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Removal of Cresols by Adsorption on Plastic Clay

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The adsorption of cresols (*ortho, meta* and *para*) on plastic clay has been investigated by means of a batch technique from their aqueous solutions. The effects of particle size and initial solute concentration have been studied and isotherm parameters are evaluated. The Freundlich Isotherm has been found to be more suitable for all the systems studied. Plastic clay is characterized with different analyses and has been found that silica and alumina are its major constituents responsible for adsorption. Thermodynamic parameters are calculated.

INTRODUCTION

The process of adsorption has been found to be an efficient and economically cheap process for removing pollutants using various adsorbents[1–3]. This has led many workers to search for low cost non-conventional adsorbents. China clay, fly ash, lignite, peat, soil, wollastonite, brick kiln ash and wood are some new adsorbents, which have been tried with varying success[4–6].

This work reports plastic clay as a good adsorbent. The main objective of this programme is characterisation of plastic clay and to explore the possibilities of using plastic clay for removing cresols from waste-water.

EXPERIMENTAL

Plastic clay was obtained from Katni, Sihora Mines (M.P.), India and was used as such after passing it through 425, 300, 150, 75 μm sieves. Cresols used were of B.D.H. Aqueous solutions of cresols were prepared by dissolving definite amount of cresols in distilled water. Batch experiments were conducted at constant temperatures of 28–30°C. The concentration of residual cresols was determined[7] with the aid of a Spectronic-20 spectrophotometer. 2 h contact time was found enough for attaining the equilibrium.

RESULTS AND DISCUSSION

Plastic clay constituents were analysed chemically (Table-1). The IR spectrum of plastic clay is observed using KBr pellet method on a Perkin-Elmer 817 model. The various bands indicate the presence of mineral matter in plastic clay (Table-2).

TABLE-1
CHEMICAL ANALYSIS OF DIFFERENT FRACTIONS OF PLASTIC CLAY

Particle size in μm	Chemical composition (% by weight)					
	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
75 μm	11.20	60.24	25.07	1.46	0.58	0.39
150 μm	16.70	53.34	23.04	1.26	0.56	0.37
425 μm	22.92	53.05	20.40	1.20	0.51	0.31

XRD studies indicate the presence of silica and alumina as the dominant constituents of plastic clay, kaolinite, gibbsite, wollastonite and haematite minerals as the dominant constituents of plastic clay. It concludes the silica and alumina as the major ingredients of sorbent.

TABLE-2
IMPORTANT IR BANDS OF PLASTIC CLAY AND THEIR POSSIBLE ASSIGNMENTS

Band position (cm^{-1})	Assignments
426	Fe—O bend
468	Si—O—Ca bend
540	Si—O stretch
750	Al—O—H bend
792	Si—O stretch (Al, Mg)- - -O—H Si—O—Al stretch
914	Al- - -O—H stretch
1008	Si—O—Al stretch
1037	Si—O—Si stretch
1635	H—O—H stretch
3392	H—O—H stretch
3452	H—O—H stretch
3525	Al- - -O—H stretch
3622	O—H stretching
3695	Al- - -O—H stretch

By decreasing the particle size from 425 μm to 75 μm the amount adsorbed increased from 57% to 80% in the case of *p*-cresol, from 44.5% to 65% in the case of *o*-cresol and from 47% to 68.5% in the case of *m*-cresol. This is due to increase in the amounts of silica and alumina content with decreasing particle size. Thus silica and alumina content of plastic clay plays a major role in removing cresols. This is in agreement with the statement (based on mathematical considerations) that if the mechanism of uptake is simply one of adsorption on a specific external site, then the rate should vary reciprocally with the first power of the diameter, whereas in intraparticle diffusion the rate should vary with the reciprocal of the square of the diameter[8].

Among the cresols the removal rate is found to decrease as follows: $p^{-} > m^{-} > o^{-}$. Higher removal rate for *p*-cresol is probably due to lone pair of electrons present on —OH which is made easily available due to electron releasing effect of —CH_3 group in *p*-cresol for silica and alumina surface, which has also no steric hindrance for chemical bonding; however removal rate for *m*-cresol and *o*-cresol may be caused by steric hindrance between the methyl (—CH_3) and hydroxyl (—OH) groups.

The hydrogen ion concentration (pH) primarily affects the degree of ionisation of the cresols and the surface properties of the sorbent. It was observed that the lower pH values produce higher removal rates and vice versa. It happens so because clay contains varying amounts of water molecules especially those which either exist as surface hydroxyl groups on adsorbed water. At lower pH values, the lone pair of electrons of the oxygen atom of the undissociated —OH groups present in the benzene ring coordinates with the highly positively charged surface.

TABLE-3
INFLUENCE OF DIFFERENT PARAMETERS ON ADSORPTION OF CRESOLS ON PLASTIC CLAY

Factors	Factor varied	System and plastic clay		
		o^{-} crosol (mg g^{-1})	m^{-} crosol (mg g^{-1})	p^{-} crosol (mg g^{-1})
Particle size (μm)	75	16.250	17.125	20.000
	150	14.750	15.625	18.500
	300	12.250	13.875	17.375
	425	11.125	11.750	14.250
pH	4.0	11.625	12.375	15.750
	6.5	11.125	11.750	14.250
	8.0	9.750	10.000	14.000
Concentration of sorbate (mgL^{-1})	250	6.400	6.850	8.750
	500	7.050	7.605	10.350
	750	9.250	9.850	12.500
	1000	11.125	11.750	14.250
Temperature (°C)	15	13.625	15.000	19.000
	28	11.125	11.750	14.250
	45	6.250	6.500	8.500

The uptake of cresols was found to decrease with an increase in temperature. The enthalpy of activation calculated from temperature data is very low which shows that adsorption is fast on clay's surface. Thermodynamic parameters are reported in Table-4. The rate of removal of cresols is observed to increase as the concentration of these sorbates increases. Moreover, a grater fraction of the solute originally present will be adsorbed in a given period of time. The results of particle size, pH, sorbate conc. and temperature are summarised in Table-3.

TABLE-4
THERMODYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES

Condition: pH 6.5, size 425 μm, (substrate) = 1000 ppm

Sorbate	Temp. (°C)	Thermodynamic parameters		
		ΔG (kcal mol^{-1})	ΔS (cal mol^{-1})	ΔH (kcal mol^{-1})
o^- cresol	15	–2.4171	–0.1467	–2.4593
	28	–2.4152	–0.0280	–2.4236
	45	–2.4147	—	—
m^- cresol	15	–2.4074	–0.3497	–2.5081
	28	–2.4029	–0.0821	–2.4276
	45	–2.40 15	—	—
p^- cresol	15	–2.3117	–3.0545	–3.1914
	28	–2.2720	–1.3731	–2.6853
	45	–2.2487	—	—

The results of present batch studies show that adsorption of cresols on plastic clay is quite satisfactory. Plastic clay can be used as column adsorber for cresolic effluents. The physical characterisation of plastic clay and the results establish its feasibility as an effective adsorbent for waste-water treatment.

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