ADSORPTION OF HYDROXY SUBSTITUTED PHENOLS ON F-300 ACTIVATED CARBON IN BATCH SYSTEM

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Abstract -

A batch system was applied to study the adsorption of some substituted phenol from aqueous solution by granular activated carbon. Removal and recovery of aromatic pollutants from water by solid adsorbents have been of considerable concern recently .The compliance of discharge limit by pollution control boards in most cost effective manner is problem the industries are facing .The GAC treatment is one of the best alternative because of its reuse by regeneration. In the present investigation various hydroxyl substituted phenols as priority pollutants were taken .Adsorption equilibrium and kinetics were studied on GAC namely F-300 . The various physico- chemical parameters associated with equiliribrium and adsorption rate are investigated. All adsorbates were analyzed by UV absorption theory. The adsorption data were analyzed by Langmuir isotherm equation and adsorbate removal rate calculated from kinetic data based on Langmuir theory.

Keywords: *Activated carbon; Adsorption isotherm; Kinetics , substituted phenol*

Introduction

Langmuir adsorption isotherm model and BET Isotherm model which shows that in F-300 adsorbate system Liquid and solid waste, are a huge and always increasing problem for the industries and the environment. Aromatic compounds belong to a group of general environmental pollutants from industry. Water pollution by synthetic aromatic compounds has increasingly leaded an important environmental issue associated negatively with the health and economy, particularly in developing countries such as China [1].The existence of their even low concentrations can be a trouble to the use or reuse of water. Industrial sources of pollutants such as phenolic resin production

(400 mg/L), refineries (50 mg/L), shale dry distillation (200 mg/L) and naphthalenic acid production (12 mg/L), etc. generate large quantities of phenols [2]

Dangerous and Toxic Waste [3, 4] is defined as those solid, semi-liquid, and liquid materials, as well as those gaseous materials in recipients, which are the result of a process of production, transformation, use or consumption which are destined to be abandoned and whose composition contains some of the substances or materials in such quantities or concentrations that represent a health risk to humans, natural resources and the environment and that need a treatment process or special elimination. The European Union made out a list of dangerous compounds, considered as contaminants, to which constantly new substances are added ("black list" of the E.U., see Table 1.1) [5].

One of the most popular and extensively researched families of compounds that are adsorbed onto activated carbon is phenols. Much emphasis has been posed on phenol and its derivatives [6]as they are highly toxic and are present in many industrial wastewaters. PAH's, dyes, herbicides, surfactants, and pharmaceuticals have also received much attention ,phenol and its derivatives also show mutagenic effect by unbinding of the DNA helix, inhibition of DNA synthesis in the human Syrian hamster embryo (SHE) cells, induction of gene mutations, chromosome aberrations, and aneuploid formations (phenol, catechol) [7]. Phenol is an important raw material in many branches of industry (e.g. electrochemical, pharmaceutical, plastic and pesticide chemical industry). Nowadays, the importance of phenol is proved by its ever-increasing global production capacity, which reached 7.8 million of tones in 2001 [8].

It has been well-known that phenol, catechol and 2-chlorophenol can induce conformational changes in the human growth hormone [9]. A connection has been also established between the presence of chlorophenols and development of the non-Hodgkin lymphatic system

neoplasmic changes [10]. As a result, the elimination or destruction of phenols from wastewaters is of great importance. Different methods designed to remove phenols have been projected. The methods include, biological treatment [11], reverse osmosis [12], physicochemical method [13], solvent extraction [14] and activated carbon are commonly used techniques for removing phenols and associated organic substances.Amongst the several techniques of phenols removal, adsorption has been found to be a proficient and economic method, and a successful and widely in use for wastewater treatment [15]. when recovery and reuse of some aromatic compounds is not technically or economically feasible, transforming those into more environmentally friendly compounds can be more appropriate.

For a raw material to be used for activated carbon production, it should have high carbon content. Agricultural waste is commonly exploited this way. Adsorption process for removal of hazardous pollutant has been used from long time Granular activated carbon adsorption is well-known and recognized technology in wastewater and drinking treatment . The activated carbon require sorbents with large surface area having large volumes of very fine pores .The presence of fine pores influences its sorption properties because the amount adsorbed on micropores surface is negligible in comparison with that for micropores and mesopores [16] .and with varying porous structure consisting of a network of interconnected macropores, mesopores and Micropores. Their surface area also presents great diversity in terms of surface charge and surface groups, depending on the original raw material and the way of activation. Large amount commercial systems currently use activated carbon as adsorbent to remove phenol in wastewater because of its exceptional adsorption capability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best existing control technologies [17]. The selection of sorbent with its surface area is also area of concern, the complete removal and /or

reduction of dissolved organic compounds of permissible concentration level has become is major task in designing and selecting advanced waste water treatment technology. The adsorption by GAC is advantageous process for removal of soluble, chemically stable and biologically non-biodegradable pollutants.

The aim of this work was to explore to study in more detail the adsorption mechanism of selected substituted phenols,in particular hydroxyl substituted phenols . An extensive characterization of selected activated carbons is presented.The F-300 granular activated carbon are used as adsorbent. The adsorption of phenol and hydroxy substituted phenol compounds from the aqueous phase has been studied onto two grades of activated carbon at 30 ± 2 ^oC. The adsorption equilibrium and kinetics data for all the systems were analysed by Langmuir ,BET adsorption isotherm .A batch reactor was selected for evaluation and kinetic data . All the adsorbates were analyzed by UV absorption spectrophotometry using UV-visible spectrophotometer from GBC Australia.

Experimental studies- characterization of activated carbon

The GAC samples were first sieved to obtain 12x16 mesh (B.S.)fraction (Particle diameter=0.1502 ± 0.0009 cm) . the uniform fraction were washed several times with distilled water until no suspended material appeared in washing , dried in oven at 100- 110 ^oC for 24 hrs and then stored in $CaCl_2$ desiccators at room temperature until the use .The GAC samples used in present investigation are given in table 1and the physical properties are given elsewhere [18] ,the SEM analysis was also carried and shown in SEM plate.

Adsorption isotherm studies

For equilibrium studies experiments were performed using 125 ml borosilicate glass bottle at room temperature on electrical shaker . In 125 ml borosilicate glass bottle which were cleaned and dried previously 100 ml the prepared solution were taken. The solution were prepared in

the range of 2 x10^{-4} mol/L.A known quantity of adsorbate solution was withdrawn for UV analysis from the bottle. The withdrawal of the adsorbate solution was so adjusted so that initial adsorbate volume is not disturbed. Then 0.100±0.0001 g accurately weighed GAC samples were introduced in each bottles The bottles are placed on the shaker for 7 days .It was found that time of 5 days was sufficient to reach.The equilibrium for the compounds used in the study. As a precautionary measure experiments were continued for the 7 days some of the points on the isotherm were also tested for their reproducibility.

The **kinetic studies** of the same adsorbent /adsorbate systems were carried out in the a assembly of 8L capacity . The initial adsorbate volume maintained to be 4L after the first required quantity of the solution for UV analysis showing the initial concentration of the adsorbates . Then 2.000g of accurately weighed GAC samples was introduced in to the constantly stirred reactor. Known quantities of the samples were withdrawn from the system at intervals 10, 20 ,30, 40 , 60, 90, 120, 150, 180, 210, 240, and 300 minutes and their respective concentrations were determined in order to evaluate the fractional approach to equilibrium.

RESULT AND DISCUSSION

The concentrations of solutions are micro molar, it appears desirable to examine the Langmuir and B.E.T. isotherm equations in the very low concentration range as studied in the investigation .The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of the adsorbate molecules on the adsorbent surface that the energy of the adsorption is constant , and there is no transmigration of the adsorbate molecule in the plane of the surface .The equation can be expressed as

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \qquad (1)$$

Rearranging eqn(1)

$$\frac{1}{q_e} = \frac{1}{Q^o b C_e} + \frac{1}{Q^o} \tag{2}$$

Thus , a plot of 1/q should be linear if Langmuir adsorption is operative. The B.E.T. isotherm method usually employs solution near the saturation concentration of the solute [19,20] but the concentration of interest in wastewater are in micromolar .The BET plots for all the systems are plotted according to equation

$$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{Q^o Z} + \frac{(Z-)}{Z}\frac{C_s}{Q^o}\frac{C_s}{C_e}$$

From the slope and the intercept it is possible to obtain Q^o

In the present work (Cs>>Ce) and (Z-1)=Z , Therefore

$$\frac{C_e}{q_e C_s} = \frac{1}{Q^o Z} + \frac{C_e}{C_s Q^o}$$

The adsorbent used in the present study was characterized with respect to proximate and ultimate analysis , surface area , pore size distribution , surface groups and pore structure by instrumentation techniques like N_2 –BET ,scanning electron microscopy (SEM) and Fourier transform spectroscopy (FTIR).The SEM micrograph (SEM Plate no.1 and 2) of F-300 sample shows layered loosely packed structure with lot of cavities ,cracks ,irregular protrusions and widely dispersed pores [21].

Table –1

PHYSICO-CHEMICAL PROPERTIES OF GAC

Activated Carbon Type	Origin	Surface Area N_2-BET (m^2/g)	Particle Density (g/cm^3)	Pore Volume (cm^3/g)	Wt (%)					
					Moisture content	Ash content	Volatile matter	Fixed carbon	Carbon	Hydrogen
F-300	Bituminous coal	970	0.730	0.850	5.3	5.4	1.7	87.6	97.63	0.18

* Information supplied by the manufacturer.

Table –2

PHYSICO-CHEMICAL PROPERTIES OF ADSORBATE

| Adsorbate		Abbrevation	M.W.	Solubility at 30°C(mol/L)	λ_{max} (nm)	ε mol^{-1} cm^2
Phenol	Phenol	P	94.11	0.8665	270	1520
o-Hydroxy phenol	Pyrocatechol	OHP	110.11	4.095	275	2368
m-Hydroxy phenol	Resorcinol	MHP	110.11	1.335	273	1933
p-Hydroxy phenol	Quinol	PHP	110.11	0.5449	289	2635

SEM Plate 1-SEM OF F-300 GAC   SEM Plate 2- SEM OF F-300 GAC

The adsorption equilibrium and kinetic studies carried out in the present work for various hydroxyl substituted adsorbate and adsorbent (GAC F-300) and the results obtained are used for calculation of monolayer capacity using langmuir adsorption equation and graphically represented in Graph-1,2,and 3.
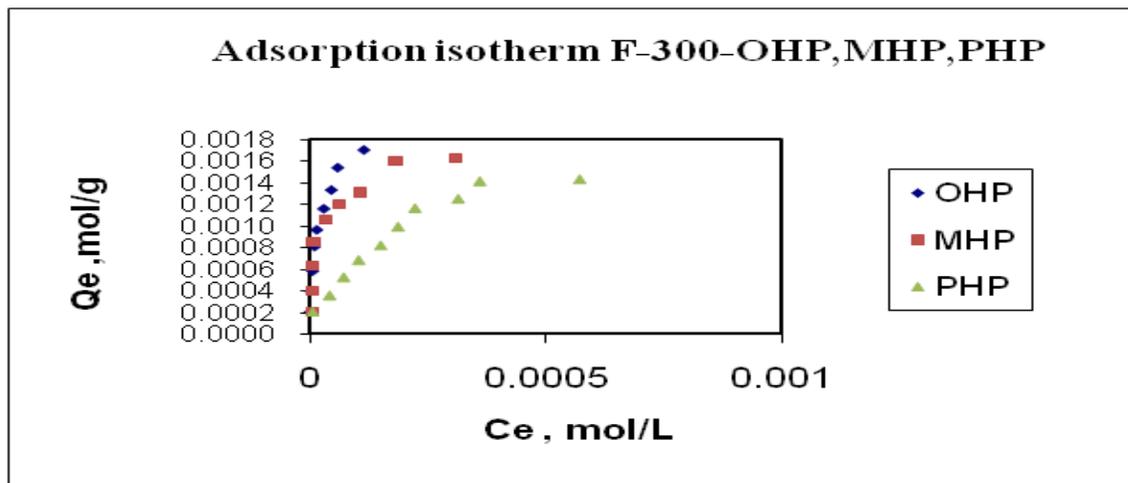
Graph 1-Adsorption isotherm ofGAC F-300 with OHP,MHP,PHP
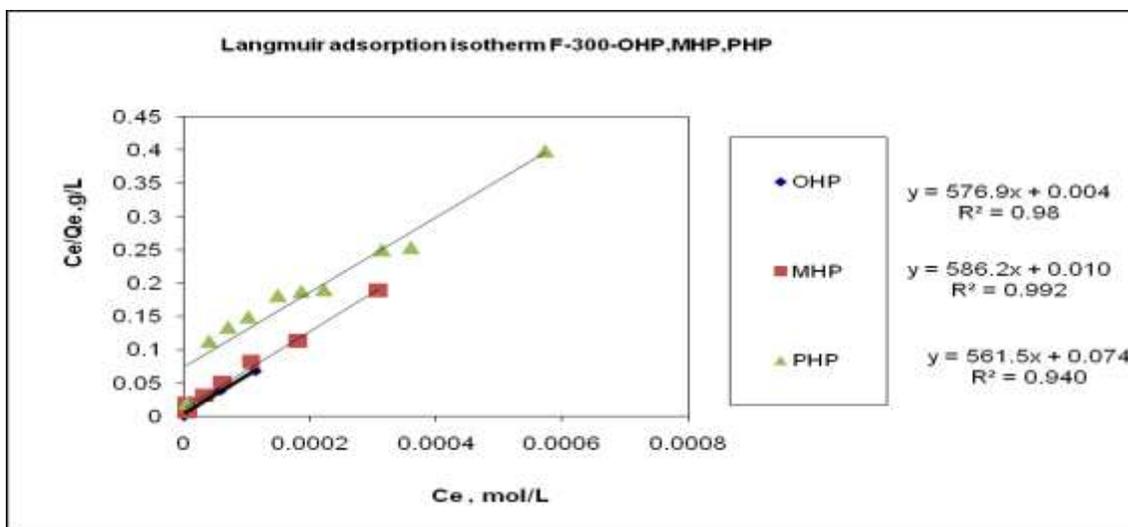
Graph 2-Langmuir adsorption isotherm of GAC F-300 with OHP,MHP,PHP
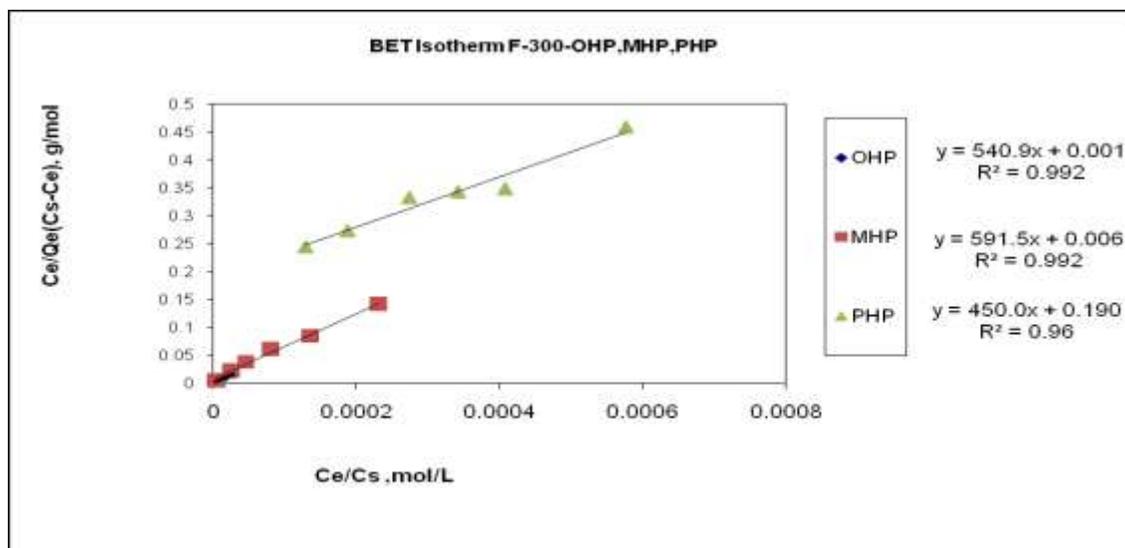
Graph 3-BET Isotherm F-300-OHP,MHP,PHP

Result and discussion

The monolayer capacity Q^0 mol/g for the above single solute system are given in below Table-3,determined with the help of Langmuir adsorption isotherm model and BET Isotherm model which shows that in F-300 adsorbate system the trend monolayer capacity is OHP>PHP>MHP>P and PHP>OHP>MHP>P respectively . The monolayer capacity is an indication of the preference of the adsorbent surface to particular adsorbate.It is observed in general that the substituted phenols are adsorbed to greater extent as compared to phenol .

Table-3

Monolayer capacity ,Adsorption –desorption constants in Adsorbent/Adsorbate system

(hydroxy substituted Adsorbates) Langmuir adsorption isotherm model(A,B,C,D) and BET Isotherm model(E,F)

Sr.N.	System	Q^o x10⁴ (mol/g)	b	Ka /min	Kd /min	Q^o x10⁴ (mol/g	z
	(Adsorbent/Adsorbate)	A	B	C	D	E	F
1	F-300/Phenol	16.59	4768	100.46	0.02106	15.49	3245
2	F-300/o-Hydroxy phenol	18.45	80895	45.1	0.00056	18.49	540900
3	F-300/m-Hydroxy phenol	17.06	59793	40.0	0.00067	16.91	98583
4	F-300/p-Hydroxy phenol	17.89	7882	128.2	0.01626	22.22	2368

Literature reports [22] a general tendency of increase in adsorption capacity with increase in molecular weight, but in this study no such clear trend is observed .

In this work only substituted hydroxyl phenols are taken for study. The solubility of the adsorbates is also known to affect the overall adsorption capacity significantly. The activated carbon surface (untreated) is non-polar and generally it has been seen that it favors non-polar adsorbates .The aqueous phase solubility values are in (Table-2) the order OHP>MHP>P>PHP ,it shows that solubility is not a single factor that affects the adsorption process.

Conclusion

The monolayer capacity is the indicator for adsorption which indicates that the adsorption capacity order followed in the studied hydroxyl substituted phenol is as given OHP>PHP>MHP>P and PHP>OHP>MHP>P respectively with Langmuir adsorption isotherm model and BET Isotherm model equations which shows that in GAC F-300 adsorbate system . The structure of the adsorbate molecule has

significant role to play on its adsorption. It has been reported that phenolic group on benzene ring are not involved in adsorption process [23],thus it shows that there is no possibility of hydrogen bonding with oxides groups on carbon surface . Literature also reports that phenolic and amino group also have adverse impact on adsorption [24].It is very clear from the result the adsorption of PHP is highest then of OHP,MHPand phenol from BET equation which is matching with almost with Langmuir equation except with PHP.

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