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Research Paper

Adsorption Efficiency of Crystal Violet Dye onto Sludge (Effluent) Obtained from Caustic Industries

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Abstract: *In the present study, sludge obtained from caustic industries was used as adsorbent for crystal violet (CV) dye removal from aqueous solution. The effects of dye initial concentration, contact time, adsorbent dosage and pH on CV adsorption onto sludge were investigated. Results showed that the adsorption of CV was favourable at pH 6 whereas the adsorption uptake was found to increase with a increase in initial concentration, contact time and adsorbent dosage. Experimental data were analyzed by model equations such as Langmuir, Freundlich isotherms and it was observed that Langmuir isotherm model was found to be best fitted in the adsorption data.*

Keywords: Sludge, Crystal violet, pH, Adsorption isotherm.

Introduction

Aqueous effluents are well known as massive industrial wastewater. The presence of very low concentrations of these effluents are highly visible and undesirable and potentially inhibiting photosynthesis. The main pollution source of coloured effluents comes from textiles, leather, printing, laundry, tannery, rubber, painting, etc., processes[1]. Untreated disposal of this coloured water into receiving water body causes damage to aquatic life and also severe damage to the human health[2-4]. Removal of colour from wastewater effluents is an important issue faced by the textile dyeing industries. Various physical, chemical and biological treatment techniques can be employed to remove dyes from wastewater. Many synthetic dyes do not easily decompose in biological treatments due to their toxic effects on micro organisms, adsorption is suitable under field condition due to the flexibility, easy operation and no/lesser sludge disposal problems, high efficiency and for treating a large volume of effluent especially in removing dyes from dilute solutions[5-11]. It is considered to be a potential technique for the treatment of wastewater and reclamation of water containing dyes. Activated carbons with large surface area have shown high adsorption capacities for many adsorbates containing dyes, but they are mainly composed of less than 2nm and thus are not effective for large sized synthetic dyes. Furthermore, the commercial activated carbon has also disadvantages such as high price, and high cost of regeneration. Activated carbon adsorption has been limited greatly[12-13]. Hence, alternative low-cost, novel, locally available adsorbents are currently used for the removal of textile dye effluents from aqueous solutions, instead of activated carbon. For instance, natural clays such as sepiolite[2-4], zeolite[14-17], montmorillonite[18-20] and bentonite[21-25] can be used in these aspects. In this study, sludge is used as adsorbent to remove the crystal violet dye. Crystal violet was used a model compound of water soluble aromatic dyes to investigate the sorption equilibria onto sludge.

Material and Methods

A commercial dye Crystal violet, as monovalent cationic dye (analytical reagent-grade), was purchased from Merck Ltd. The chemical structure of Crystal violet is illustrated in Figure 1. All the reagents used were of analytical-reagent grade. Doubly distilled water used to prepare all the solutions.

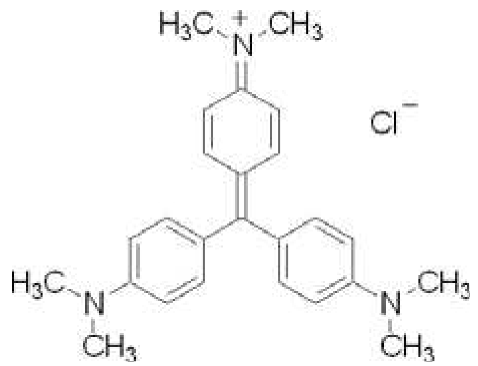

Figure 1: Chemical structure of Crystal violet

Adsorption equilibrium experiments

For equilibrium studies, the batch technique was used because of its simplicity. Solutions of 5,10,15,20 and 25 mg/L crystal violet, as the initial concentration, were treated with known amount of adsorbent. The mixtures were agitated on shaker incubator continuously for 180 min, as the equilibrium time, at 25°C. After 180 min, the suspension was centrifuged at 4000 rpm and the filtrates were analysed for residual crystal violet concentration by UV-visible spectrophotometer. The amount of crystal violet uptake by sludge in each flask was calculated using the mass balance equation.

Results and discussion

Effect of contact time and initial crystal violet concentration

The effect of initial dye concentration and contact time on the adsorption rate of crystal violet onto sludge is shown in Figure 2. As shown, when the initial CV dye concentration is increased from 5 to 25 mg/L the amount of CV dye adsorbed per unit weight of the sludge (mg/ g), at equilibrium conditions and the constant temperature as 25°C, increased from 18.8235 to 24.3902 (25 mg/l). Therefore, the adsorption percentage decreases and the extent of adsorption increase with increasing initial dye concentration. This is obvious from the fact that the initial CV concentration provides an important driving force to overcome all of mass transfer resistance. Furthermore, the increase of loading capacity of sludge with increasing initial CV concentration may be due to higher interaction between CV dye and adsorbent. For constant dosage of adsorbent, at higher initial concentrations, the available adsorption sites of adsorbent became fewer and hence the removal of CV dye depends upon the initial concentration. The removal of dye by adsorption onto sludge was found to be rapid at the initial period of contact time, and then to become slow with the increase of contact time. Fast diffusion onto the external surface was followed by fast pore diffusion into the intraparticle matrix to attain rapid equilibrium.

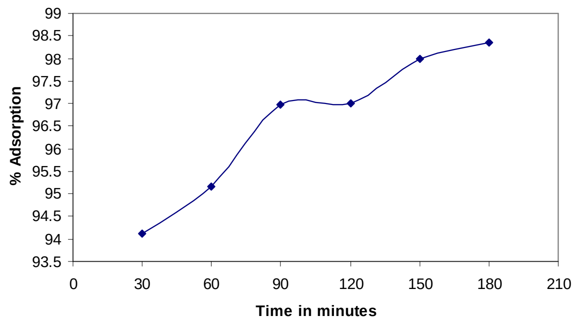

Figure 2: Effect of contact time on removal of crystal violet dye using sludge

Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process. As shown in Figure 3, a consistent increase in adsorption capacity of the sludge was noticed as the pH increased from 2 - 6, whereas in the range 2 - 10, after 6 the adsorption amount was only slightly affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of crystal violet at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites.

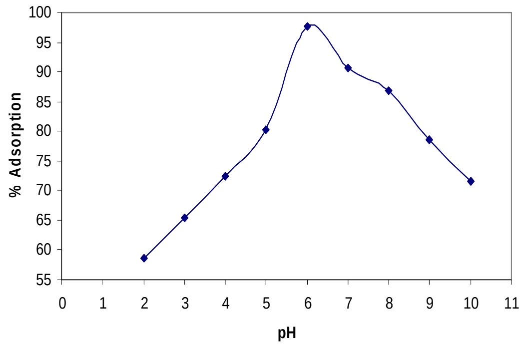

Figure 3: Effect of pH on removal of crystal violet dye using sludge

Effect of adsorbent dose

In order to study the effect of adsorbent mass on the adsorption of crystal violet, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 25 mg/L. Figure 4 shows the effect of adsorbent dose on the removal of crystal violet. Along with the increase of adsorbent dosage from 50 - 300 mg/L, the percentage of dye adsorbed increased. Above 300 mg/L of adsorbent dose, the adsorption equilibria of dyes were reached and the removal ratios of dyes kept almost invariable.

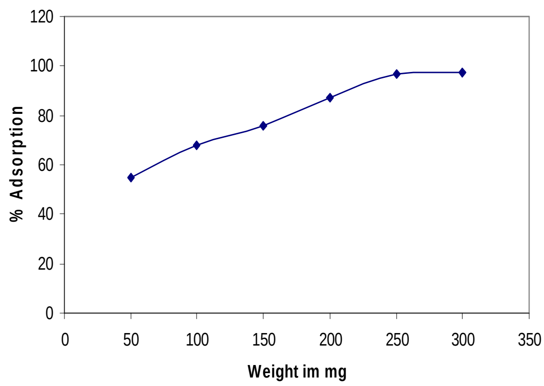

Figure 4: Effect of adsorbent dose on removal of crystal violet dye using sludge

Freundlich Isotherms

Freundlich isotherm is log qe=log Kf+1/n log Ce
Where qe is the amount of dye adsorbed per unit weight of adsorbent (mg/g), Kf is the measure of sorption capacity and l/n is sorption intensity; Ce is equilibrium concentration of residual dye in solution. Figure 5 shows the Freundlich adsorption isotherms for sludge. The straight line nature of

the plots indicates that the process followed was of Freundlich adsorption type.

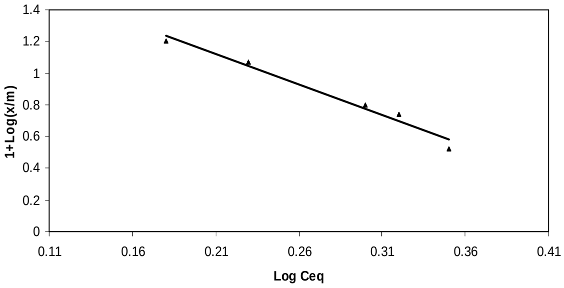

Figure 5: Fruendlich plot on removal of crystal violet dye using sludge

Langmuir isotherm

It is represented experimentally by the expression.
$P/(x/m) = 1/(K_1K_2) + P/K_2$
where K_1 and K_2 are proportionality constants, P-initial concentration (Ceq), x/*m*- amount of dye adsorbed at equilibrium (mg/g), qe. A plot of Ce/qe *versus* Ce will give a straight line. The slope of this is $1/K_2$ and intercept on the y−axis will give $1/K_1K_2$. Figure 6 indicates adsorption of dye on sludge is best fit with Langmuir model and so we infer that it followed Langmuir adsorption isotherms.

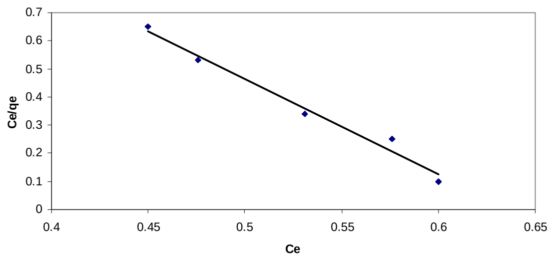

Figure 6: Langmuir plot on removal of crystal violet dye using sludge

Lagergren kinetics

Lagergren also proposed kinetics for the adsorption. According to him, if a plot of time in minutes *versus* log10 (qe−q) gives a straight line and it follows the first order kinetics. If a plot of time in minutes *versus* t/q gives a straight line and it follows the pseudo second order kinetics. Where,
qe–Maximum *x/m* value at maximum time
q –minimum *x/m* value at minimum time
x–amount of dye adsorbed
m–Mass of the adsorbent

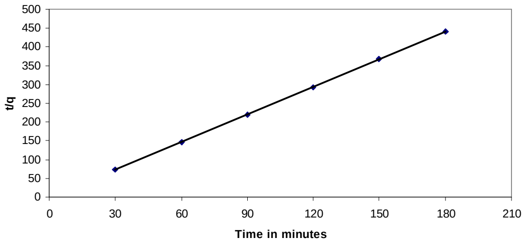

Figure 7. Pseudo second order plot on removal of crystal violet dye using sludge

Figure 7 indicated adsorption of dye on sludge gave the straight line, so it followed the pseudo second order.

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 sludge were measured within the wave number range of 400 - 4000 cm^{-1}. As can be inferred from figure 8 a and b the adsorption frequencies were shifted to higher wave numbers with the adsorption of dyes on sludge. From these findings it is presumed that the dyes were incorporated within the adsorbent through interaction with the active functional groups.

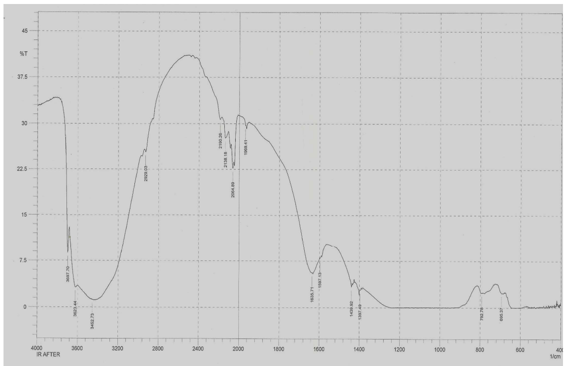

Figure 8.a FTIR spectrum of sludge

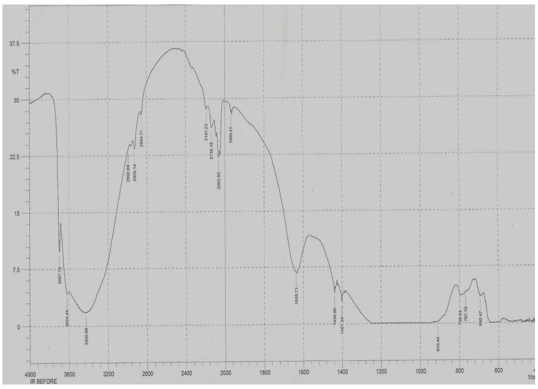

Figure 8.b FTIR spectrum of sludge after adsorption CV dye

b. Scanning Electron Microscope analysis (SEM)

The surface morphology of sludge 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× magnification are given in figures 9 a and b. At such magnification, sludge particles showed rough areas of surface within which micro pores were clearly identifiable. Comparison of these micrographs showed that the adsorption of dyes occurred on the surface of the sludge.

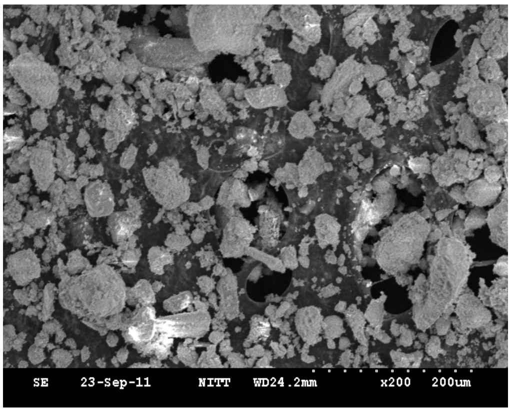

Figure 9.a: SEM micrograph of sludge

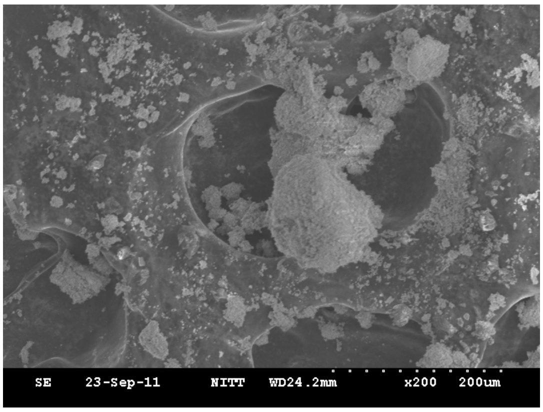

Figure 9.b SEM: micrograph of sludge after adsorption of CV dye

c. X-Ray Difraction analysis (XRD)

The Xray Diffraction studies of the sludge 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 10 a and b. 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.

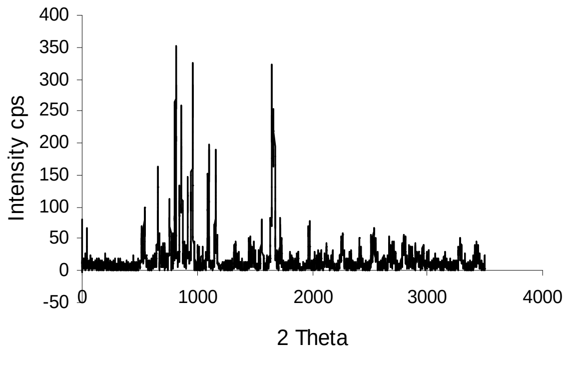

Figure 10.a: XRD pattern of sludge

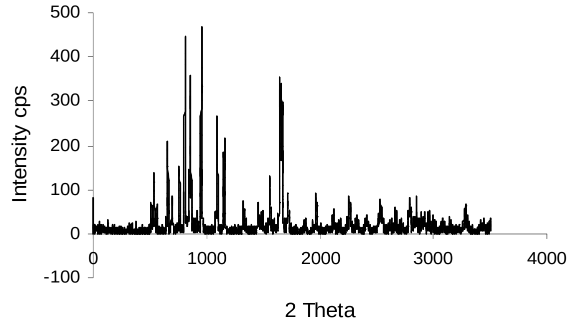

Figure 10.b: XRD pattern of sludge after adsorption of CV dye

Conclusion

In this study adsorption of crystal violet dye from aqueous solution was investigated using sludge came out from caustic industries as an adsorbent. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, contact time, and adsorbent dosage. The result also indicated that the uptake of crystal violet took place at a pH range of 2-6. Then the adsorption of crystal violet decreased with increasing pH. Equilibrium data fitted well in a Langmuir isotherm equation, confirming the monolayer sorption capacity of crystal violet onto sludge with a monolayer sorption capacity of 24.3902 mg/L (25 mg/L).

References

1. Mishra G, Tripathy M. Acritical review of the treatments for decoloutization of textile effluent. *Colourage,* 40: 35-38(**1993**).

2. Baskaralinggam P, Pulikesi M, Elango D, Ramamurthi V, Sivanesan S. Adsorption of acid dye onto organobentonite, *J.Hazard. Mater,* 128: 138-144(**2006**).

3. Ozcan A, Oncu E M, Ozcan A S. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto BTMA–natural sepilite, *Colloid Surf. A: Physicochem. Eng. Aspects*, 277: 90-97(**2006**).

4. Ozcan A, Oncu E M, Ozcan A S. Adsorption of Acid Blue 193 from aqueous solutions onto DEDMA-sepiolite,*J. Hazard. Mater*, 129: 244-252(**2006**).

5. Ravikumar K, Deebika K, Balu K. Decolourization of aqueous dye solutions by a novel adsorbent: application of statistical designs and surface plots for the optimization and regression analysis, *J. Hazard. Mater,* 122: 75-83(**2005**).

6. Ravikumar K, Pakshirajan K, Swaminathan T, Balu K. Optimization of batch process parameters using response surface methodology for dye removal by a novel adsorbent. *Chem. Eng. J,* 105: 131-138(**2005**).

7. Gupta V K, Ali I, Suhas, Mohan D. Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-lost adsorbents. *J. Colloid Interf. Sci.,* 265: 257-264(**2003**).

8. Gupta V K, Mittal A, Krishnan L, Gajbe V. Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Sep. Purif. Technol,* 40: 87-96(**2004**).

9. Mittal A, Kurup Krishnan L, Gupta V K. Use of waste materials-bottom ash and de-oiled soya, as potential adsorbents for the removal of amaranth from aqueous solutions. *J. Hazard. Mater,* 117: 171-178(**2005**).

10. Mittal A. Use of hen feathers as potential adsorbent for the removal of a hazardous dye, Brilliant Blue FCF, from wastewater. *J. Hazard. Mater*, 128: 233-239(**2006**).

11. Bhattacharyya KG, Sharma A. Azadirachta inica leaf powder as an effective biosorbent for dyes: a case study with aqueous CongoRed solutions. *J. Environ. Manage,* 71: 217-229(**2004**).

12. Ozcan A S, Oncu E M, Ozcan A. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto BTMA–bentonite, *Colloid Surf. A: Physicochem. Eng. Aspects*, 266: 73-81(**2005**).

13. Ozcan A, Oncu E M, Ozcan A S. Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite, *J. Colloid Interf. Sci.,* 280: 44-54(**2004**).

14. Kılınç A S, Ozge, Alpat, Senol A, Husamettin A. The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite. *J. Hazard. Mater,* 151(1): 213-220(**2008**).

15. Armagan B, Turan M, Celik M S. Equilibrium studies on the adsorption of reactive azodyes into zeolite. *Desalination*, 170: 33-39(**2004**).

16. Benkli Y E, Can M F, Turan M, Celik M S. Modification of organozeolite surface for the removal of reactive azodyes in fixed-bed reactors. *Water Res,* 39: 487-493(**2005**).

17. Wang S, Li H, Xu L. Application of zaolite MCM-22 for basic dye removal from wastewater, *J. Colloid Interf. Sci.,* 295: 71-78(**2006**).

18.Wang C C, Juang L C, Hsu T C, Lee C K, Lee J F, Huang F C. adsorption of basic dyes onto motmorillonite. *J. Colloid Interf. Sci.,* 273: 80-86(**2004**).

19. Selvam P P, Preethi S, Basakaralingam P, Thinakaran N, Sivasamy A, Sivanesan S. Removal of rhodamine B from aqueous solution by adsorption onto sodium montmorillonite. *J Hazard Mater*, 155(1-2): 39-44(**2008**).

20. Wang L, Zhang J p, Wang A q. Removal of methylene blue from aqueous solution using chitosan-g-poly (acrylic acid) /montmorillonite superadsorbent nanocomposite. *Colloids Surf. A: Phys. Eng. Asp.,* 322(1-3): 47-53(**2008**).

21. Turabik M. Adsorption of basic dyes from single and binary component systems onto bentonite: Simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method. *J Hazard Mater,* 158(1): 52-64(**2008**).

22. Eren E, Afsin B. Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces. *Dyes and Pigments*, 76(1) 220-225 (**2008**).

23. Ozcan A, Çigdem, Erdogan Y, Ozcan, A S. Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19. *J Hazard Mater,* 140(1/2): 173-179(**2007**).

24. Banat S F. Al-Asheh S. Al-Anbar S, Al-Refaie S. Microwave- and acid-treated bentonite as adsorbents of methylene blue from a simulated dye wastewater. *Bull Eng Geol Env.,* 66: 53-58(**2007**).

25. Ghiaci M, Kalbasi R J, Abbaspour A. Adsorption isotherms of non-ionic surfactants on Na-bentonite (Iran) and evaluation of thermodynamic parameters. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 297: 105-113(**2007**).