



Competitive Adsorption of dyes (crystal violet, methylene blue, malachite green) on chlor-alkali waste (slurry)

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ABSTRACT

The objective of this work is the study of adsorption of dye solution of three dyes (crystal violet, methylene blue & malachite green) using chlor-alkali waste. Removal of these dyes from aqueous solution using chlor-alkali waste has been investigated. Liquid phase adsorption experiments were conducted. Batch adsorption studies are carried out by observing the effect of experimental parameters, namely, pH, amount of adsorbents, contact time and initial concentration. Adsorption capacity of chlor-alkali waste is determined for competitive adsorption of dyes. Optimum conditions for dye removal are studied like pH value, contact time required, amount of adsorbent, initial concentration, etc. Dyes are present in various Industrial effluents like Textile Industries, Sewage water, Water treatment plants. This work can have use in Design of adsorption setup for dyes removal.

Keywords: Adsorption, Dyes, chlor-alkali waste, pH.

INTRODUCTION

Textile industries have shown a significant increase in the use of synthetic complex organic dyes as colouring materials^[1]. Different processes for colour removal typically include physical, chemical and biological schemes. Some processes, such as electrochemical techniques and ion pair extraction, are relatively new for textile waste treatment, while others have been used in the industry for a long time. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances^[2]. Adsorption has been used extensively in industrial process for separation and purification. A wide variety of materials such as natural zeolite^[2], shale oil ash^[3], peat^[4], various silicas^[5], activated clay^[6], banana pith^[7], natural manganese mineral^[8], goat hair^[9], alum sludge^[10] and mixtures of fly ash and soil^[11] have been investigated as low-cost alternatives to activated carbon^[12]. This study was calculated to investigate the adsorption capacities of chlor-alkali waste adsorbent from chlor-alkali industry in Nagapattinam, Tamilnadu for dye removal from wastewaters.

EXPERIMENTAL SECTION

Adsorbate:

Commercial quality dyes were obtained from Aldrich and used without any further purification. A stock solution of dyes was prepared in double distilled water.

Adsorbents:

The adsorbent, raw chlor-alkali waste was collected from Nagapattinam, Tamil nadu. It was sieved with 200 mesh (75 μ m) size and dried at 110°C and kept in bottles for use.

Methods:

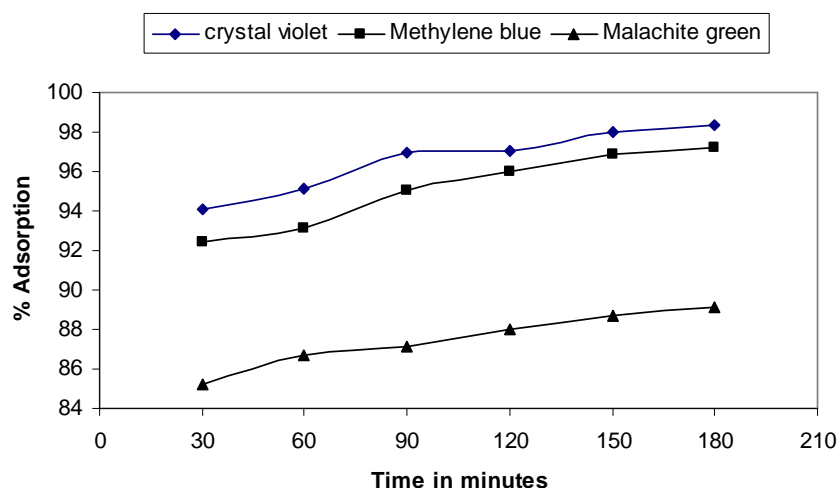
Adsorption experiments were conducted in which aliquots of dye solution with known concentrations were introduced into glass bottles (100 cm³) containing accurately weighed amounts (0.250 g) of the adsorbent. The bottles were shaken at 25°C using immersed water bath for a prescribed length of time to obtain equilibrium. The adsorbent was then removed by centrifuge at 4000 rpm. The equilibrium concentrations of dyes were determined by a UV-visible spectrometer (Shimadzu UV 160).

RESULTS AND DISCUSSION**Effect of Contact time:**

The effect of contact time can be seen from table 1 and figure 1 for the dyes. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 3 hours from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 3 hours (180 min). It is basically due to saturation of the active site which do not allow further adsorption to take place .

Table 1. Effect of contact time on removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste

Contact time (t) minutes	% Adsorption of crystal violet	% Adsorption of methylene blue	% Adsorption of malachite green
30	94.1176	92.4323	85.2389
60	95.1589	93.1265	86.6754
90	96.9876	95.0075	87.1235
120	97.0132	95.9989	88.0098
150	97.9854	96.8745	88.6785
180	98.3432	97.2346	89.1298

**Figure 1. Effect of contact time on removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste****Table 2. Effect of pH on removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste**

pH	% Adsorption of crystal violet	% Adsorption of methylene blue	% Adsorption of malachite green
2	58.5432	84.4376	62.8965
3	65.3245	87.9876	64.6234
4	72.3145	91.1287	69.9994
5	80.2367	95.3256	73.2476
6	97.5609	93.5698	80.1276
7	90.5674	89.2156	87.6785
8	86.9087	81.6753	83.2116
9	78.6543	76.9834	78.9056
10	71.5423	71.0078	72.5698

Effect of initial pH of the solution:

The effects of initial pH on dye solution of three dyes removal were investigated by varying the pH from 2 to 10 were presented in table 2 and figure 2. At pH - 2 the removal was minimum but it increased along with increasing initial pH (2-6) of dye solution. For malachite green it was maximum at pH -7 as we see in the figure 2. In case of

methylene blue the pH-5, greater is removal by adsorption. For congo red the maximum adsorption observed at pH-6. For all the three dyes there is no significant increase in amount adsorbed after pH 7. Infact adsorption found to decrease with increase in pH of solution from 7 and above. Thus as the pH increased from 2-6, more negatively charged surface was available thus facilitating greater dye removal. We see that the trend is increasing with increasing pH from 2-6, so very useful to industrial application because almost neutral pH.

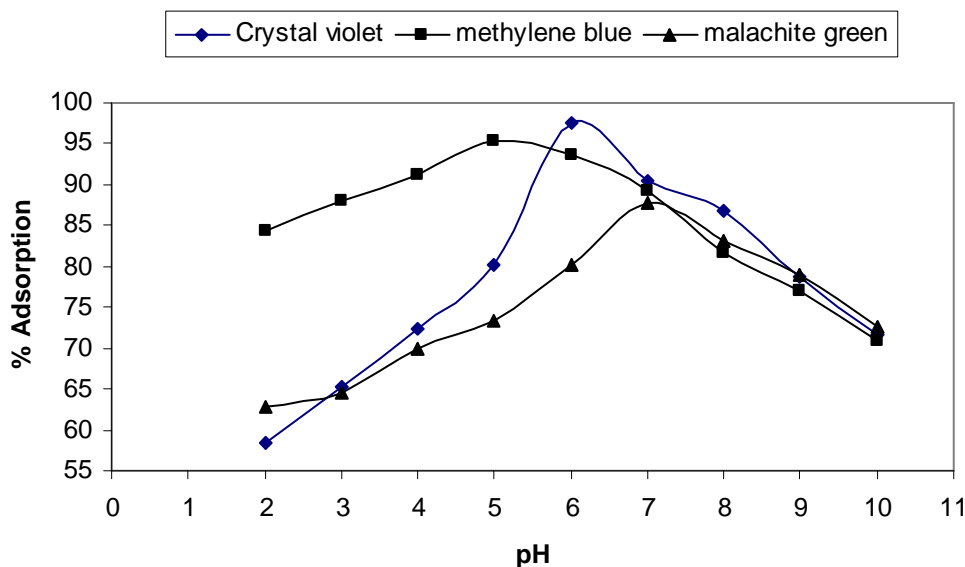


Figure 2. Effect of pH on removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste

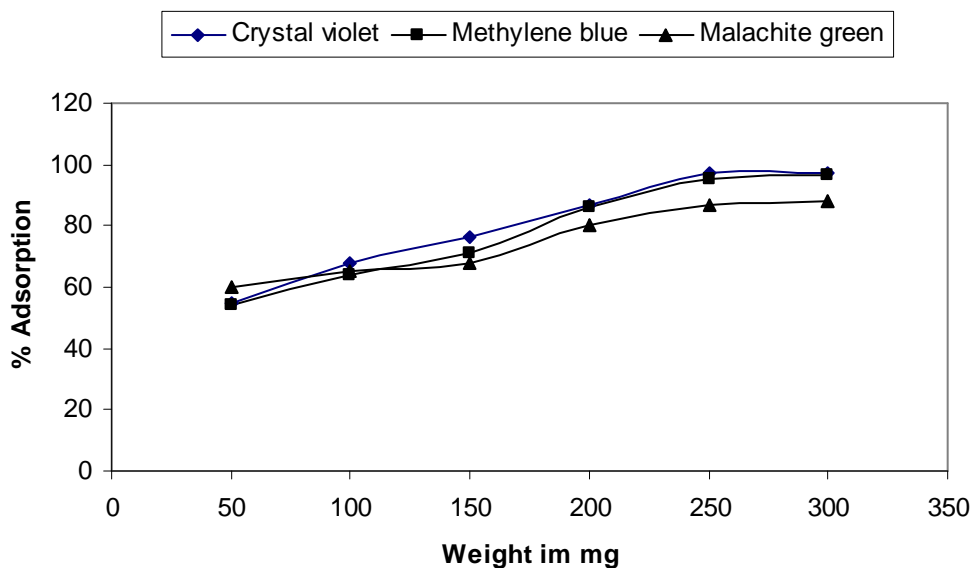


Figure 3. Effect of adsorbent dosage on removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste

Effect of adsorbent dosage:

From figure 3 we see that the optimum dose for the dyes were 250mg/50ml. Though at 300mg/50ml, there is slight increase in %adsorption value but if we get nearly the same result as we get at adsorbent dosage of 250mg/50ml then going for 300mg/50ml will be expensive and loss of adsorbent. It is obvious as with increasing amount the active sites for adsorption of three dyes.

Adsorption Isotherm:

The adsorption of the dyes on chlor-alkali waste was studied by using the following two isotherm equations:

- Langmuir
- Freundlich

a. Langmuir isotherm

The Langmuir isotherm can be expressed by the equation,

$$C_e / q_e = (1 / q_0 b) + (C_e / q_0)$$

where, C_e = Concentration of dye at equilibrium (mg/L).

q_e = Amount of dye adsorbed at equilibrium time (mg/g).

q_0 = Adsorption capacity of the adsorbent (mg/g).

b = Langmuir constant (L/mg).

In this study, linear plot of C_e/q_e vs C_e was obtained which showed that the adsorption followed Langmuir isotherm model (Figure 4). The applicability of Langmuir isotherm suggested a monolayer coverage of dyes on the surface of chlor-alkali waste.

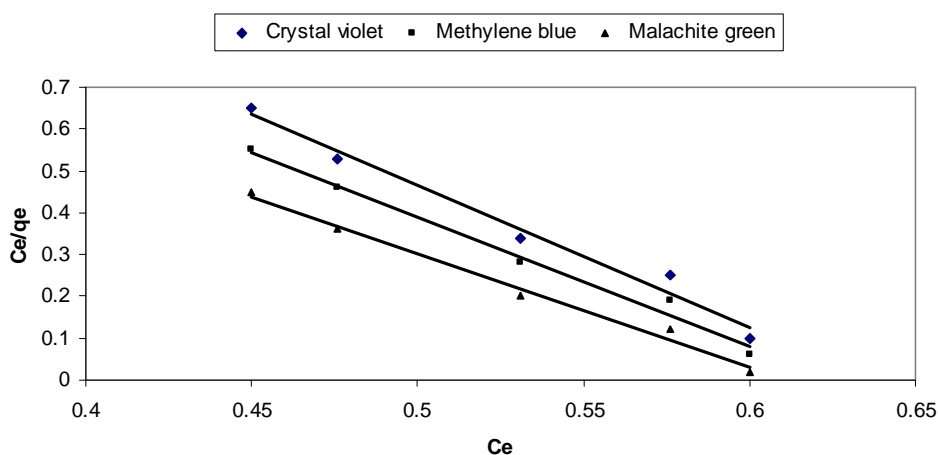


Figure 4. Langmuir plot for the removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste

b. Freundlich Isotherm

The Freundlich equation can be derived by assuming that the free energy of adsorption decreases logarithmically as adsorption density increases. The Freundlich equation is used for heterogeneous surface energies. The linear form of Freundlich equation is given by the following expression

$$\log (x/m) = \log K_f + 1/n \log c_e$$

where x = Amount of dye adsorbed at equilibrium (mg).

m = Weight of the adsorbent used (g).

c_e = Equilibrium dye concentration (mg/L).

K_f and n are Freundlich constants.

Linear plots of $\log_{10} x/m$ versus $\log_{10} c_{eq}$ was obtained in this study which showed that the adsorption follows Freundlich isotherm model. Values of K_f and n were calculated from the intercept and slope, respectively, of the plots (Figure 5). Since the 'n' value in the range of 1 to 10 indicates beneficial adsorption, the value of n suggests that chlor-alkali waste may be considered as an effective adsorbent for crystal violet, methylene blue and malachite green dyes.

Kinetics of adsorption:

Pseudo-second order kinetics

Experimental data were clearly fitted to the pseudo-second order kinetics model,

$$t / q_t = 1 / (k_2 \cdot q_e^2) + t / q_e$$

where k_2 (g/mg/min) is the second order rate constant, q_t (mg/g) is the amount adsorbed at time t (min) and q_e is the amount of adsorbed at equilibrium (mg/g). This model is more likely to predict the kinetics of adsorption

with chemical sorption being the rate-controlling step. The values of rate constants (k_2), calculated from the linear plots of t/q versus t (Figure 6), along with q_e values.

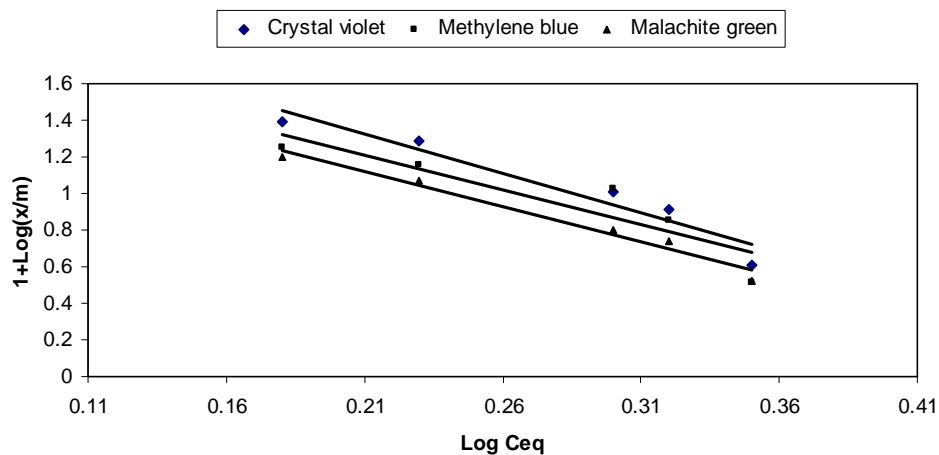


Figure 5. Freundlich plot for the removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste

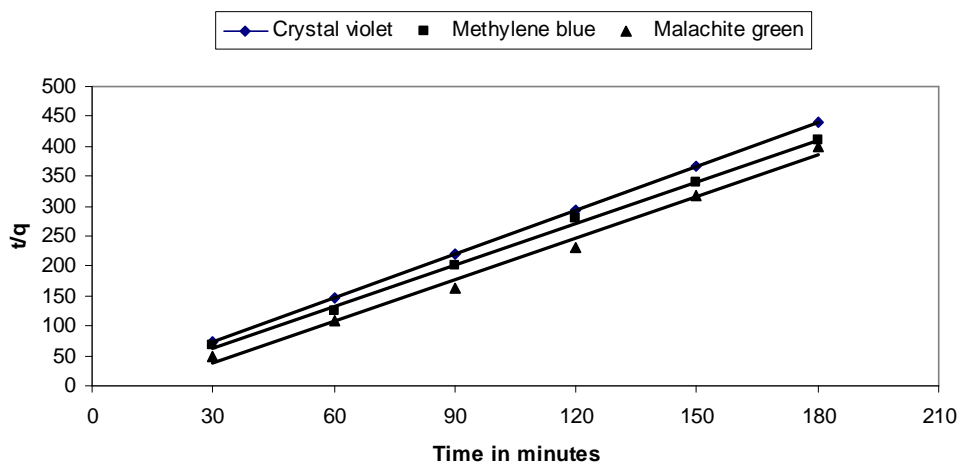


Figure 6. Pseudo-second order (Lagergren) plot for the removal of crystal violet, methylene blue and malachite green dyes using chlor-alkali waste

Instrumental analysis:

a. Fourier transform infrared analysis

Fourier transform infrared (FTIR) spectroscopy was used to determine the vibration frequency changes in the functional groups of chlor-alkali waste. The spectra of the chlor-alkali waste were measured within the wave number range of $400 - 4000 \text{ cm}^{-1}$. As can be inferred from figure 7 a,b,c and d the adsorption frequencies were shifted to higher wave numbers with the adsorption of dyes on chlor-alkali waste. From these findings it is presumed that the dyes were incorporated within the adsorbent through interaction with the active functional groups.

b. Scanning Electron Microscope analysis (SEM)

The surface morphology of chlor-alkali waste was examined using scanning electron microscopy (SEM), and the corresponding SEM micrographs obtained, before and after adsorption of dyes, at an accelerating voltage of 15 kV (Hitachi SE 900) at $5000\times$ magnification are given in figures 8 a,b,c and d. At such magnification, chlor-alkali waste particles showed rough areas of surface within which micropores were clearly identifiable. Comparison of these micrographs showed that the adsorption of dyes occurred on the surface of the chlor-alkali waste.

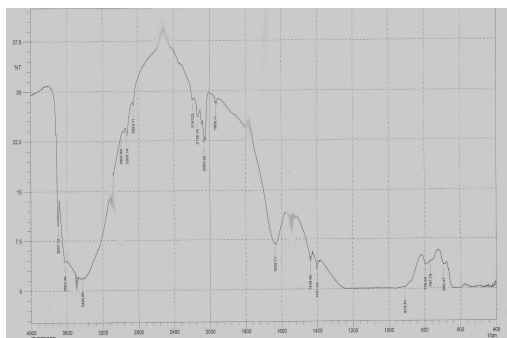


Figure 7.a FTIR spectrum of chlor-alkali waste

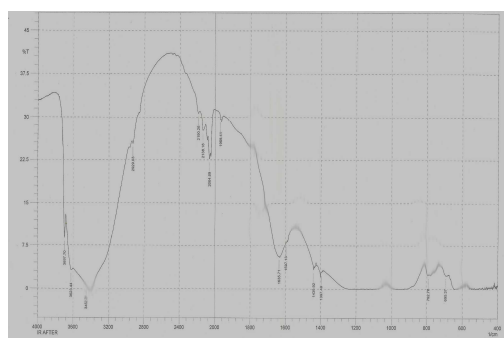


Figure 7.b FTIR spectrum of chlor-alkali waste after adsorption of CV dye

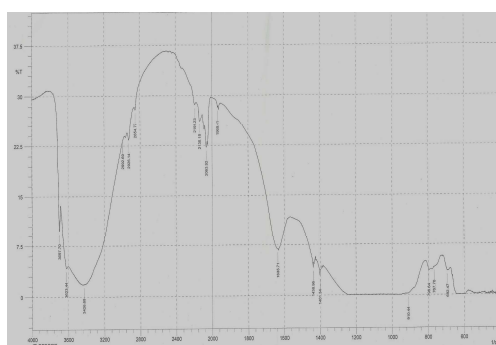


Figure 7.c FTIR spectrum of chlor-alkali waste after adsorption of MB dye

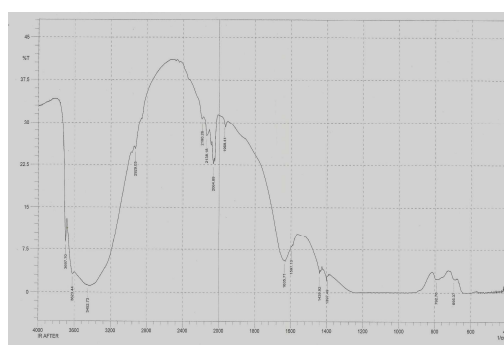


Figure 7.d FTIR spectrum of chlor-alkali waste after adsorption of MG dye

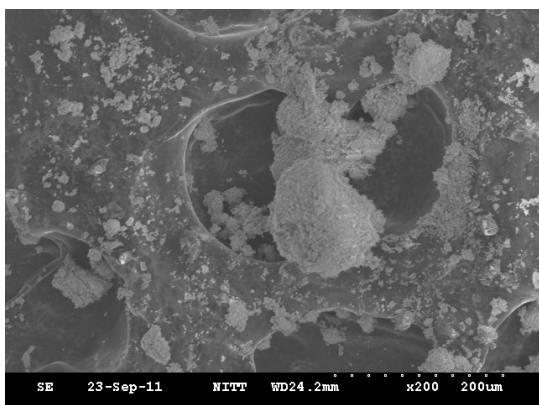


Figure 8.a SEM micrograph of chlor-alkali waste

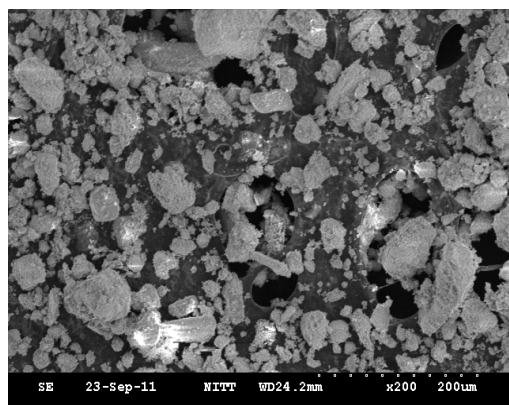


Figure 8.b SEM micrograph of chlor-alkali waste after adsorption of CV dye

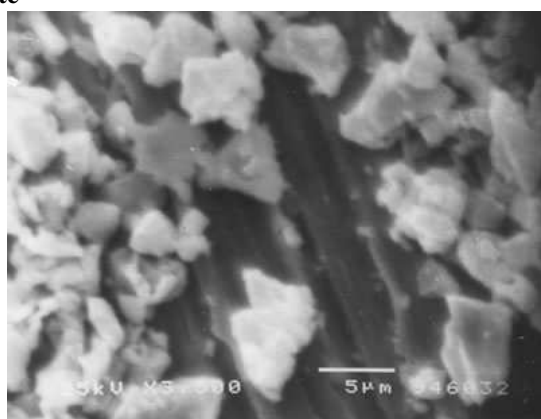


Figure 8.c SEM micrograph of chlor-alkali waste after adsorption of MB dye

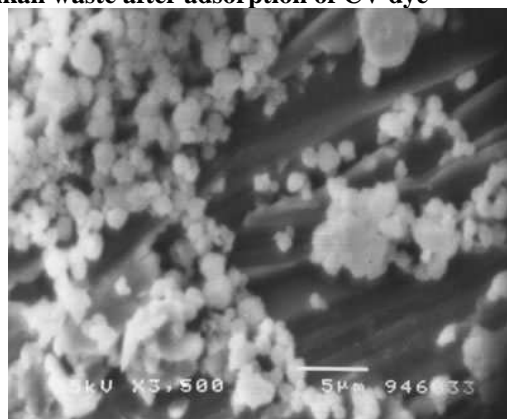


Figure 8.d SEM micrograph of chlor-alkali waste after adsorption of MG dye

c. X-Ray Diffraction analysis (XRD)

The X-ray Diffraction studies of the chlor-alkali waste were carried out using Rigaku corporation, Japan, X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III. The diffraction patterns obtained, before and after adsorption, are shown in figures 9 a,b,c and d. It is evident from the figures that there is no appreciable change in the spectra of adsorbent after adsorption. This may be due to the fact that adsorption does not alter the chemical nature of the surface of the adsorbent. That is, the adsorption forces in the present case are of physical in nature. The XRD pattern of the adsorbent, before and after adsorption, supports the adsorption process.

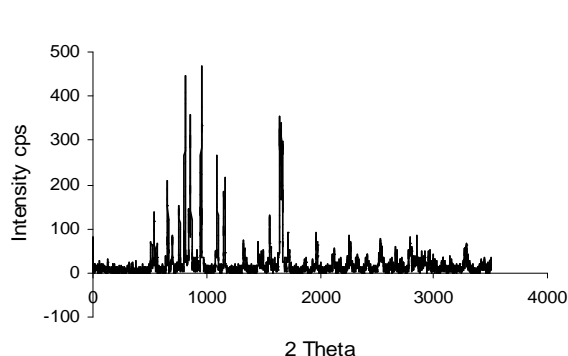


Figure 9.a XRD pattern of chlor-alkali waste

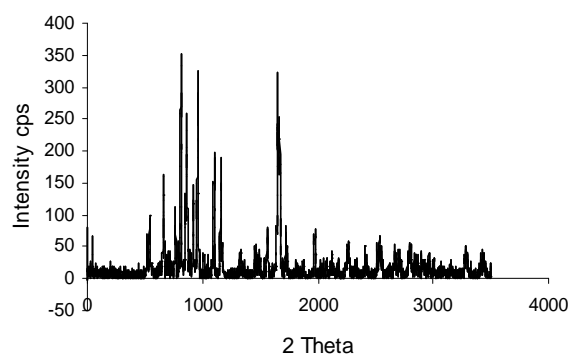


Figure 9.b XRD pattern of chlor-alkali waste after adsorption of CV dye

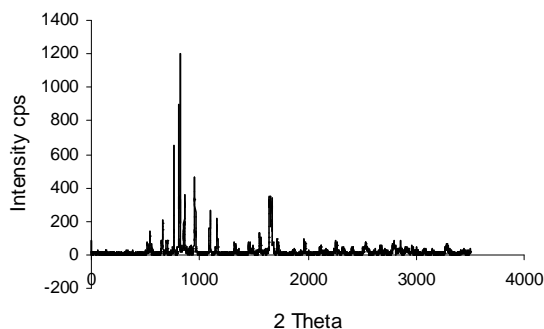


Figure 9.c XRD pattern of chlor-alkali waste after adsorption of MB dye

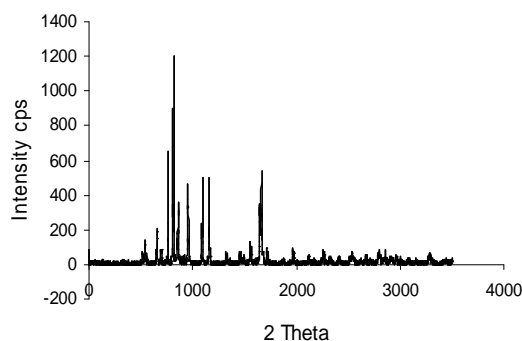


Figure 9.d XRD pattern of chlor-alkali waste after adsorption of MG dye

CONCLUSION

The present study shows that chlor-alkali waste can be used as an effective adsorbent for the removal of crystal violet, methylene blue and malachite green dye from aqueous solution. The maximum adsorption capacities were obtained (97.5609, 95.3256 and 87.6788 %) by using chlor-alkali waste at pH 6,5 and 7 with adsorbent dose of 250 mg and with agitation time of 180 minutes. The adsorption follows pseudo second order kinetics and data fits the Langmuir and Freundlich adsorption isotherms. The data may be useful in designing and fabrication of an economic treatment plant for the removal of crystal violet, methylene blue and malachite green dye from wastewaters.

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