TRANSITION METAL COMPOSITE FOR THE REMOVAL OF PAHs FROM AQUEOUS PHASE: ADSORPTION KINETICS AND ISOTHERM STUDIES

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Abstract:

This work describes the zinc ferrite nano particles as an efficient adsorbent in the removal of PAHs (ploy cyclic aromatic hydrocarbons) namely Acenaphthene (ACE), Anthracene (ANT) and benzo[a] pyrene (BAP) from aqueous media. The batch experiments were employed to determine the effect of initial adsorbate, adsorbent concentration and contact time. The adsorption of ACE, ANT and BAP reached equilibrium after 60,70 and 80 minutes respectively. q_e exp = 18.12, 18.36 and 18.78 µg/g respectively.The higher adsorbate concentrations were associated with increase in the percentage removal and the value of q_e. The adsorption followed pseudo second order kinetics and experimental data fitted using the Langmuir isotherm model.

Keywords: Zinc ferrite nano particles, adsorption, polycyclic aromatic hydro carbons, Pseudo second order kinetics.

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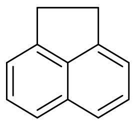
1. Introduction

The transition metal composite namely zinc ferrite spinel structure has tremendous applications in the various fields of chemistry. $ZnFe_2O_4$ has normal spinel structure where Zn^{+2} ions preferably occupy the tetrahedral A sites and Fe^{+3} ions the octahedral B sites[1,2]. The absence of Fe^{+3} ions in the A sites results in weak anti ferromagnetic exchange interactions within Fe^{+3} in B sites, making $ZnFe_2O_4$ antiferromagnetic below 9K[3,4]. The enhanced magnetization originates from super exchange interactions ascribed to the inversion of Fe^{+3} and Zn^{+2} ions in the tetrahedral (A) and octahedral (B) sites [5,6].

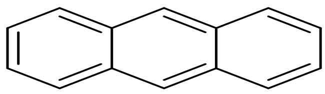
Polycyclic aromatic hydro carbons (PAHs) are tenacious in the environment and are highly carcinogenic, toxic, mutagenic and have immuno toxic effects. PAHs are organic compounds consisting of essentially carbon and hydrogen arranged in aromatic rings[7].

Acenaphthene[ACE] of PAH with molecular weight 154 is used to make plastics, dyes and pesticides. It is found in the exhaust from automobiles and in cigarette smoke. It can irritate the skin and eyes. Breathing Acenaphthene can irritate the nose and throat and causes coughing and wheezing. ACE can cause methemoglobinema [8,9].



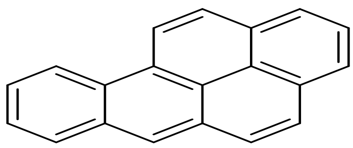
1,2-dihydroacenaphthylene

Anthracene [ANT] is a PAH with molecular weight of 178 is used as dye precursor and is used as scintillator for high energy electron, photon and α particle detector. It is also present in insecticides, wood preservatives and coating materials [10,11].



anthracene

Benzopyrene is a high molecular weight PAH with 252 molecular weight is a mouse metabolite and carcinogenic agent. It can cause lung, skin and bladder cancer. It is present in charbroiled food, cigarette smoke [12,13].



benzo[*pqr*]tetraphene

Several conventional methods are available for the removal of PAHs. But adsorption is inexpensive simple design, accepted at wide pH range and easy operation with high performance.

The application of nano zinc ferrite in the adsorption of ACE, ANT and BAP is discussed in detail with respect to adsorption kinetics and isotherm models.

2. MATERIALS AND METHODS

The zinc ferrite nano particles were synthesized and used as per the procedure [14]. ACE, ANT and BAP analytical standards were obtained from Aldrich. The solvent is acetonitrile of HPLC grade. Amorphous silica, tetra methyl ammonium hydroxide, sodium meta silicate were used as it is without further purification. Ultra pure water was obtained from Milli-Q system.

Batch adsorption experiments

To investigate the effects of the initial concentration, dose of adsorbent, contact time. The experiments were conducted in amber flasks at 25^0C with agitation at 150 rpm. All the experiments were conducted in duplicating employing 5 ml of the mixed solution of three PAHs and 0.05g of adsorbent. At every 10 minutes the samples were allowed to rest and centrifuged at 3500 rpm for 2 minutes. The concentrations are determined using an HPLC instrument Shimadzu,Japan. For each analysis, a blank solution was prepared with $ZnFe_2O_4$ adsorbent and a control solution was prepared using PAHs mixture alone.An aliquot of 20μL of the solution was injected into an HPLC system. The tests were conducted for 120 minutes.The concentration of PAHs are maintained and varied to 25μgL^{-1}, 50μgL^{-1},75μgL^{-1} and 100 μgL^{-1} respectively and readings are noted. The quantity of PAH adsorbed is calculated using expression.

$$q_e = \frac{(C_o - C_e)V}{m}$$

Here q_e = quantity of PAHs adsorbed in μgg^{-1}

C_o = initial concentration of PAHSs in μgL^{-1}

C_e = equilibrium concentration of PAHs in μgL^{-1}

V = Volume of the solution in L

m = mass of mesoporous adsorbent in grams

Preparation of PAHs standard solution

A 5ml volume of stock 1000mgL^{-1} stock solution of the each PAHs was transferred to a 250ml volumetric flask and the volume was made up distilled water, giving final concentration of 20mgL^{-1} in water / acetonitrile (98:2 V/V). The resulting solution was transferred to volumetric flask and agitated at 300rpm for 30 minutes in order to ensure a homogeneous distribution of the PAHs. The adsorption studies were performed after dilution of this stock solution using the the same water/ acetonitrile ratio.

The exact standard method was used to calculate the concentration of PAH in the sample. The duplicate injections of PAH s standard solution at various concentrations was determined by linearity method. Linear regression was employed to construct calibration curves and the linear correlation coefficients (r^2) values very much nearer to 1.

Kinetic study and adsorption isotherms

The studies were interpreted using pseudo first order and pseudo second order kinetic models. After the equilibrium is attained the isotherms were constructed to fit the data into Langmuir and Freundlich isotherm models.

3. RESULTS AND DISCUSSION

RESULTS

The effect of initial concentration

The effect of initial concentration of PAHs on the adsorption by zinc ferrite nano particles was clearly explained in the figure 1. Various concentrations of PAHs in the range of 100 to1000 μg L^{-1}are observed for the adsorption of PAHs by zinc ferrite nano prticles.

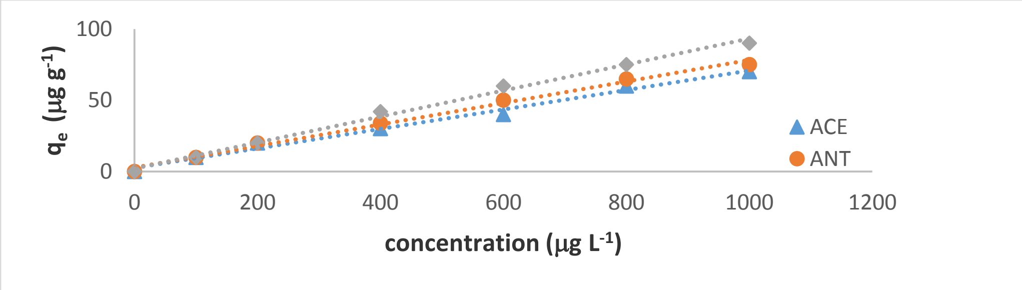


Figure 1: Effect of initial concentration of PAHs on the adsorption

Effect of contact time

From the figure 2 it is observed that equilibrium is attained after 60,70,and 80 minutes respectively for PAHs namely ACE, ANT and BAP respectively. At equilibrium the percentage removal obtained for adsorption of the PAH s are 90.46, 90.12 and 90.94 respectively.

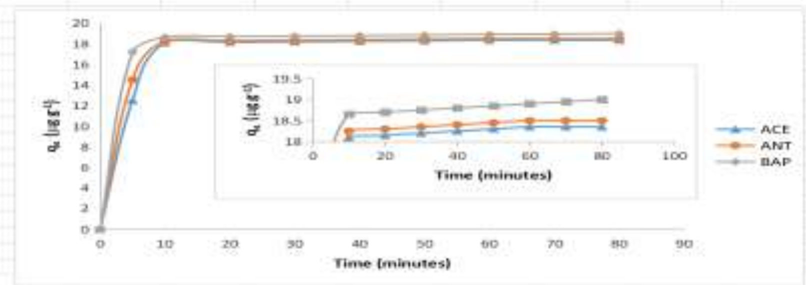


Figure 2: Effect of contact time on adsorption

Effect of adsorbent dose

Effect of adsorbent dosage on the adsorption of PAHs was studied by varying the dosage from 0.1 to 0.8 g L^{-1}. From the figure 3, The maximum adsorption efficiency was achieved at 0.5g L^{-1} for the respective PAH with $ZnFe_2O_4$.

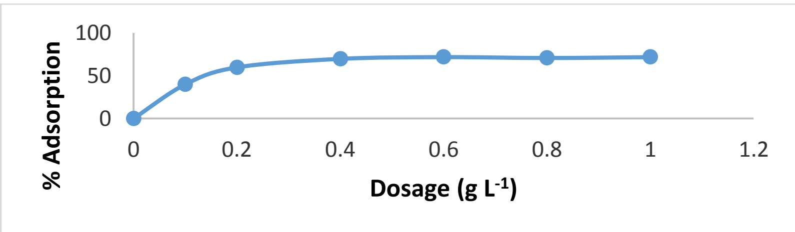


Figure 3: Effect of adsorbent dosage ($ZnFe_2O_4$)

Adsorption kinetics

The kinetic studies are useful to determine the nature of adsorption. Pseudo first order and pseudo second order kinetic models are conducted and PSO is shown in Table 1.

$$q_t = q_e . e^{-k_1 t}$$

Here q_t and q_e are the amount of PAHs (µg g^{-1}) adsorbed at time 't' and at equilibrium respectively. k_1 is the rate constant for pseudo first order sorption.

$$q_t = \frac{t q_e^2 k_2}{1 + t q_e k_2}$$

k_2 is the rate constant for pseudo first order sorption.

Table 1: Pseudo first order and pseudo second order kinetic models on adsorption of PAHs by zinc ferrite nano particles

PAH	Parameters of pseudo first order kinetics				Parameters of pseudo second order kinetics			
	q_e (exp) µg g^{-1}	q_e (cal) µg g^{-1}	k_1 (min^{-1})	r^2	q_e (exp) µg g^{-1}	q_e (cal) µg g^{-1}	k_2 g µg^{-1} m^{-1}	r^2
ACE	18.12	18.36	1.03	0.395	18.12	18.22	1.54	0.954
ANT	18.36	18.20	0.99	0.298	18.36	18.30	1.08	0.966
BAP	18.78	18.71	1.15	0.596	18.78	18.79	2.91	0.985

The experimental data were fitted to the data obtained using PFO and PSO kinetic models in order to calculate the adsorption kinetic parameters. The best fit of the experimental data was obtained with pseudo second order model, as shown by higher linear correlation coefficients, compared to those found using pseudo first order models.

Adsorption isotherms

Langmuir and Freundlich are the most commonly used and typically employed in adsorption process. Langmuir model represents one of the non linear sorption and proposes that uptake occurs by mono layer sorption on a homogeneous surface without interaction between the adsorbed molecules.

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e}$$

q_{max} = maximum adsorption loading (µg g^{-1}) and b is a constant related to energy of adsorption.

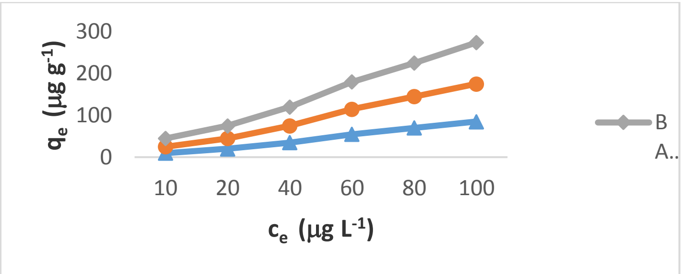


Figure 4: Langmuir adsorption kinetics

The Freundlich is adsorption process those are not restricted to the formation of a monolayer, and the adsorption is nonlinear, $q_e = k_F C_e^{1/n}$ Here k_F is adsorption capacity and "n" is adsorption intensity The models with a heterogeneous distribution of energetic active sites and interaction between the adsorbed molecules.
are expressed in figures 4 and 5 respectively.

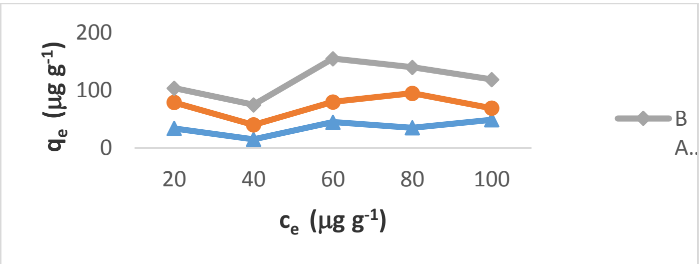


Figure 5: Freundlich adsorption isotherms

Table 2 explains Langmuir and Freundlich adsorption isotherms and their constants in detail.

Table 2: Langmuir and Freundlich isotherm models on adsorption of PAHs by zinc ferrite nano particles

PAH	Parameters of Langmuir isotherm model			Parameters of Freundlich isotherm model		
	Q_{max} µg g^{-1}	b Lµg^{-1}	r^2	K_F µg g^{-1}	1/n	r^2 g µg^{-1} m^{-1}
ACE	150.44	0.013	0.928	4.38	0.65	0.868
ANT	149.02	0.012	0.944	3.78	0.66	0.908
BAP	165.24	0.015	0.948	5.35	0.62	0.893

4. DISCUSSION

It is seen that the quantities of PAHs adsorbed increases when initial concentration is high. This behaviour is explained by adsorption occurring mainly at the outermost sites of $ZnFe_2O_4$ surface when the initial adsorbate concentration was low. The adsorption capacity reflects the satisfactory textural and structural properties of adsorbent[15,16]. The adsorption is a mass transfer phenomenon. Here the adsorbate ions are transferred from the entire liquid phase to adsorbent's surface. The effect of time helps to determine the adsorption mechanism and the rate controlling steps like mass transport or chemical reaction process[17]. The maximum adsorption efficiency at 0.5g L^{-1} is obtained. This indicates that the removal of PAHs at a particular dosage of adsorbent is effective. This behaviour is observed due to the presence of large number of vacant sites at initial stages and PAH s are attracted to these vacant sites[18,19]. There fore with time a stage is reached at which these sites are totally occupied and equilibrium condition is achieved between adsorbent surface and adsorbate. Maximum adsorption was observed at a lower PAH concentration, because at this concentration more number of active sites may be available over the surface of $ZnFe_2O_4$ nano particles for adsorption[20,21]. As the data is very much fit into pseudo second order kinetics it can be further utilized in deriving the entropy, enthalpy and spontaneity of the reaction using Arrhenius equation. From the table 1 and 2 it is observed that parameter values are obtained for both the models and experimental data were more closely fitted using the Langmuir model, for which the linear correlation coefficients obtained were higher. The values of Q_{max} and b are in the following ascending order for adsorption of PAHs[22,23]. [Ace] < [Ant] < [BAP]. Hence it is understood that adsorption process is endothermic and spontaneous with an apparent increase of randomness at the solid/ solution interface, during the adsorption process.

5. CONCLUSION

Using the zinc ferrite nano particles different PAHs were removed to good extent in aqueous phase. The order of removal was found to be dependent on the molecular weight, size, structure and aromaticity of PAHs. The higher rate of degradation in aqueous phase is due to higher absorbing affinity of PAHs towards nano ferrites. The adsorption kinetics followed a non linear pseudo second order model and best fits for the isotherms are obtained using Lagrange theoretical model. The results indicated that $ZnFe_2O_4$ could be used as an adsorbent material for the removal of PAHs from surface water or waste waters. The studies describe the positive aspects of using efficient synthesized magnetic nano particles in the removal of PAHs.

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