Activated carbon, economically.

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