

SORPTION OF METHYL SUBSTITUTED TOXIC PHENOLS ON COAL FLY ASH

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Introduction

Of all the methods, adsorption appears to offer the best prospects for overall treatment [1]. Activated carbon is most widely used sorbent but its use is limited due to its high cost. Flyash is new non-conventional sorbents having good adsorption quality. Most of the chemical contaminants are of organic origin. Phenols are among the most common water pollutants. The results of experiments designed to show the influence of chemical and physical parameters on the equilibrium sorption of phenols from aqueous solution are presented.

Experimental

O-cresol (OCL), m-cresol (MCL) and p-cresol (PCL) were used as sorbate in this study. Sorption isotherm experiments were performed by agitating 1.0 g of different fraction of flyash (FA) with 35 cm³ of various concentrations of the phenolic solutions (C = 500-142.85 mg/dm³) in 100 cm³ conical glass stoppered flasks in a temperature controlled shaking thermostat at desired temperature (30°C, 40°C and 50°C ± 0.1°C) and pH values (2.0, 4.0, 6.5, 8.0 and 10.0) for 2h to reach equilibrium. Samples were centrifuged at 10,000 rpm. The supernatant liquid was analysed for phenols spectrophotometrically (Spectronic 20D).

Results and Discussion

Out of the several isotherm model, Langmuir's isotherm equation, i.e.

$$\frac{C_e}{q_e} = \frac{k}{Q_0} + \frac{C_e}{Q_0}$$

where C_e is equilibrium concentration and Q₀ and k are Langmuir constants related to sorption capacity and equilibrium constant respectively is used for equilibrium modelling. From linear plots, the constants were calculated for different particle sizes, pH and temperature and are given in Table 1-3.

Effect of Particle size - There is strong chemical bonding between lone pair of electron present on the -OH group in the phenols and the central ion of silicate (Si⁺⁴) as well as the weakly acidic alumina surface. As size of FA decreases, amount of major constituents, i.e., alumina and

silica increases and so sorption capacity decreases (Table-1) as follows -

$$FA(45\mu m) > FA(100\mu m) > FA(150\mu m)$$

Among phenols, variation is as follows

$$PCL > MCL > OCL$$

This is because of substitution with steric hindered -CH₃ group on benzene ring increase the distance between the plane of ring and the surface of sorbent. The lone pair of electrons present on -OH is made easily available due to electron releasing effect of the -CH₃ group in PCL for silica and alumina surface which also has no steric hinderance for chemical bonding.

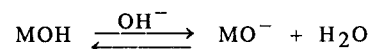
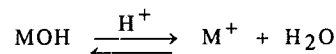
Effect of pH - The sorption capacity of FA at different pH values decreases (Table-2) as follows -

$$pH 2.0 > pH 4.0 > pH 6.5 > pH 8 > pH 10.0$$

Among phenols, variation is as follows

$$PCL > MCL > OCL$$

This may be explained on the basis of formation of a positively charged surface in an acid medium and a negatively charged oxide surface in basic medium from hydroxylated oxide surface to FA which can be presented as



At lower pH, the lone pair of electrons on oxygen atom of undissociated -OH group present in the benzene ring coordinate with highly positively charged surface. But at higher pH values, the undissociated phenoxide ion is repelled by highly negatively charged oxide surface.

Effect of temperature - The amount of phenols sorbed on FA increases by increasing temperature indicating process to be endothermic. The sorption capacity also increases suggesting that the active surface centres available with sorption have increased with temperature [2]. So variation of sorption capacity at different temperature (Table-3) can be explained on the basis of above fact.

Thermodynamic parameters - ΔG°, ΔH° and ΔS° are calculated by Langmuir equation using

$$\Delta G^{\circ} = -RT \ln K$$

$$\Delta H^{\circ} = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln \frac{k_2}{k_1} \text{ and}$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T}$$

In these equations, R is gas constant, k, k₁ and k₂ are equilibrium constant at T, T₁ and T₂ temperature respectively. The negative value of ΔG° indicate the spontaneous nature of process while positive values of ΔH° and ΔS° indicate the endothermic nature (Table-3).

Conclusion

Increasing temperature and decreasing particle size and pH increases the sorption capacity of FA for phenols. Isotherm studies indicate the sorption capacity of sorbent towards sorbate and nature of system. This helps to design a treatment plant for phenolic effluents where continuous removal or recovery can be achieved on a large scale.

References

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Table 1. Sorption isotherm parameters for different fractions of flyash. Conditions: pH 6.5; Temperature- 30°C

Sorbate	Particle size of sorbent (μm)	Langmuir parameters	
		Qo (mg g ⁻¹)	K (mg/dm ³)
OCL	150	3.111	46.67
	100	3.828	61.25
	45	4.708	80.04

MCL	150	3.589	44.86
	100	4.464	55.03
	45	5.536	78.89
PCL	150	4.598	36.78
	100	5.136	38.52
	45	6.721	50.41

Table 2. Sorption isotherm parameters at different pH values. Conditions: Size - 150 μm; Temperature - 30°C

Sorbate	pH	Langmuir parameters	
		Qo (mg g ⁻¹)	K (mg/dm ³)
OCL	2.0	3.833	57.50
	4.0	3.565	57.04
	6.5	3.111	46.67
	8.0	2.790	46.04
	10.0	2.608	45.64
MCL	2.0	4.273	49.14
	4.0	3.922	47.06
	6.5	3.589	44.86
	8.0	3.108	43.51
	10.0	2.898	43.47
PCL	2.0	5.379	43.03
	4.0	5.000	42.50
	6.5	4.598	36.78
	8.0	4.436	35.49
	10.0	4.124	35.05

Table 3. Sorption isotherm and thermodynamic parameters at different temperatures. Conditions: pH-6.5 Size-150 μm

Sorbate	Temp. (°C)	Langmuir parameters		Thermodynamic parameters		
		Qo	K	ΔG° (kcal/mol)	ΔS° (cal/mol)	ΔH° (kcal/mol)
OCL	30	3.111	46.67	-2.314	24.50	5.11
	40	3.826	61.22	-2.559	25.59	5.45
	50	4.867	80.31	-2.795	-	-
MCL	30	3.589	44.86	-2.290	22.07	4.397
	40	4.358	56.65	-2.511	23.87	4.961
	50	5.372	72.52	-2.725	-	-
PCL	30	4.598	36.78	-2.170	15.09	2.402
	40	5.222	41.78	-2.321	19.13	3.668
	50	6.269	50.15	-2.513	-	-