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Removal of Pollutants from Industrial Effluents Using Plastic Clay and Pyrophyllite

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Attempts were made to remove Cr(VI) from tannery effluents, PO_4^{3-} from gelatin industry effluent and $C_2O_4^{2-}$ from oxalic acid manufacturing unit effluent by plastic clay and pyrophyllite adsorbent. The adsorption of Cr(VI), PO_4^{3-} and $C_2O_4^{2-}$ was found to be appreciable in both adsorbents but removal was higher in plastic clay for Cr(VI) and $C_2O_4^{2-}$. Removal of PO_4^{3-} was higher on pyrophyllite. The percentage removal of Cr(VI), PO_4^{3-} and $C_2O_4^{2-}$ in industrial waste waters was 43.8, 49.6 and 53.4 on plastic clay and 21.9, 53.1, 34.3 on pyrophyllite respectively. The equilibrium data fit well within the Langmuir and Freundlich isotherms.

Key words: Removal of pollutants, Industrial, Effluents, Plastic clay, Pyrophyllite.

INTRODUCTION

Tannery industry in India has made tremendous strides in developing newer and quicker processing techniques. Recently, the industry has switched over to chrome tanning from vegetable tanning. Large quantities of chromium sulphate is used in this process resulting in high concentration of Cr(VI) in effluents. The effluent contains both hexavalent and trivalent forms of chromium. High concentration of Cr^{6+} in water is lethal for fish, corrosive to flesh and a potential carcinogen to human being[1–3].

The effluent from oxalic acid manufacturing unit (OAMU) is discharged in water streams leads to acidity and digestive problems along with stone and ulcer formation in digestive track.

The effluent of gelatin manufacturing unit discharge phosphate in water streams leads to eutrophication problems[4]. The tolerance limit for drinking water specified by WHO and ISI for Cr(VI), PO_4^{3-} and $C_2O_4^{2-}$ are 0.05 mg L^{-1}, 5 mg L^{-1} and 1 mg L^{-1} respectively[5, 6].

The present paper aims to develop an adsorption technique for removal of Cr(VI) from tannery effluent, PO_4^{3-} from gelatin industry effluent and $C_2O_4^{2-}$ from OAMU effluent and to study the sorption capacity of plastic clay and pyrophyllite to adsorb these pollutants from effluents and assess their ability as potential commercial adsorbents.

EXPERIMENTAL

For the present study industrial effluents in the untreated forms, were collected from tannery industry (at Tannery and Footwear Corporation of India Ltd., Kanpur). Gelatin industry (at Shaw Wallace Gelatines. Ltd., Jabalpur) and OAMU (at Seoni Chemicals, Seoni). The pH of effluents was examined by Systronic 331 Digital pH meter. The concentration of Cr(VI) in tannery effluent and PO_4^{3-} in gelatin effluent was analysed[7] spectrophotometry and $C_2O_4^{2-}$ in OAMU was analysed titrimetrically.

Plastic clay and pyrophyllite used as adsorbents are obtained from the mines of Jabalpur and Katni district. They were sieved through standard test siever into 150 pm particle size and dried for 2 h at 110°C in an electric oven and stored in a dessicator for use.

Batch sorption experiments were carried out by agitating 2.0 g of adsorbents with 50 mL of effluent at four different concentrations 24.3 mg L^{-1}, 48.6 mg L^{-1}, 72.9 mg L^{-1} and 97.2 mg L^{-1} for Cr(VI), 7.15 mg L^{-1} 14.3 mg L^{-1}. 21.4 mg L^{-1} and 28.6 mg L^{-1} for PO_4^{3-}, 237.5 mg L^{-1}, 285.0 mg L^{-1}, 332.5 mg L^{-1} and 475.0 mg L^{-1} for $C_2O_4^{2-}$ in an electric shaker for 2 h. The sorbents were centrifuged and the supernatant were analysed.

RESULTS AND DISCUSSION

The pH of tannery effluent, gelatin industry effluent and OAMU effluent were examined and found to be 5.7, 6.8 and 4.4 respectively. The concentration of Cr(VI) in tannery effluent was 97.2 mg L^{-1}. The concentration of PO_4^{3-} in gelatin effluent was 28.6 mg L^{-1} and the concentration of $C_2O_4^{2-}$ in OAMU effluent was 475 mg L^{-1}.

The amount adsorbed at equilibrium for Cr(VI) increases form 0.345 mgg^{-1} (56.7%) to 1.05 mgg^{-1} (43.8%) on plastic clay and from 0.22 mgg^{-1} (37.4%) to 0.53 mgg^{-1} (21.9%) on pyrophyllite with increasing the concentration of Cr(VI) from 24.3 mg L^{-1} to 97.2 mg L^{-1} (Fig.1).

With increase in concentration from 7.15 mg L^{-1} to 28.6 mg L^{-1} sorption of PO_4^{3-} increases from 0.10 mg g^{-1} (60.1 %) to 0.35 mg g^{-1} (49.6%) on plastic clay and 0.11 mgg^{-1} (63.0%) to 0.38 mgg^{-1} (53.1%) on pyrophyllite (Fig.2).

Adsorption studies further revealed that adsorption of $C_2O_4^{2-}$ increases from 3.84 mgg^{-1} (64.8%) to 6.34 mgg^{-1} (53.4%) on plastic clay and 2.62 mgg^{-1} (44.2%) to 4.07 mgg^{-1} (34.3%) on pyrophyllite on increasing the concentration of $C_2O_4^{2-}$ from 237.5 mg L^{-1} to 475 mg L^{-1} (Fig. 3).

It is clear from Table-1, the percentage adsorption increases on diluting the effluent. In the case of lower concentration, the ratio of the initial number of moles of adsorbates to the available surface area is low and subsequently the fractional adsorption becomes independent of initial concentrations. However, at higher concentration the available sites of adsorption become fewer and hence the percentage removal of sorbates depend upon the initial concentration[8].

In our earlier communication we have studied the effect of particle size, concentration, pH and temperature on the removal of Cr(VI), PO_4^{3-} and $C_2O_4^{2-}$. Similar observations were recorded for their removal with effluents also. The

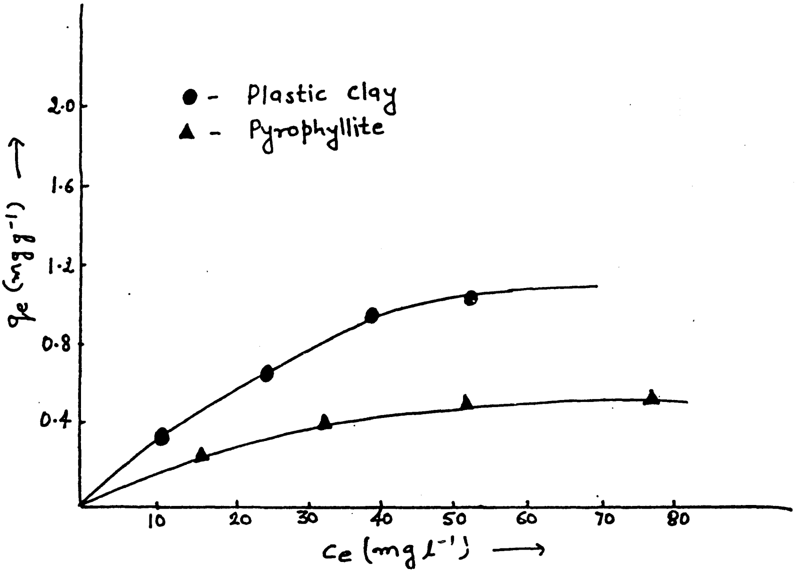


Fig. 1. Adsorption of Cr(VI) in tannery effluent at 5.7 pH, 150 μm size and 25°C

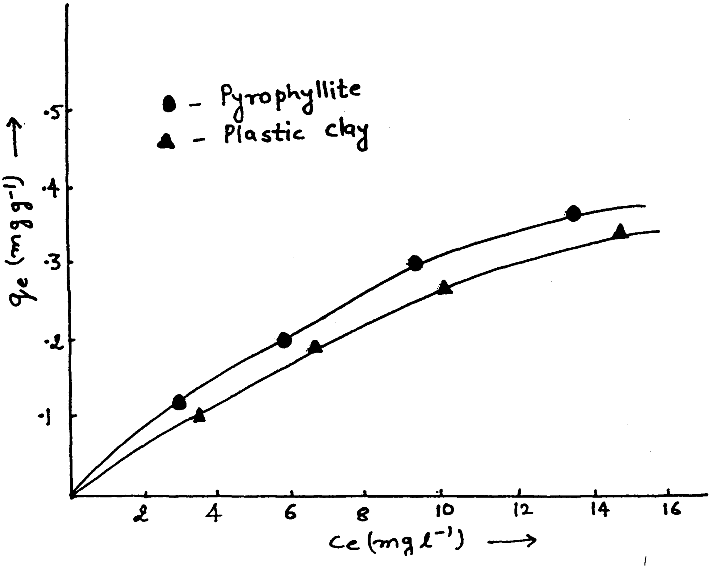


Fig. 2. Adsorption of PO_4^{3-} in gelatin industrial effluent at 6.87 pH, 150 μm size and 25°C

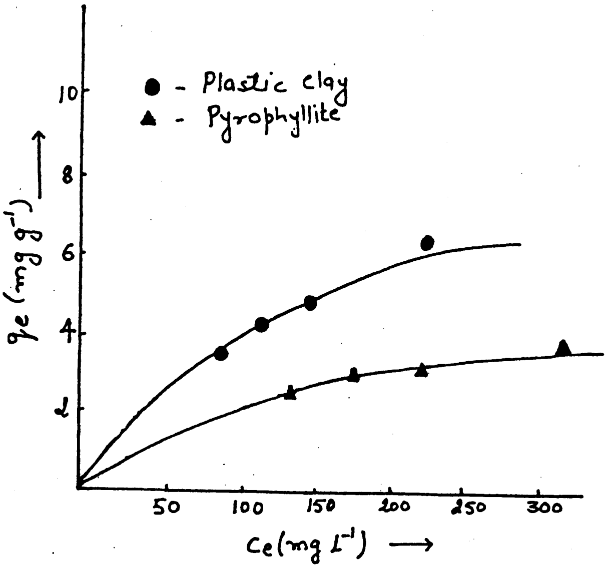


Fig. 3. Adsorption of $C_2O_4^{2-}$ in OAMU effluent at 4.4 pH, 150 μm particle size and 25°C

TABLE-1

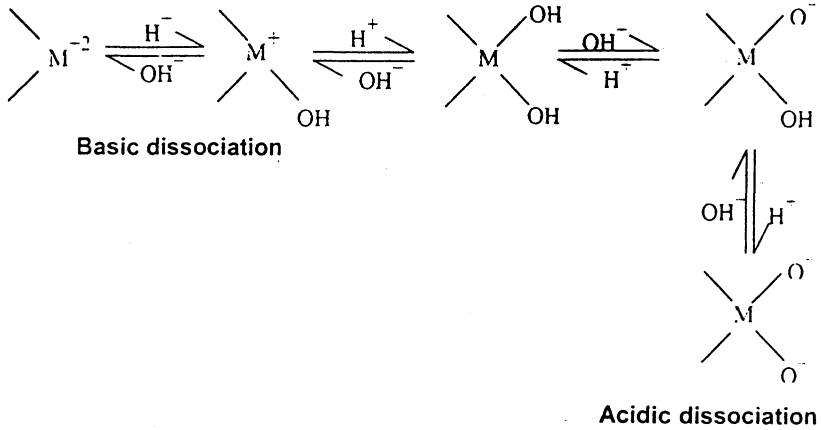
REMOVAL OF Cr(VI), PO_4^{3-}, $C_2O_4^{2-}$ IN INDUSTRIAL EFFLUENTS BY PLASTIC CLAY AND PYROPHYLLITE

Sorbate	Concentration (mg L^{-1})	Plastic clay (%)	Pyrophyllite (%)
Cr(VI)	24.30	56.7	37.4
	48.60	51.0	32.0
	72.90	47.4	27.1
	97.20	43.8	21.9
PO_4^{3-}	7.15	60.1	63.0
	14.30	55.2	59.0
	21.40	52.8	56.0
	28.60	49.6	53.1
$C_2O_4^{2-}$	237.50	64.8	44.2
	285.00	61.1	41.7
	332.50	56.9	37.5
	475.00	53.4	34.3

main constituents of plastic clay and pyrophyllite are the oxides of silica and alumina, while other constituents are present in traces. It is thus expected that the Cr(VI), PO_4^{3-} and $C_2O_4^{2-}$ will be mostly removed by the main constituents of adsorbents. It is found that smaller sized fractions of adsorbents are more efficient in removing the adsorbates. It must be due to increase in the amount of silica and alumina with decrease in particle size.

The removal of dichromate, phosphate and oxalate on plastic clay and pyrophyllite increased with time until equilibrium was attained. Equilibrium was attained in 120 minutes in each case for both the adsorbents.

It is clear that the adsorption of dichromate, phosphate and oxalate ions decreases as the pH increases. The adsorption at low pH values may be attributed to the large number of H^+ ions present at low pH values which can neutralize the negatively charged surface or convert a neutral group to a positively charged group. The enhancement of the adsorption of sorbates is because of the decrease in the forces of repulsion between adsorbent and adsorbate. The oxides present in the adsorbents used, undergo surface hydroxylation and form surface hydroxyl compounds, which give positively or negatively charged surface as a result of their subsequent acid-base dissociation in the following manner[10].



where M represent Al, Si, Fe, etc. It is obvious from the above equilibria, that with decrease in the pH of the solution, the positive charge density on the surface increases and hence the extent of adsorption of anions increases as a result of coulombic attractive forces.

The decrease in the adsorption capacity of plastic clay and pyrophyllite with temperature indicates an exothermic adsorption process. The equilibrium time is independent of solution temperature for all the six systems. Thermodynamic parameters like heat of adsorption and the energy of activation play an important role in predicting the adsorption behaviour and both are strongly temperature dependent.

The various thermodynamic parameters were calculated with the help of the following equations:

$$\Delta G^0 = -RT \ln K \qquad \ldots(1)$$

$$\Delta H^0 = R(T_2 \cdot T_1/T_2 - T_1) \ln (K_2K_1) \qquad \ldots(2)$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0/T \qquad \ldots(3)$$

where R is the constant, K, K_1 and K_2 are equilibrium constants at different temperatures for both systems. The negative value of the free energy, ΔG^0, is indicative of the spontaneity of the adsorption process. The negative value of the enthalpy change ΔH^0, suggests the exothermic nature of the adsorption process. The negative entropy change, ΔS^0 indicates the faster interaction with the active sites of adsorbents[11]. It also indicates that there is no configurational change and the surface compound is stable[12].

Isotherm Analysis: The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. Out of the several isotherm equations available, Langmuir and Freundlich isotherm equation[13, 14] were found most suited for the present equilibria.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir expression is represented in the following equation:

$$\frac{C_e}{q_e} = \frac{K}{Q^0} + \frac{C_e}{Q^0} \qquad \ldots(4)$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount adsorbed at equilibrium (mgg^{-1}) and K, Q^0 can be related to the equilibrium constant and sorption maxima respectively. The plot of C_e/q_e vs C_e gives straight line showing the applicability of Langmuir isotherm. The values of Q^0 and K at different concentrations have been determined from the slope and intercept of the plot and are given in Table-2. This clearly shows the formation of monolayer coverage of the sorbate at the outer surface of the sorbent.

TABLE-2

SORPTION ISOTHERM PARAMETERS OF Cr(VI), PO_4^{3-}, $C_2O_4^{2-}$ FOR PLASTIC CLAY AND PYROPHYLLITE

Sorbate	Sorbent	Freundlich parameters		Langmuir parameters	
		K_f (mg g^{-1})	1/n	Q_0 (mg g^{-1})	K (mg L^{-1})
Cr(VI)	Plastic clay	0.316	0.657	2.142	55.71
	Pyrophyllite	0.173	0.685	1.130	49.72
PO_4^{3-}	Plastic clay	0.047	0.756	1.144	29.72
	Pyrophyllite	0.054	0.692	1.375	31.62
$C_2O_4^{2-}$	Plastic clay	3.162	0.484	1.818	32.72
	Pyrophyllite	1.659	0.540	1.160	31.32

The Freundlich equation is used for heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly due to variation in the heat of adsorption. The Freundlich equation has the general form,

$$Q_e = K_f C_e^{1/n} \qquad \ldots (5)$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \qquad \ldots (6)$$

The constants are listed in Table-2 for the batch systems. The value of K_f and 1/n at different concentrations were determined from the slope and intercept of the linear plots of Q_e vs log C_e.

The experimental data also showed the effect of concentration on the sorption capacity. The initial concentration of sorbate affected the sorption capacity. As observed from the Fig. 1 to 3 the sorption capacity rapidly increases on increasing initial concentration and then no significant change occurred.

Conclusion

On the basis of isotherm constants analysis, it was confirmed that the plastic clay and pyrophyllite sorbent exhibits promising adsorption characteristics for dichromate, phosphate and oxalate ions and can be used as a suitable sorbent for pretreatment of these effluents before discharging to main stream.

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