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Removal of Phenol onto Fly ash by QSAR

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Abstract

The removal of phenol from wastewaters is a widely researched topic and many methods have been tried out to either effectively separate or phenol or remove it from the wastewaters. This review paper briefly discusses the different methods briefly, the advantages and disadvantages or limitations associated with these methods, along with the effects of different factors on the adsorption process are discussed. The main focus of the paper is to study the Quantitative structure-activity relationships (QSAR) model for the adsorption of phenols onto fly ash.

Keywords: QSAR, Phenols, Flyash

Introduction

The economic development of any country is heavily dependent on industries. Industries provide employment opportunities and also increase the per capita income in the country. However, the harmful and toxic effluents coming out of industries, both organic and inorganic pose a severe threat to the environment in many ways. The removal of these chemical pollutants from the effluents is therefore very important. Industries producing dyes, pharmaceuticals, petroleum products, personal care products, and chemicalsrelease organic pollutants into the water. One of the important organic pollutants is phenols. Large amounts of wastewater produced from the industries contain phenol in significantly higher concentration. Phenols or phenolic compounds are very toxic and their accumulation in the environment should be prevented. Consumption of water containing even low levels of phenolic compounds causes damage to the liver and also ailments such as diarrhea, mouth ulcers, and hemolytic anemia.Drinking water containing even very low concentration of phenol imparts odor to it and makes drinking water non potable. They are also protoplasmic poisons (1). According to the United States Environmental Protection Agency (EPA or USEPA), the limit of phenol discharge into waste water is 0.1 mg/L. According to the schedule VI of the general standards for discharge of environmental pollutants, in India, the Central Pollution Control Board (2) has set a limit of 1.0 mg/L for release of phenolic compounds through wastewater into inland surface water and a limit of 5.0 mg/L into public sewers, and a limit of 5.0 mg/L into marine coastal areas. However, even a concentration of 5.0 mg/L of phenol in marine water, under some conditions, could be lethal enough for marine life (1). Taking this into cognizance, it becomes imperative to treat the wastewater in a very effective and efficient manner.

Many researches on methods to remove phenols from wastewater, before they are discharged from the industry, have been carried out. These include chemical methods, extraction methods, and adsorption techniques, use of membranes, physicochemical processes and also biological treatments.All these methods, except the adsorption technique, were found to be not so efficient (3). Other drawbacks include huge investments, operational costs, cost of regeneration, and also the disposal of the residues formed in the process. The choice of a particular method also takes into account the economic aspect. The adsorbents used for the adsorption of phenol could be either from natural sources or synthetic ones. The adsorbents include peat, chitin and chitosan (3), biomass (4), activated carbon (5, 6), amberlite resin (7), bentonite (8), silica gel and activated alumina (9), and activated carbon zeolites (10).

Use of adsorbents is a very promising technique for the removal of phenols from the wastewater, since it is very efficient, and the solvents can be readily recovered. Another benefit of the use of adsorbents is the removal of color and odor in addition to the removal of phenols. Liquid phase adsorption technique is preferred, since it a very simple process and a wide range of adsorbents are readily available. Adsorption can be

either physical or chemical in nature. In physical adsorption the bonds between the adsorbent and the compound getting adsorbed (adsorbate) are weak and the process is reversible. This implies that the adsorbent can be recovered and reused. The process, involving physical adsorption, can be carried out at lower temperatures. In chemical adsorption, the bonds formed are strong, the process is irreversible, and the adsorbent cannot be recovered and reused. Nowadays several studies have focused on adsorbents, derived from natural resources, which are economical, like rice husks, biomass, waste fertilizers, saw dust, peat, fly ash, etc., and can be used after simple chemical treatments

There are many thermal power stations in India that use coal for power generation. Fly ash is the product of combustion of coal. Fly ash is a very economical adsorbent which can be utilized in many ways, such as in removal of phenols from wastewaters, in cement concrete, roads, light weight aggregates, etc. (11). The other advantage associated with fly ash is that there is no requirement any expensive pretreatment. Additionally, they are readily available in large quantities and a very low price, hence, do not require regeneration process. The use of fly ash for the removal of phenols was carried out by many researchers (12-15). Totally different results were, however, reported in these studies, regarding the preferential adsorption of phenol with respect to its analogues. This was the outcome of different factors influencing the adsorptions (16). Hence, it becomes necessary to understand the different factors that affect the adsorption.

Factors Affecting Adsorption of Phenol onto Fly Ash

Adsorbate

Phenols exist as anions in aqueous solutions above pH 6. Hence they get adsorbed to the positively charged regions of the surfaces. Molecular size, molecular weight, pKa, cross sectional area, effective molecular volume, nature of the substituents (electron withdrawing or electron donating), solubility, and dispersive forces between π-electrons in phenol molecules influence the adsorption rates of phenols (17-20).

Adsorbent

The physico-chemical nature of the fly ash influences the adsorption rate. Additionally the specific surface area, carbon content and the particle size of the coal fly ash adsorbent were found to affect the rate of adsorption of chlorophenols (21). Hence, a proper classification of the adsorbent (fly ash) and the determination of its properties are essential. Increase in the dosage of the fly ash led to an increase in the amount of phenol removed (17). Variations in the combustion conditions or source of coal lead to variations in the composition of fly ash, as a result of which, the adsorption is influenced (30).

pH

The pH of a solution has a direct effect on the charges present on the surface of the adsorbent, the extent of ionization of the adsorbate. A pH of 5 was found to be most effective for the adsorption of phenol (22).

Particle Size

Micropores present on the surfaces lead to larger surface areas. Also it is obvious that smaller particle sizes have larger effective surface areas. Adsorption, being a surface phenomenon, is related to the surface area. In the removal of phenol using charcoal from burnt wood, it was found that the percentage of phenol removed increased with a decrease in particle size of the adsorbent (23). However, adsorbents with smaller particle sizes are not suitable for continuous column processes (17).

Concentration of Adsorbate

An increase in the concentration of the adsorbate, at a specific temperature results in an increase in the adsorption. Linear forms of Freundlich and Langmuir adsorption isotherms are generally express the relation between the concentrations of the adsorbates and rate of adsorption of phenols (22, 24, 25).

Contact Time

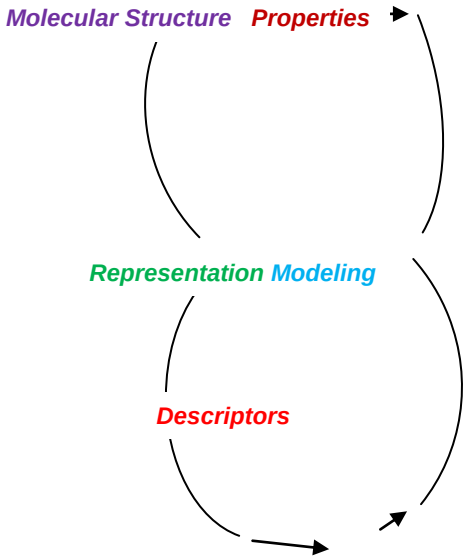
The time period over which the adsorbate remains in contact with the adsorbent also affects the adsorption, till a state of equilibrium is attained (22, 24, 26, 27). However, factors such as pH, temperature, particle size of the adsorbent, etc., also decide the time required to attain equilibrium.

There are so many factors influencing the adsorption process simultaneously. Hence to increase the efficiency of adsorption and obtain ……

Quantitative Structure-Activity Relationship for Adsorption of Phenols onto Fly Ash

Quantitative structure-activity relationship (QSAR) helps in predicting the adsorption of a particular phenol molecule based on its structure. It is a modeling program in which the adsorption of an organic compound can be predicted without experimentation, based on system descriptors. Adsorption isotherm constants have to be incorporated into QSAR and a protocol has to be devised, by which for a given process, the constants for isothermal adsorption and QSAR can be applied. An adsorption process can be quantitatively predicted based on the models developed using adsorption isotherm constants. The adsorption of phenol onto fly ash depends on the chemical and physical properties of both, phenol and fly ash. The dependent variables in QSAR for adsorption of phenols onto fly ash include the isotherm constants and the kinetic rates for the process. The independent variables include intrinsic factors such as the electronic effects, steric hindrance, and hydrophobicity of the phenol molecules (28). A good QSAR should be able to readily and reliably predict the rate of adsorption based on the structural properties of the adsorbates and the experimental conditions. To achieve this, a QSAR having a diverse parameterization, obtained from a set of compounds possessing carefully chosen parameters, helps to understand the mechanisms involved in the process in a better way. The key factors in QSAR include hydrophobicity, electronic effects, and steric hindrance (29). The other

advantage of the prediction of the adsorption of organic compounds quantitatively, is in the event of accidental spills, where there is no data on the adsorption isotherms of the spilled chemicals available. There are many steps involved in QSAR, which include collecting data, molecular descriptors, selecting and obtaining the correlations, developing a model, and finally evaluating the model.



Flowchart Showing the Steps in Predicting Molecular Properties from Chemical Structure

Parameters representing intrinsic properties of the compounds (e.g., hydrophobic, electronic, steric, chemical, physical properties) were incorporated into the QSAR asindependent variables, while the parameters that were experimentally derived in this adsorption system (e.g., isotherm constants) were incorporated as dependent variables using SPSS 12.0 software (SPSS., Inc., Chicago, IL, USA). Classical QSAR procedure, as developed by Hansch, was followed for the development of correlations (Hansch and Fujita 1995). Linear, polynomial, and multilinear correlations were employed to describe the data

Some Condition should be Taken for Following QSAR

1. No collinearity of independent variables (for MLR correlations)
2. R2 ≥ 0.7
3. F-Ratio values must meet a 95% confidence limit
4. Standard error considered
5. Q2 determined for goodness of predictability

Independent variables were linearly correlated; variables that produced a R2 value of 0.4 or higher were considered collinear and were excluded from the QSAR analysis**. Conditions 2** and**3** were helpful in identifying poor correlations. The F-Ratio was determined using thenumber of compounds in each correlation (k) and two total data sets (n), observed andcalculated values. The degrees of freedom were calculated for the variance between (v1 =n-1) and within (v2 = (n*k)-n) the data sets and compared to an upper 5% distributiontable to determine the significance of the observed and calculated data sets. As the F Ratio values become larger than the F-distribution values, the data sets are considered to be more similar. Therefore, high F-Ratio values indicate the predicted data from the QSAR correlation is in agreement with the observed data

Condition 5 is an essential step in measuring the validation of the correlations thatresult from the QSAR process. When performing a Q2 analysis, it is ideal to introduce anew compound to test the predictability of the QSAR correlation

Selected Parameters Used in the QSAR Training Set of Monosubstituted Phenolic Compounds

	M.W	LOGKow	Absorbance Experimental
Phenol	94.1	1.48	1.85
2-chlorophenol	128.5	2.15	2.375
4-chloro	128.5	2.18	2.174
2-Nitro	141	-1.306	2.174
3-Nitro	141	-0.73	2.089
4-Nitro	141	-0.73	2.157
2-Iodo	220	2.59	1.987
3-Iodo	220	2.59	2.219
4-Iodo	220	2.59	2.144
3-cyano	123.1	0.42	2.051

ANNOVA

One Sample t- test

One-Sample Statistics

	N	Mean	Std. Deviation	Std. Error Mean
M.W	10	155.72	46.414	14.678
LOGKow	10	1.12	1.564	.495
a	10	2.12	.141	.045
V5	0[a,b]	.	.	.

a. t cannot be computed because the sum of caseweights is less than or equal 1.

b. t cannot be computed. There are no valid cases for this analysis because all caseweights are not positive.

One-Sample Test

Test Value = 0						
	t	df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	
					Lower	Upper
M.W	10.609	9	.000	155.720	122.52	188.92
LOGKow	2.271	9	.049	1.123	.00	2.24
a	47.598	9	.000	2.122	2.02	2.22

Correlations

		a	M.W
Pearson Correlation	a	1.000	.152
	M.W	.152	1.000
Sig. (1-tailed)	a	.	.338
	M.W	.338	.
N	a	10	10
	M.W	10	10

Model Summary[b]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics					Durbin-Watson
					R Square Change	F Change	df1	df2	Sig. F Change	
1	.152[a]	.023	-.099	.148	.023	.189	1	8	.675	2.380
a. Predictors: (Constant), M.W										
b. Dependent Variable:										

Conclusion

Process is repeated for each compound within the training set and equation 3.1 is used to calculate the value of Q2: larger values indicate a betterability for the QSAR correlation to predict the observed values within the given system. Ideally the Q2 should be close to the value for the adjusted R2, thus indicating that the new correlation did not cause a significant shift in the predicted data.

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