

Removal of Azure C Dye from Aqueous Solution Using Natural Clay Adsorbent

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Abstract: *The adsorption of Azure C cationic dye by bentonite clay was firstly studied in a batch system for various dye concentrations. The adsorption was studied as a function of contact time, and adsorbent dose, under batch adsorption technique. The concentration of the solution before and after adsorption was measured spectrophotometrically. The equilibrium data fit with Langmuir, Freundlich models of adsorption and the linear regression coefficient R² was used to elucidate the best fitting isotherm model.*

Keywords: about four key words separated by commas.

1. Introduction

Textile industry is one of the most complicated industries among manufacturing industry [1]. There are several classes of organic pollutants [organic dyes, pharmaceuticals, polycyclic aromatic hydrocarbons, polychlorinated pesticides, polychlorinated dibenzodioxins, and biphenyls] that by the seriousness of the risks they pose to environment and human health are considered priorities for environmental monitoring by the most important environmental agencies [2]. Photo-oxidation technique is one of the important techniques that is used in many fields its high efficiency in the removal of the toxic effects of the environmental pollutants [3]. Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Colour stuff discharged from these industries poses certain hazards and environmental problems. Wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man[4] There are various conventional methods of removing dyes from waters. Among these methods, adsorption is by far the most versatile and widely used method because of its low cost, ease of operation[5-6] A number of agricultural waste and by-products of cellulose origin have been studied for their capacity to remove dyes from aqueous solutions[7], such as peanut hulls[8], maize bran[9], sawdust[10], clay sugar beet pulp[11], crab peel[12], granular kohlrabi peel[13], raw barley straw[14], eggshell[15], aquacultures shell powders[16]. Activated carbon is regarded as the most effective material for removal the dyes [17], but due to its high cost and 10 – 15 % loss during regeneration, unconventional adsorbents like, wood [18], silica [19], clay and activated clay [20-21], agricultural residues [22] etc. have attracted the attention of several investigations for the removal of dyes. In the present work, the ability of charcoal to remove cationic dye, by adsorption, was considered. The effects of contact time, initial dye concentration on the amount of Colour removal were investigated.

2. Materials and Method

2.1. Adsorbents

Natural bentonite

The bentonite clay was supplied from the state company for Geological Survey and Mining – Iraq. The bentonite had the following composition with particle size less than (75) µm. Information and analysis for the surface were supplied by the same company and described below in Table (1). The molecular formula of bentonite could be written as: Mg₂Al₁₀Si₂₄O₆₀(OH)₁₂[Na, Ca]. (13)

Table 1: The molecular formula of bentonite could be written as: Mg₂Al₁₀Si₂₄O₆₀(OH)₁₂[Na, Ca]. (13)

Constituent	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	L.O.I
Wt%	56.77	15.67	4.48	3.42	0.60	1.11	5.02	12.49

2.2. Adsorbate

Azure C is an organic compound that is used as a dyestuff. It is traditionally used as a dye for materials such as silk, leather, and paper. It is known high solubility in water, λ_{MAX} = 611.5nm C₁₃H₁₂CLN₃S), other name (Basic violet 3). Fig (1) shows the scheme structural formula of dye.

2.3. Batch Mode Adsorption

Batch mode adsorption studies for individual dye were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose. Solution containing 100 ml adsorbate and 0.1 g adsorbent was taken in 250 ml capacity conical flask and agitated at 200 rpm in water bath shaker at predetermined time intervals. The adsorbate solution was centrifuge at (3000 rpm) for (30min). The percentage of dye removal (R in %) and quantity of CV (Q_e) was calculated using Eq. 1 and 2 respectively. ⁽²³⁾:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$Q_e = \frac{C_0 - C_e}{m} * V \quad (2)$$

Figure 1: scheme structural formula of dye

Where C₀ and C_e are the initial and the equilibrium concentrations (mg L⁻¹) of CV in solution, respectively Q_e, is

the amount of dye adsorbed per unit of clay mg/g, V is volume L of solution and m is the mass of adsorbent (g) used in each r experiment. The residual dye concentrations of each solution were determined by measuring their characteristic absorbance using a double beam UV-Vis Spectrophotometer (Schimadzu, uv-160A) at a wavelength (611.5nm). The spectrum for 25mg/L azure C adsorption was shown in Fig 1. The calibration curve at this wavelength was established as a function of azureC dye concentration in Fig. 2

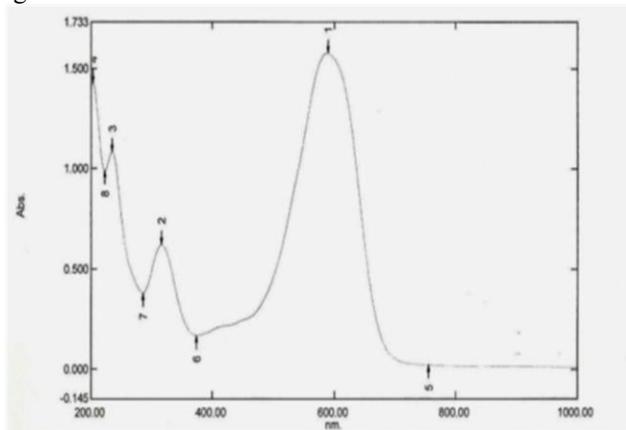


Figure 2: UV-Visible absorption spectrum for (25) mgL⁻¹ azureC dye solution

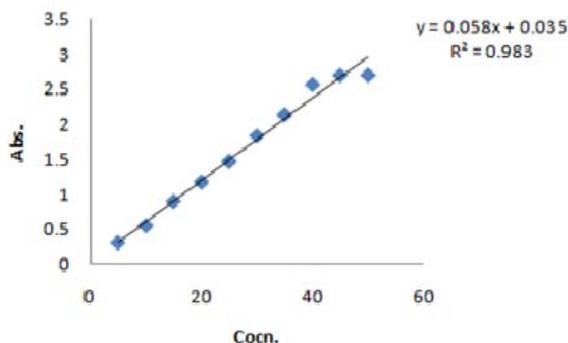


Figure 3: Calibration curve of azureC dye (5-50) ppm, pH 7, 25C⁰.

2.4. Effect of variable parameters

2.4.1. Dosage of adsorbent

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

2.4.2. Initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 5 to 50 mg/L. All other factors are kept constant.

2.4.3. Contact time

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

3. Results and Discussion

3.1. The Effect of Shaking Time

The time-dependent behavior of dye adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 5-50 min. The concentrations of dye were kept as 100 mg/L and the amount of adsorbent added was 0.1 g. The adsorption data for the uptake of azure C versus contact time was represented in Fig 4. The removal of azure C by adsorption increased with time and attained a maximum value in 40 min and thereafter it remained constant for all the concentration studied. This mean that uptake attained equilibrium at 40 min for natural and modified bentonite at the same conditions. Therefore, a 75min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent experiments⁽²⁴⁾. Although the rate behavior of bentonite was similar.

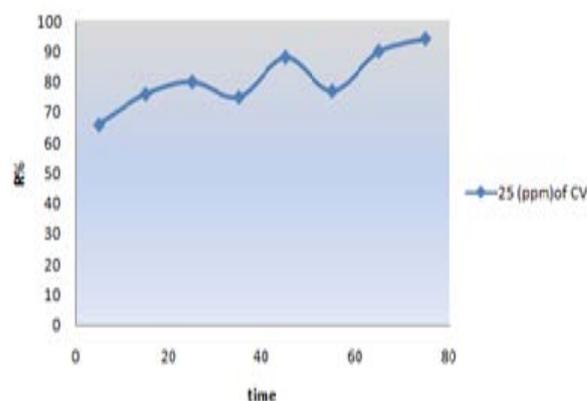


Figure 4: The Effect of contact time on azure C adsorption on natural bentonite

A rapid adsorption is observed at 5 minutes and thereafter a gradual increase in adsorption occurs with increasing contact time up to 75 minutes, after which a maximum value of adsorption is attained. After this time, the amount of dye adsorbed was not significant, very small decreases in the amount of the dye adsorbed were observed, indicating to desorption process. Therefore, the time of 75minutes is fixed as the optimum contact time. Similar results have been reported for the adsorption [25].

3.2. Adsorbent dosage

In order to study the effect of adsorbent dosage on dyes removal as the adsorption capacity with fixed initial concentration of type of dye, pH, temperature, shaking time and activated charcoal as an adsorbent, Different weight of dosage was used (0.02, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.4 g). The maximum removal of dyes was observed with the dosage (0.3 g) used for all subsequence experiments.

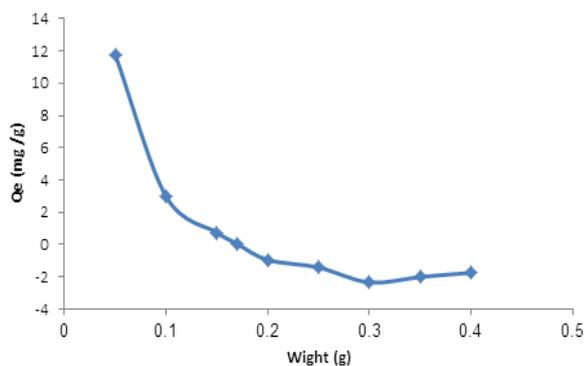


Figure 5: Show the adsorbent dosage bentonite

3.3. Adsorption isotherms

Adsorption isotherms play a very important role for understanding adsorption mechanism. The variation of the dye concentration with the same mass of the adsorbent is used to determine an adsorption mechanism. Fig (6) shows the adsorption isotherm which was of S-type. This indicating a vertical or flat orientation of adsorbate, and the adsorbate is mono functional. The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) adsorption isotherm models were applied to describe the dye-organoclay system, equations (5), (6) [26-27].

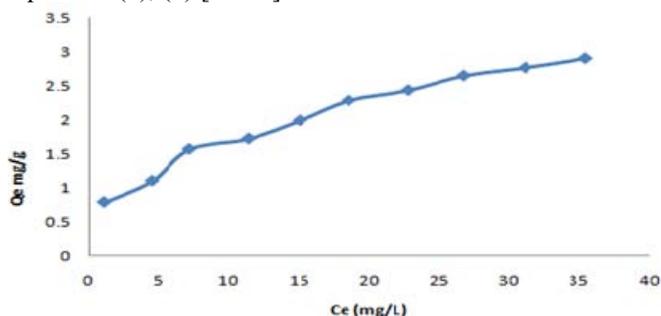


Figure 6: Adsorption isotherms of DY50 on bentonite and modified clay at 25 °C pH7

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (5)$$

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

Where Q_m is Langmuir constant related to the capacity and K_L is related to the energy of adsorption, $1/n$ and K_f are Freundlich constants related to the intensity of adsorption and adsorption capacity respectively. Fig (7) and (8) show the linear plots of Langmuir and Freundlich respectively. To confirm the favorability of the adsorption process, the separation factor (R_L) is calculated by using the [equation (7)] and presented in Table (2). The values of R_L are found to be between 0 and 1 and confirm that the ongoing adsorption process is favorable. R_L values indicate that the type of isotherm is irreversible ($R=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or unfavorable ($R_L > 1$) [28]

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Table 2: the parameters of Freundlich and Langmuir isotherms

parameters of Freundlich	T (°C)	1/n	KF	R2
	25	0.522	0.617	0.96
Langmuir parameter	T (°C)	q L	R_L	R2
	25	0.953	0.866	0.977

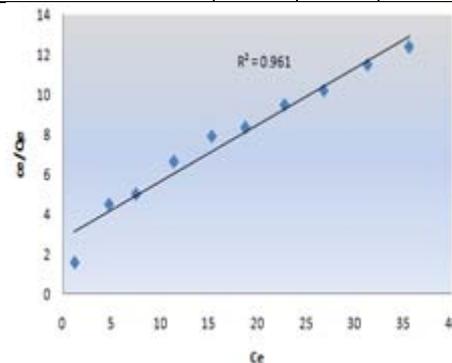


Figure 7: The linear plot of Langmuir isotherm at 25 °C

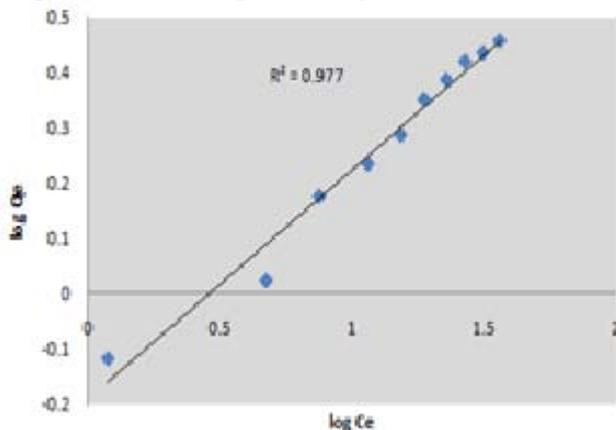


Figure 8: The linear plot of Freundlich isotherm at 25 °C

The values of $n > 1$ indicate favorable adsorption conditions. The values of linear R^2 coefficient were high (> 0.9) for Freundlich isotherm indicating the useful values of its constants. So the adsorption isotherm for the present system is explained better by Freundlich isotherm model.

4. Conclusion

This research purely focused on the Azure C Dye from Aqueous Solution, this research discussed detailed results about the Effect of contact time on azure C adsorption on natural bentonite, Adsorption isotherms play a very important role for understanding adsorption mechanism, Adsorption isotherms of DY50 on bentonite and modified clay at 25 °C pH7, In the present work, the ability of charcoal to remove cationic dye, by adsorption, was considered. The effects of contact time, initial dye concentration on the amount of Colour removal were investigated.

References

- [1] Gupta, V. K., Mittal, A., Krishnan, L., Gajbe, V., Sep. Purif. Technol., 2004, 40, 87-96.
- [2] Kareem, S. H., and Ennas, A.B., J. Baghdad Sci., 2013, 9(4),680-688

- [3] Rahmatollah, R., Mahboube, R., and Marziye, K., "Study of tetracarboxylporphyrin covalently to silica in the removal of crystal violet aqueous solution", Iran, Tehran, 213-223, (2003).
- [4] "Low cost biosorbents for dye removal", CES Technical Report 113, (2004).
- [5] Min-Yu, T., Su-Hsia, L., "Removal of methyl orange dye from water onto raw and acid activated montmorillonite in fixed bed,". Desalination, vol. 201, p. 71-81, 2006.
- [6] Malik, P.K., "Use of Activated carbons prepared from sawdust and rice- husk for adsorption of acid dyes: a case study of acid yellow 36", Dyes Pigments, vol. 56, p. 239- 249, 2003.
- [7] Nafeesa, J. K., (Adsorption study for Triflurain on Iraqi α - Alumina), J. Baghdad, Sci., vol 9(1)2012
- [8] Brown, P., Jefcoat, I.A., Parrish, D., Gill S., and Graham, E., (Advances in Environmental Research), Ed, 4, 19-29(2000).
- [9] K. K. Singh, M. Talat and S. H. Hasan, Bioresource Technology, 97, 2124-2130(2006).
- [10] Taty-Costodes, V. C., Fauduet, H., Porte, C., and Delacroix, A., Journal of Hazardous. Materials, B105, 121-142(2003).
- [11] Reddad, Z., Gerente, C., Andres Y., and Cloirec, P.L., J, Environmental Sci., and Tec., 36,2067-2073 (2002).
- [12] Vasanth, K. K., (Dyes and Pigments),74, 595-597(2007).12.
- [13] Ministry of Industry and Minerals State Company of Geological Survey Mining,2000. "Physical and Chemical specifications of Geological Raw Materials and Processed products
- [14] Yavuz Ö., and Aydin A. H. 2006. 'Removal of Direct Dyes from Aqueous Solution Using Various Adsorbents', Polish J of En S. 15, (1) ,155-161.
- [15] Venkatraman, B. R., Hema, K., Nandhakumar, V. and Arivoli, S. 2011."adsorption thermodynamics of malachite Green Dye onto Acid Activated low cost" J. Chem. Pharm. Res., 3(2): 637-649.
- [16] IhanGulgonul, (2012)" Evaluation of Turkish bentonite for Removal dyes from textile wastewaters", Physicochem.Prolo. Miner.Process.48((2),369-380).
- [17] Tilaki, R.A. (2012) "kinetic Study on adsorption of Reactive Yellow dye by Bentonite and Organo-bentonite ", Res. J. cahem. Environ., 16,156-165.
- [18] Ucun, H. (2011)"Equilibrium, thermodynamic and kinetics of reactive black 5 bio sorption on loquat Seed "Sci Res and Essays,6,4113-4124.
- [19] Ding.Z.,Zhu.H.,Lu,GQ.et al, (1999)"Photo catalytic properties titania pillared clays by different drying method", J. Colloies & Interface. Sci, 209,193-199.
- [20] Raffiea Bseri J., PalanisamyP. N. and Sivakumar P. 2012."Comparative Studies of the Adsorption of Direct Dye on Activated Carbon and Conducting Polymer Composite ", E-J Ch, 9(3): 1122-1134.
- [21] Laila.Al., Feras F., Mohammad. A, and Omar. A. 2012. "adsorption from equous solution onto natural and acid activated bentonite ", A J Envi Sci, 8 (5): 510-522
- [22] Ozlem. C, and Demet. B.2001." Adsorption of Some Textile Dyes by Hexadecyltrimethylammonium Bentonite", Turk J Chem 25, 193 – 200
- [23] Mesut.T., Nihal.B. 2009. " Adsorption studies of aqueous basic dye solution using sepiolite "Gebze institute of technology, TURKEY.
- [24] Ahmad A, Hameed B H and Aziz N. 2007."adsorption of reactive dye on palm- oil industry wast" J. Hazard. Mater. 141(6): 70-76
- [25] Bellir K., Benchelktt L. M, and Meniai A. 2010. "Removal of Methylene Blue from aqueous solutions using an Acid Activated Algerian Bentonite: Equilibrium and Kinetic Studies). IRES. 5-7.
- [26] Langmuir I. 1918. (Characterization and Chemical Modification of the Silica Surface) J. Amer. Chem. Soc. 40, 1361.
- [27] Freundlich, H. 1906 (Comparative adsorption of levodopa from aqueous solution on different activated carbons), Phys. Chemie. 57, 384.
- [28] Haycock M J and Parfitt G D, Chemistry of Interfaces, Ellis Horwood Ltd. Chichester. 1981. Fasut S.D.and. Aly D.M. 1987."Adsorption processes for water treatment ", Butterworth
- [29] M. Husseien, A., Amer A., Azza EI- Maghraby, and Nahla, A., J, of Applied, Sci., Research; 3 (11): 1352-1358(2007)