

Removal of Acridine Orange from Waste Water using Different Natural clays

Dler. M. Salh

Chemistry Department, Faculty of Science and Educational Science, Sulaimaniyah University, Kurdistan Region, Iraq

Corresponding Author E-mail: dlerchem@yahoo.com

Abstract-- In the present work, different natural clays were used as solid adsorbents for the elimination of the hazardous Acridine Orange AO from wastewater. The adsorption of AO dye at a fixed initial concentration of 100 ppm on the Qwlapalk Clay (QC) and 200ppm on the Commercial Bleaching Clay CBC were carried out. The study was done in a batch system to optimize operation variables; working temperature, time and pH, for the same adsorbent quantity of QC and CBC dye solution. This procedure is particularly suitable for purification of wastewater from Acridine Orange at relatively short period of time and with low cost.

1. INTRODUCTION

Wastewater management is one of the challenging issues in the world. The traditional aim of wastewater treatment is to enable wastewater to be disposed safely, without a danger to public health, polluting watercourses or causing other nuisance. Increasingly another important aim of wastewater treatment is to recover energy, nutrients, water and other valuable resources from wastewaterⁱ. Chemistry plays a major role in providing many different materials, protocols and techniques for purification of wastewater. Wastewater can be polluted by many different chemicals; organic and inorganic. Acridine Orange can be regarded as one of the chemical substances that is present in wastewater.

Acridine Orange, we briefly denote as AO, is a heterocyclic dye containing nitrogen atoms which is widely used in the fields of printing, dyeing leather, printing ink, and lithographyⁱⁱ, it has also been used extensively in biological stain. Toxicological investigation indicates that aminoacridine has mutagenic potentialⁱⁱⁱ. In literature, there are various methods and techniques that can be used for elimination of organic dyes; among them is the adsorption process.

Many materials, like fly ash and walnut shell activated carbon silicates and porous glass,.....etc, were used as adsorbents for adsorption of wastewater contaminants like methylene blue, methyl red, malachite green, ethylene dibromide, sulfosulfuron, imazaquin, sulfentrazone, neutral bromacil, chlorotoluron, and so on ^{4,5,6 and 7}. Among the adsorbents are clays, which show a remarkable affinity for pollutants. These pollutants become bound up in the clay through the process of adsorption⁴.

Organic Compounds Contamination presents in the hydrosphere are of particular concern for the freshwater, coastal, and marine environments because of their non biodegradability and potential carcinogenic nature of the majority of these compounds^{iv}.

In literature, AO was eliminated using many different techniques, like; electrochemical degradation of AO in aqueous solution by anodic oxidation with a Ru-doped Pt electrode, this technique was applied to the remediation of wastewater containing AO^v, or in another procedure chemical oxidative was used to degraded the AO in aqueous by Fenton's reagent (Fe²⁺ and H₂O₂)^{vi}.

Other techniques include using adsorption on adsorbent material like clay for removal of AO from solutions, one of these procedures was done under identical conditions (Graphene oxide) used for elimination of AO as the adsorbent, and it was found a highly effective adsorbent, and its absorbing capability is further enhanced through its in situ reduction with sodium hydrosulfite as the reductant^{vii}. Different type of clays were investigated for adsorption of AO among of them Na-beidellite and low charged swelling clay were studied for this purpose^{viii ix}. Magnetic nanoparticles is another approach that are used for removing of AO, and about 60–90% AO was recovered and achieved by rotary evaporating the dye bearing nanoparticles in acetone, were the last could be recycled for additional dye removal^x

In the present study, a type of clay in the Qwlapalk region of Kurdistan region of Iraq was chosen as a cheap material with and compared to commercial bleaching clay (CBC) for the purpose of elimination of one of the types of dyes which is Acridine Orange

2. MATERIALS AND EXPERIMENTS

Natural clay sample was taken from Qwlapalk of Kurdistan region of Iraq, then purified, crashed and sieved, (the mesh size of 63 μm was chosen). Another type which is CBC was used. AO was of analytical grade (99.99%) and used without further purification. Other chemicals were commercial products of analytical grade or reagent grade. Elemental analysis or chemical analysis was recorded using X-Ray Fluorescence spectrometer (model Qubix-XRS). UV-vis spectra were taken with TU-1800S UV-Vis spectrophotometer, with 1cm path length quartz cell. The pH of the solutions was adjusted by using Hanna pH-meter with combined glass electrode (910600) Orion Comb pH, Water bath Thermostat Shaker (GFL 1083) was used and Micro pipettes (variable and fixed).

The calibration curve of AO was obtained by preparation of a series standard solutions of AO and measured its Absorbance by a UV-Vis Spectrophotometer at $\lambda_{max} = 492$ nm,

Batch adsorption experiments were performed by preparing two sets of 100 mL flasks containing 0.1 gm of both clays each alone with 50 mL 100 ppm for QP and 200 ppm for CBC sample of A.O at certain temperature on shaking thermostat with constant speed of 150 rpm using thermostat water bath for the pre-determined period to reach equilibrium. At the end of predefined time interval the adsorbent clays were removed from aqueous solutions by centrifuging at 3000 rpm for 10 minutes. The progress of adsorption was monitored by determining the residual concentration of AO in supernatant by UV-vis spectrophotometer at $\lambda_{max} = 492$ nm. This procedure repeated for four different temperatures (20, 30, 40 50 °C).

The pH was then adjusted for a series of flask containing 0.1 gm of both clays each alone with 50 mL (100 ppm for QP and 200 ppm for CBC) sample of AO at the optimum time and temperature for (2, 4, 6, and 8) by using 0.1M NaOH or HCl. The rest of the experiment was then followed according to the same mentioned procedure.

A series of flask containing 0.1 gm of both clays each alone with 50 mL for different standard solutions of AO were prepared from their stock solutions 1000 ppm at the optimum time and temperature. The rest of the experiment was then followed according to the same procedure.

3. RESULTS AND DISCUSSION

Samples of both types of clays were analyzed by X-Ray Fluorescence to determine their chemical composition. The result of chemical analysis for clay composition is shown in table I.

Table I
Chemical composition of the clay samples

Sample	L.O .I	SiO ₂	Al ₂ O	Fe ₂ O	CaO	MgO	Na ₂ O	K ₂ O
Qwlap alk	30.5 0	25.4 0	4.60	2.9 4	34.0 0	1.5 8	0.1 6	0.4 1
White Clay	Nil.	76.4 0	13.6 0	1.4 0	12.2 0	2.0 6	0.0 6	0.2 0

Operating conditions were optimized in order to achieve the best result of waste removal. Time and temperature were studied by varying working temperature 20, 30, 40, and 50 °C over a period of time from 0 to 500 min. As in Figure 1 and Figure 2, the best elimination capacity as AO% removal of the waste obtained at 300 min and 30 °C for both types of clay QP and CBC.

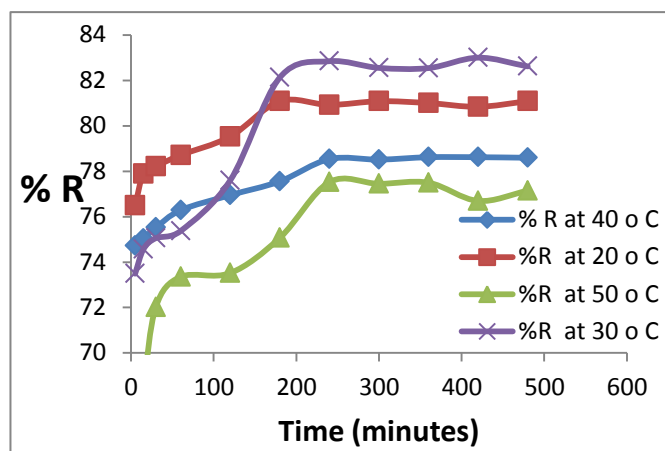


Fig. 1. Equilibrium time and temperature, – Optimization for QP

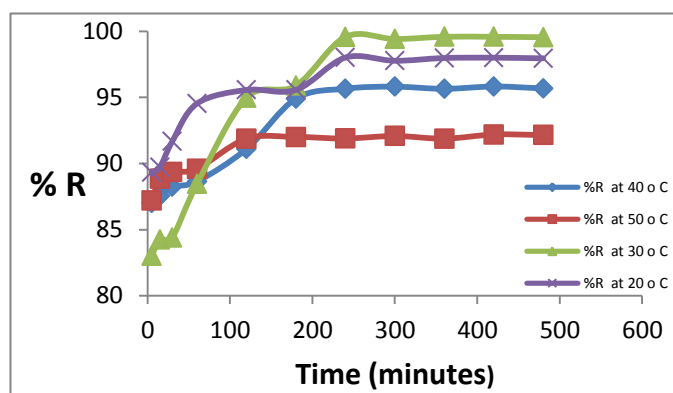


Fig. 2. Equilibrium time and Temperature – Optimization for CBC

pH of each solution was also investigated, it was found that the optimum pH were pH=4 for CBC and pH= 8 for Q.C figure (3).

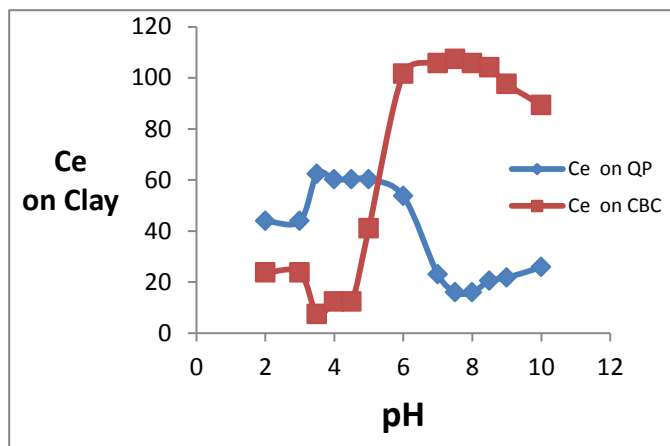


Fig. 3. Optimization of pH

Kinetic studies

The kinetics of adsorption describes the rate of AO adsorption and desorption on both type of clays (QP and CBC) and this rate controls the equilibrium time. The kinetics of

adsorptions must be optimized by operating conditions for the full-scale batch process.

The kinetic parameter, like rate constant of adsorption, gives which is helpful for the prediction of adsorption rate, important information for designing and modeling the processes. The kinetics of the adsorption data analyzed using pseudo-first-order and pseudo-second-order models.

Pseudo-first-order model

The Lagergren first-order model was used to treat the kinetic data:

$$dq/dt = k_1 (q_e - q) \dots \dots \dots (1)$$

Integrating equation (1) with respect to integration conditions:

$q = 0$ to $q = q_t$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$\text{Log}(q_e - q_t) = \text{Log} q_e - k_1 t / 2.303 \dots \dots \dots (2)$$

The slope of the plot of $\text{Ln}(q_e - q_t)$ against time t can be used to obtain the first-order rate constant $k_1 \text{ min}^{-1}$, as shown in Figure 4 and 5 for both clays QP and CBC respectively.

The adsorption first-order rate constants were found to be in the range of $(0.00365 - 0.00603) \text{ min}^{-1}$ and $(0.003775 - 0.01513) \text{ min}^{-1}$ in the temperature range of 20°C to 50°C for adsorption of AO by QP and CBC, respectively. The pseudo-first order equation can be used to describe the adsorption process, if there should be good linear relationship between $\text{Ln}(q_e - q_t)$ and t . In the present study, the plot of $\text{Ln}(q_e - q_t)$ versus time t was not linear over the entire time range Figure 4 and 5, indicating that more than one mechanism involved in adsorption.

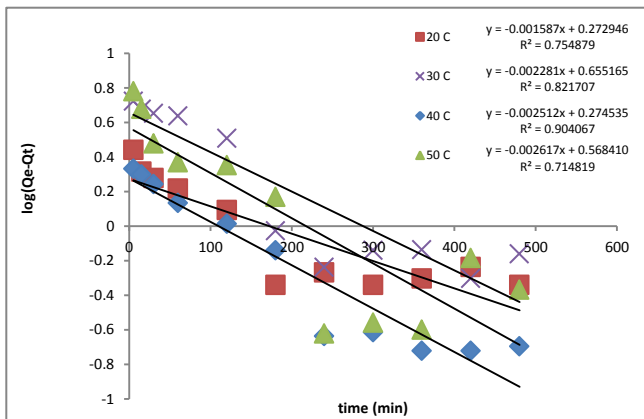


Fig. 4. Pseudo-first-order kinetics for AO adsorption by QP

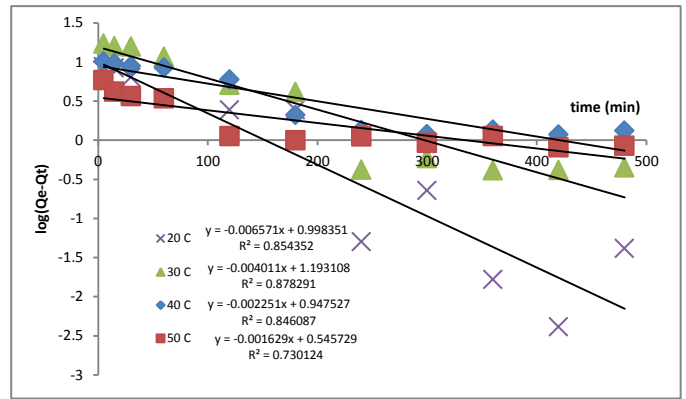


Fig. 5. Pseudo-first-order kinetics for AO adsorption by CBC

Pseudo-second-order model

Adsorption kinetics by the pseudo-second-order model was explained as follows:

$$dq/dt = k_2 (q_e - q)^2 \dots \dots \dots (3)$$

Integrating equation (3) for the boundary conditions:

$q = 0$ to $q = q_t$ at $t = 0$ to $t = t$ is simplified as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \dots \dots \dots (4)$$

The second-order rate constant represented by k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) and determined from the plot of t/q_t against t , as shown in Figure 6 and 7. The correlation coefficients of the pseudo-second-order kinetic model were higher than 0.9997. The pseudo-second-order adsorption mechanism was predominant for adsorption of metal ions by both types of clays (QP and CBC). The plot of t/q_t against t present multi linearity for AO adsorption by both clays (QP and CBC). The adsorption second-order rate constants were found to be in the range of $(0.00639 - 0.02427) \text{ min}^{-1}$ and $(0.001982 - 0.01309) \text{ min}^{-1}$ in the temperature range of 20°C to 50°C for adsorption of AO by QP and CBC, respectively.

The best the kinetic data found to be describe by the pseudo second order reaction rate model. The applicability of this model showed that sorption process is complex and involves more than one mechanism. The rate constant k_2 , the correlation coefficient R^2 and removal capacity at equilibrium state (q_e) were calculated and presented in table (2 and 3).

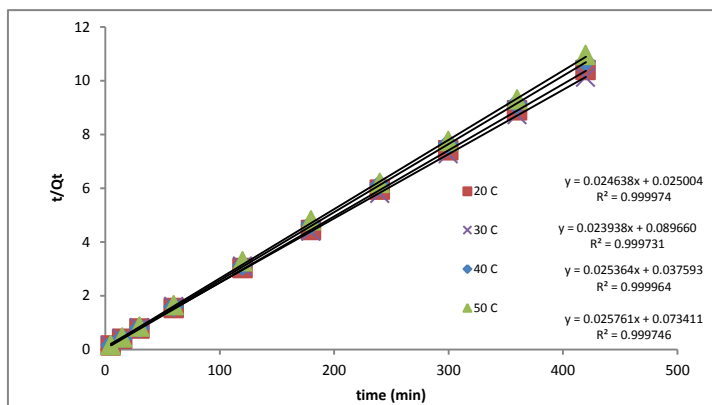


Fig. 6. Pseudo-second-order kinetics for AO adsorption by QP

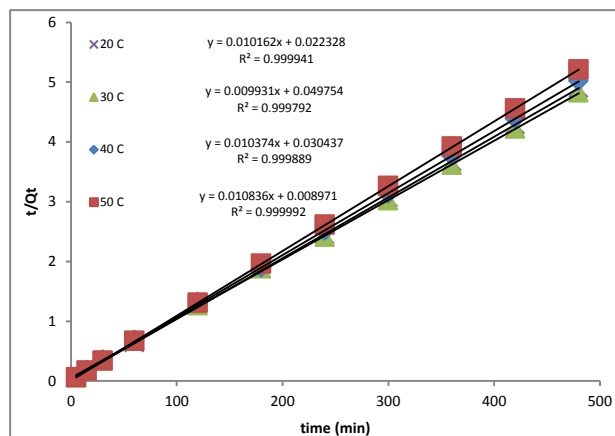


Fig. 7. Pseudo-second-order kinetics for AO adsorption by CBC

Table II
Pseudo-first-order and Pseudo-second-order model comparison adsorption rate constants for AO by QP

			Peseudo First Order kinetics			Pseudo Second Order Kineticis		
Temp	Initial Conc. ppm(Co)	Qe exp.	Qe calc. (mg/g)	k1 (min-1)	R2	Qe calc. (mg/g)	k2 (g/mg.min)	R2
20	100	41	1.87	0.00365	0.75	40.59	0.02427	0.9999
30	100	42	4.52	0.00525	0.82	41.77	0.00639	0.9997
40	100	39.5	1.88	0.00578	0.9	39.43	0.01711	0.9999
50	100	39	3.7	0.00603	0.71	38.82	0.00904	0.9997

Table III
Pseudo-first-order and Pseudo-second-order model comparison adsorption rate constants for AO by CBC

			Peseudo First Order kinetics			Pseudo Second Order Kineticis		
Temp	Initial Conc. ppm(Co)	Qe exp.	Qe calc. (mg/g)	k1 (min-1)	R2	Qe calc. (mg/g)	k2 (g/mg.min)	R2
20	200	98	9.96	0.01513	0.85	98.4	0.004626	0.9999
30	200	100	15.6	0.009237	0.87	100.69	0.001982	0.9997
40	200	97	8.86	0.005184	0.85	96.39	0.003536	0.9998
50	200	93	3.51	0.003775	0.73	92.28	0.01309	0.9999

Effect of Adsorption on % Removal

The effect of adsorption and removing of AO was found that it can be seen by increasing the dye concentration from 100 to 500 ppm added to fixed amount of both type of clays (0.1gm). The removal efficiency started with the range 95 – 99 % until the sample solution reach about 100 to 200 ppm concentration of A.O as shown in Figures 8 and 9. The efficiency of removal of A.O between 100 to 200 ppm of AO was decreased to about 75 – 80%, beyond 200 ppm, that by

increasing the concentration of A.O more than 200 ppm in the sample solutions it was retained to increased the amount removed again to reach maximum percentage about 97% , and the reason of this decreasing the amount of removal after 75ppm then after 250ppm retain to increased the amount of A.O removed, was that at low concentrations the adsorption of A.O on both types of clay is monomer adsorption while at the high concentrations of AO the adsorption leading to dimer

formations and make the removal amounts reach high percentage again^{xi}.

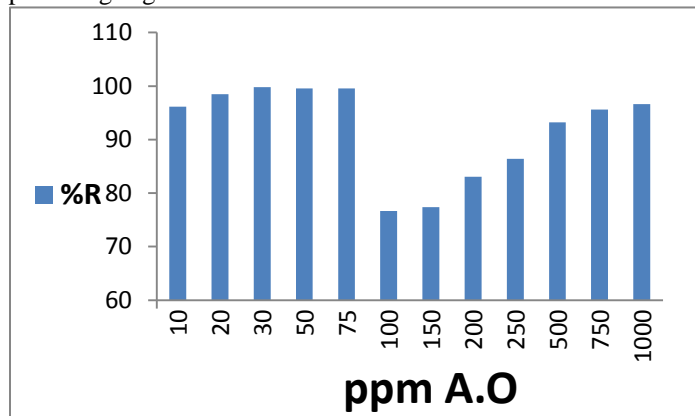


Fig. 8. Effect of adsorption dose on % removal of AO by QP

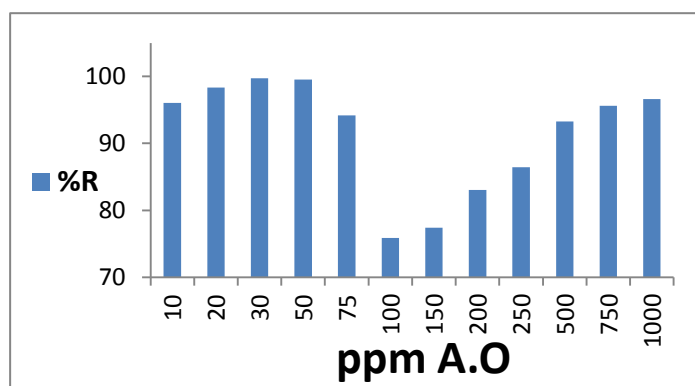


Fig. 9. Effect of adsorption dose on % removal of AO by CBC

4. CONCLUSION

The present work investigated elimination one of the toxic dyes which has a mutagenic potential, like Acridine Orange, It was found that the proposed method is simple, cheap and useful with obtaining reliable results, like the best elimination capacity as AO% removal of the waste obtained at 300 min and 30 °C for both types of clay **QP** and **CBC**, and the pH study investigate that the optimum pH were pH= 8 for **Q.C** and pH=4 for **CBC**. The adsorption kinetics of can be well described by the pseudo-second-order model equation.

ACKNOWLEDGMENT

I would like to express my gratitude to Khalid M. Omer and Bakhtyar K. Aziz for their fruitful discussions.

REFERENCES

- [1] Dr. Michael R. Templeton; Prof. David Butler "An Introduction to Wastewater Treatment" 2011, p(8-9)
- [2] Xie, Y.; Chen, F.; He, J.; Zhao, J.; Wang, H. J. Photochem. Photobiol. A: Chem. 2000, 136, 235.
- [3] Brinker, C. J.; Cornils, B.; Bonet, M. Ullmann's Encyclopedia of Industrial Chemistry, part A27; Triarylmethane and Diarylmethane Dyes; 6th ed.; Wiley-VCH: New York, 2001
- [4] A.A. Nazari Moghaddam, G.D. Najafpour, A.A. Ghoreyshi and M. Mohammadi, J. World Applied Sciences, 2010, 8 (2): 229-234

- [5] Y.C. SHARMA^{1*}, UMA S.N. UPADHYAY² and F. GODE, J. Applied Science in Environmental Sanitation, 2009, Vol. 4,1: 21-28
- [6] T. SANTHI , S. MANONMANI , T.SMITHA, International Journal of Engineering Science and Technology Vol. 2(3), 2010, 287-295
- [7] D. Zadaka, Y.G. Mishael, T. Polubesova, C. Serban, S. Nir, J. Applied Clay Science 36 (2007) 174–181
- [8] Prof. Peter Hauser (Ed.). Decolorisation of Textile Dyeing Effluents Using Advanced Oxidation Processes, Advances in Treating Textile Effluent. October, 2011 ISBN: 978-953-307-704-8,
- [9] Raskesh, S. Ananda* and Sowbhagya. International J. of Chem. And Appl. 2012, Vol. 4, No. 3, p.227-239
- [10] Chiing-Chang Chena, Ren-Jang Wub, Yi-You Tzengb and Chung-Shin Luc*. J. Chinese Chemical Society, 2009, 56, 1147-1155
- [11] Ling Sun, Hongwen Yu, Bunshi Fugetsu. J. Hazardous Materials. 203– 204, (2012) 101– 110
- [12] D. Garfinkel-Shweky and S. Yariv. J. Clay Minerals (1999) 34, 459-467
- [13] Guocheng Lv, Zhaohui Li*, Wei-The Jiang, Po-Hsiang, Jiin-Shuh Jean, Kao-Hung Lin. J. Chem. Engineering, 174(2011), 603-611
- [14] Shahnaz Qadri, Ashley Ganoee, Yousef Haik. J. Hazardous Materials. Vol. 169, 2009, 318–323
- [15] L. Antonov a.*, G. Gergov b, V. Petrov c, M. Kubista d, J. Nygren. J. Talanta 49 (1999) 99–106