

Adsorption and Kinetics of Alizarin dyes on Siliceous Rocks

Rasha Ali Mohammed, Ammar Jasim Mohammed

Chemistry Department- College of Education Ibn Al - Haytham Pure Sciences- University
of Baghdad/Iraq
chemistprof@gmail.com

Abstract

The study involves removing of [Alizarin Red S (ARS) and Alizarin yellow R (AYR)] by using Iraqi Siliceous Rocks Powder (SRP). Adsorption isotherms were studied and the factors which influence it, such as temperature and salt effect. Adsorption isotherms of (ARS) were found to be comparable to Temkin equation. Adsorption isotherms of (AYR) were found to be comparable to Freundlich equation. The adsorption process on this surface was studied at different temperatures. The results showed that the adsorption of (ARS,AYR) on surface increased with increasing temperature (Endothermic process). According to the above results the thermodynamic functions (ΔH , ΔG , ΔS) were calculated. The adsorption quantity increasing for (ARS, AYR) with increasing the saline solution .The Kinetics of the adsorption of (ARS,AYR) on surface was studied . The Kinetic experimental data properly correlated with (First and second-order kinetic) model.

Key word :- Adsorption- Siliceous Rocks- Cationic dyes- Alizarin Red S (ARS) Dye -Alizarin yellow R (AYR) Dye.

Introduction

The dyes are widely used , but they are polluting and harmful , (ARS) dye causing cancerous diseases which affects the lung Respiratory system^[1] The presence of (AYR)is involved in a huge amount in the manufacture of textile fabrics ,paper printing and cosmetics ,as this processor ends in waste water, so they dye poses severe health risks and environmental degradation and is classified form azo dyes with the least degradable ,toxic, mutagenic and carcinogenic^[2].

So many studies have been conducted on how to removal this dyes from water in different ways^[3-10]. Adsorption on surface pored was one way other methods were used, such as:(silica^[11], silica gel^[12]).

In this research the dyes (ARS, AYR) removal from aqueous solution by adsorption on Iraqi Siliceous Rocks powder(SRP).they are white color porous and high surface area, low density.



Fig.1: Siliceous Rocks powder (SRP)

Experimental

Materials (ARS ,AYR ,NaCl)were supplied by (BDH)and deionized water had been used . (Figuer.2) shows the structures of (ARS,AYR).

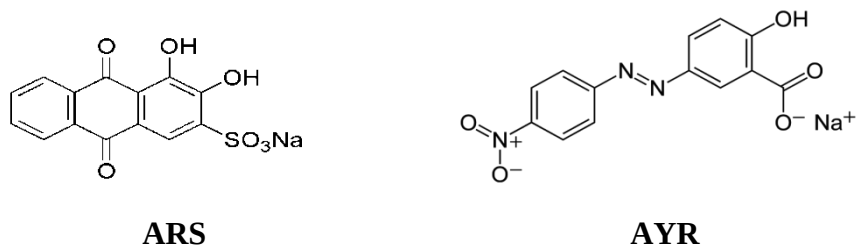


Fig. 2: Structures of ARS and AYR^[13,14]

Rocks The Siliceous Rocks Were provide by (The State Company of Mining and Geological Survey).The rocks were brought from Ukashat west of Iraq . The chemical composition of the rocks as it showed in Table (1) by the company .

Table 1: Result of Rocks Analyses

Constituent	%wt
SiO ₂	66.01
Al ₂ O ₃	2.12
Fe ₂ O ₃	0.63
TiO ₂	0.05
P ₂ O ₅	0.93
CaO	8.44
MgO	6.47
Na ₂ O	0.62

K₂O	0.13
Loss on ignition	14.61

The rocks powder it was washed excessive amounts of deionized water to remove the soluble materials . it was dried for (6 hours) at 60C^o[15] .The surface was then cracked into small parts . The particle size of (75µm) was used for the surface in this work.

Method

- 1- Technique: UV technique was used to determine the absorption as function for concentration. the wavelengths of absorption were (425,360) nm for Alizarin Red S ,Alizarin yellow R respectively.
- 2- Contact time : to determine required time for equilibrium between adsorbent and adsorbate, some certain concentration were mixed with (0.02gm) of SRP and they were put into water bath shaker under 20C^o, samples were taken from the solution in different sequenced times to determine the change in the concentration with time passing.
- 3- Adsorption isotherms: to determine the absorption isotherms for dyes solutions, (0.02gm)of the surface six round flask was weighed and then added to each (50ml) flask of dyes (ARS,AYR) with certain concentration. These flasks were placed in a water bath at (20 C^o) for(ARS=40min,AYR=210min). After the separation of the mixture ,adsorption was absorbed by UV spectrophotometer .

The adsorption quantities were calculated by used following equation ^[16] :

$$Q_e = \frac{(C_o - C_e)V}{m}$$

Q_e= the quantity of adsorbate(mg/g).

V= volume of solution (L).

C_o= initial concentration (mg/L).

C_e= equilibrium concentration(mg/L).

m= mass of the surfaces(g).

The previous step were repeated at different temperatures to follow the adsorption of the dyes on the surface when the temperatures changed .

Results and discussion

1- Effect of contact time

for the increase of adsorption as a function of time , the result show the contact time for (ARS,AYR) dyes at (40min,210min) respectively.

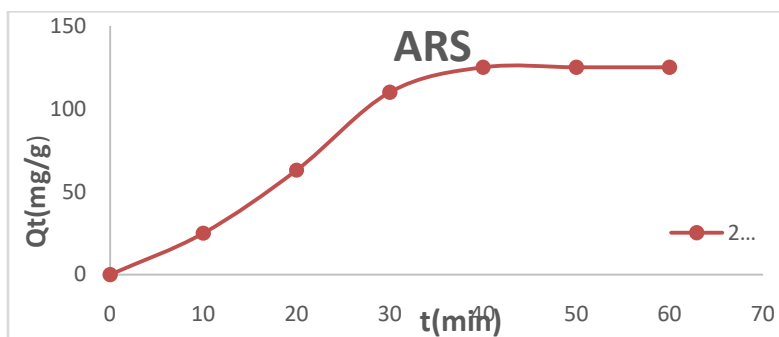


Fig. 3: Effect of contact time on(ARS) adsorption on SRP (Temperature = 20°C, rotations per minute=90rpm, Concentration of dye= 200 ppm, equilibrium time =(40min).

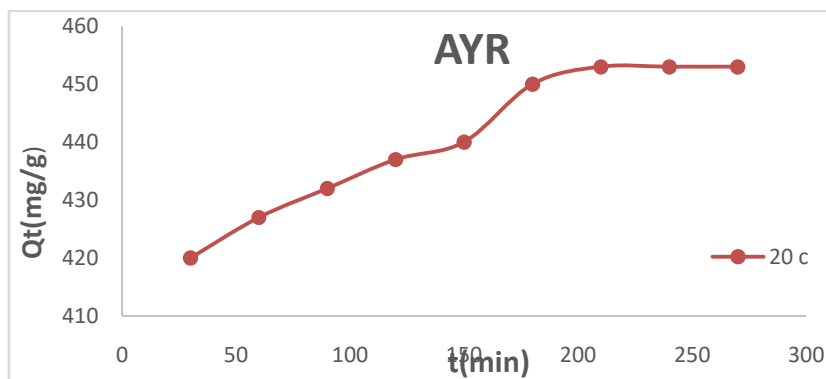


Fig. 4: Effect of contact time on(AYR)adsorption on SRP (Temperature = 20°C, rotations per minute=90rpm, Concentration of dye= 35 ppm, equilibrium time =(210min).

2- Adsorption isotherms

The adsorbed quantity (Q_e) for each equilibrium Concentration was calculated . Q_e Vs C_e plotted to show the general scheme of adsorption isotherms as show in figures (5) .

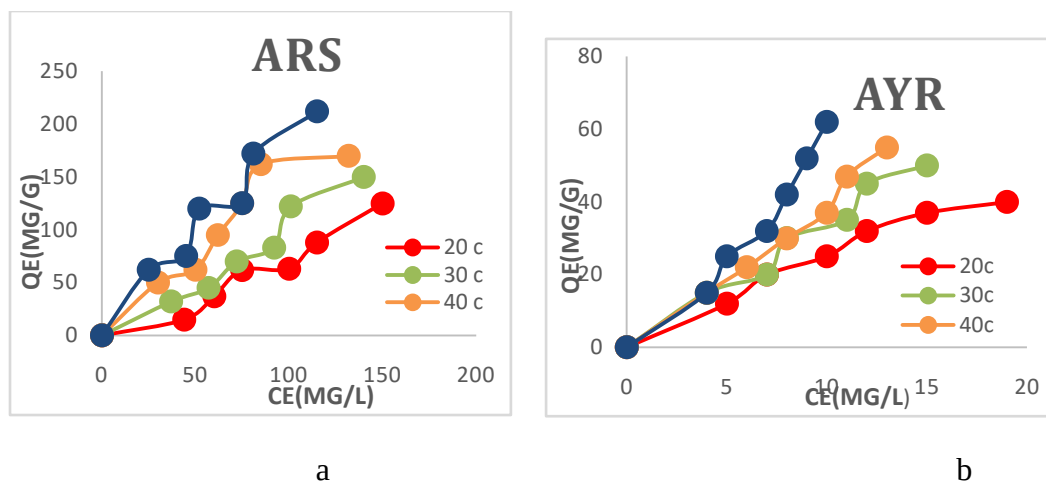


Fig. 5: (a,b) Adsorption isotherms of(Alizarin Red S ,Alizarin yellow R) dyes on SRP at different temperature.

The general scheme of adsorption isotherm of (ARS,AYR) on SRP surface pointing out these ware of (S_3) class according to Giles classification where the orientation of the adsorbate particles on the surface is bevel vertical ^[17]. Depend Temkin equation ∴

$$Q_e = b_T \ln k_T + b_T \ln C_e \quad \dots \dots \dots \text{Temkin equation}$$

Where b_T, k_T = Temkin constant

Q_e Vs $\ln C_e$ was plotted as shown in figure 6:(a,b) .Temkin constant were calculate for (ARS,AYR)dyes as shown in Table(2).

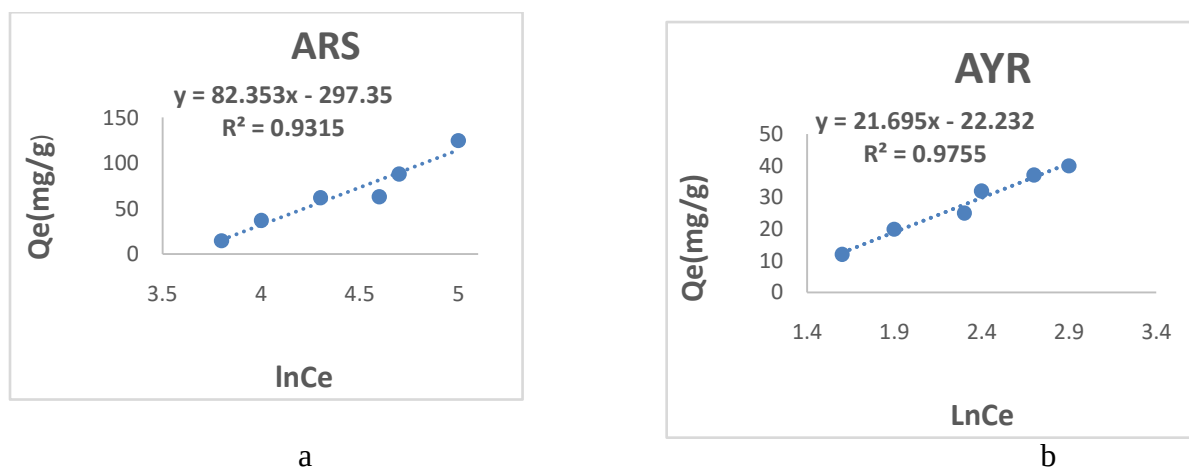


Fig. 6(a,b): Linear application of Temkin equation

Table 2 : The value of Temkin constant (b_T, k_T) for adsorption of (ARS,AYR) dyes on SPR

293K			
Dyes	b_T	$\text{Ln}k_T$	R^2
ARS	82.353	0.0270	0.9315
AYR	21.695	0.3589	0.9755

Depend Freundlich equation .

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \dots \dots \dots \text{Freundlich equation}$$

where k_f , n = Freundlich constant

$\ln Q_e$ Vs $\ln C_e$ was plotted as shown in figure 7:(a,b) .Freundlich constant were calculate for (ARS,AYR) dyes as shown in Table(3).

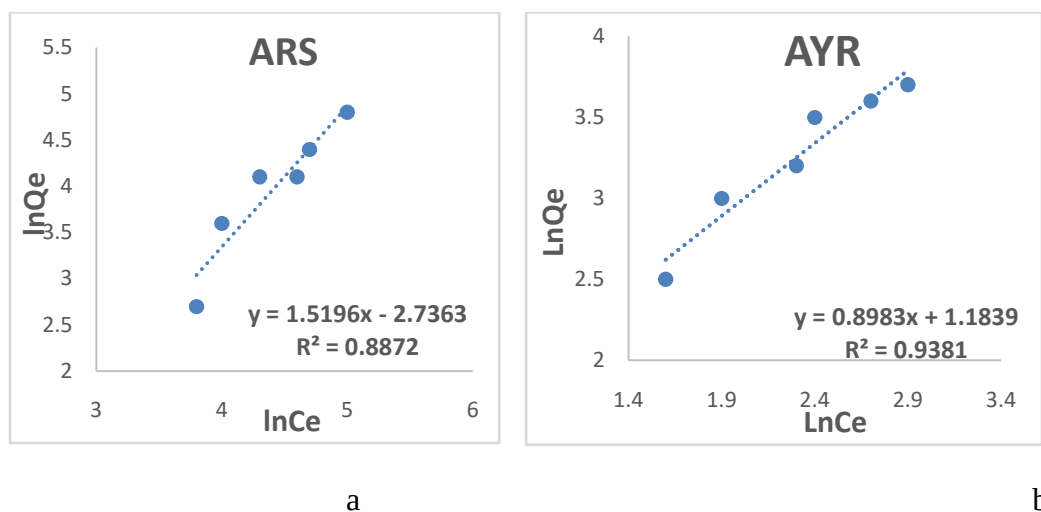


Fig. 7(a,b): Linear application of Freundlich equation

Table 3: The value of Freundlich constant (k_f, n) for adsorption of (ARS,AYR) dyes on SPR

293K			
dyes	k_f	n	R^2

ARS	0.0648	0.6580	0.8872
AYR	3.2670	1.1132	0.9381

The adsorption quantity increases at (ARS,AYR)dyes when increasing temperature (Endothermic process) .

The value of (ΔH) calculated by using Vant Hoff- Arrhenius equation :

$$\ln X_m = \frac{-\Delta H}{RT} + \text{Constant}$$

Where X_m : Maximum adsorbed quantity .

R : gas constant .

T: temperature .

$\ln X_m$ Vs Inverted temperature ($1/T$) was plotted as show in (figure 8) and (Table 4) .

The value of ($\Delta G, \Delta S$) were calculated as shown in Table (5), depending on following equations:

$$\Delta G = - \frac{nRT \ln Q_e}{C_e}$$

$$\Delta G = \Delta H - T\Delta S$$

Table 4: The value of $\ln X_m$, T for (ARS,AYR) dyes on SPR

T(K))	ARS		AYR	
	X_m (mg/g) When $C_e=100$ (mg/L)	$\ln X_m$	X_m (mg / g) When $C_e= 10$ (mg/L)	$\ln X_m$
293	63	4.14	25	3. 21
303	120	4.78	32	3.46
313	165	5.10	37	3.61
323	198	5.28	62	4.12

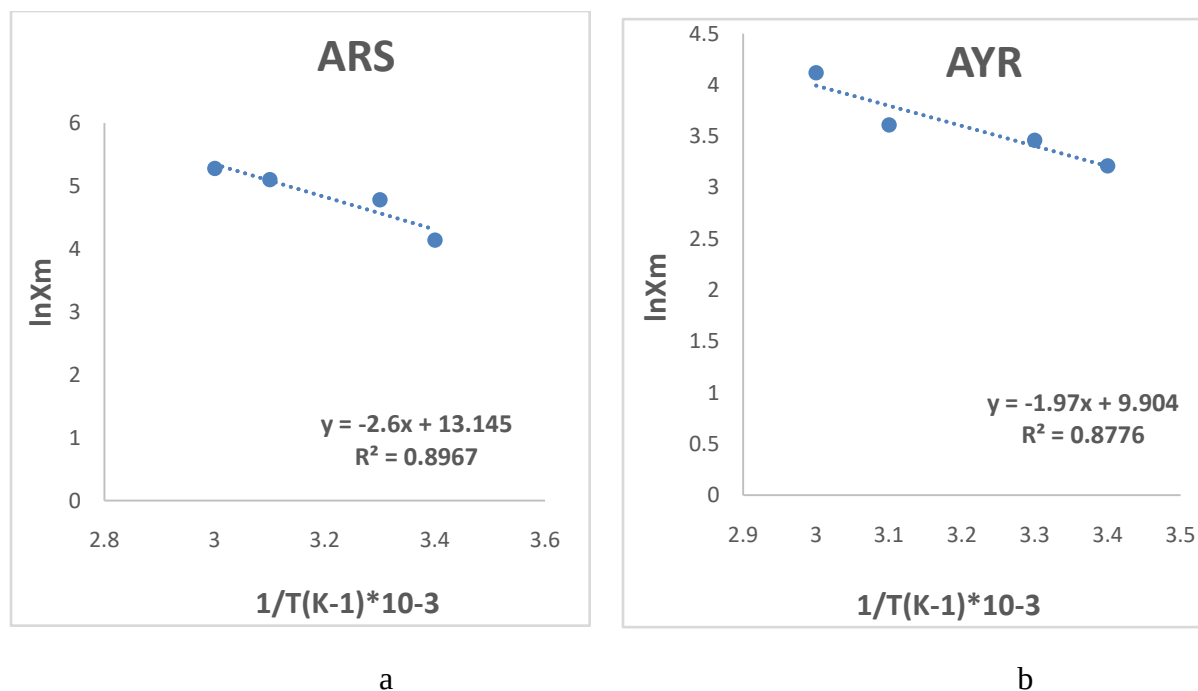


Fig. 8:(a, b) Vant Hoff curves for adsorption of (ARS,AYR) dyes on the surface

Table 5: The values of the thermodynamic functions of the dyes at (293 K)

Dyes	$\Delta H (J\backslash mole)$	$\Delta G (J\backslash mole)$	$\Delta S (J\backslash mole.K)$
ARS	21.62	1125.51	-3.77
AYR	16.38	-2232.09	7.67

The positive value of ($\Delta H, \Delta G$) while (ΔS) were negative values for (ARS) dye . The adsorbent molecules arranged on the surface ^[18].

The negative value of (ΔG) , while ($\Delta H, \Delta S$) they were positive for (AYR) dye . Prove that the adsorbed molecules were increasing randomly ^[19].

3- Effect of salt

The adsorption was studied in different salt (0.02gm) to (ARS,AYR) dyes as shown in figure (9).

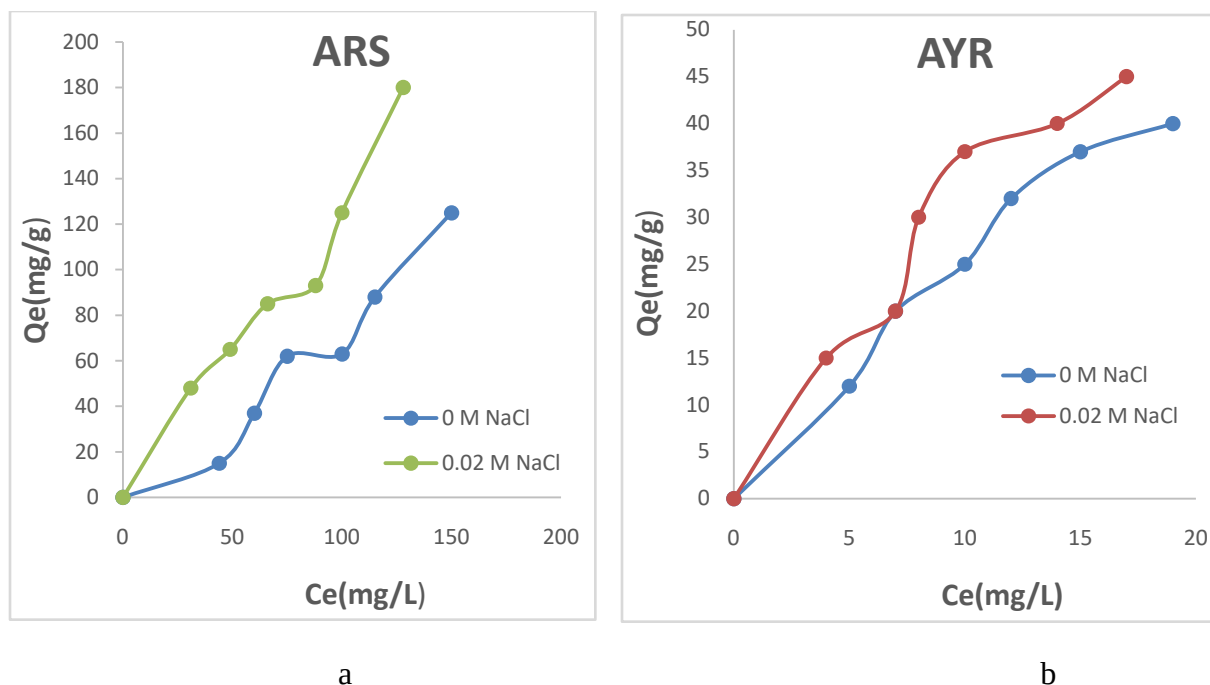


Fig. 9: (a,b) Effect of salt on Adsorption of (ARS,AYR) dyes on SRP at T = 298 K

Increasing of adsorption with increase of salt is refer to that the SRP surface is ^[20].

4- Adsorption Kinetic

Kinetic studies for dyes (ARS,AYR), by used (Largergreen equation) :

$$\ln (q_e - q_t) = \ln q_e - k_{ad} t$$

where q_e and q_t : are the adsorption capacity at equilibrium and at time (t) respectively (mg/L).

K_{ed} : the rate constant of pseudo first- order kinetic adsorption (min^{-1}).

The adsorption results that the adsorption kinetics followed pseudo first- order kinetics model , as shown in figure (10), table(6) shown value the rate constant of adsorption.

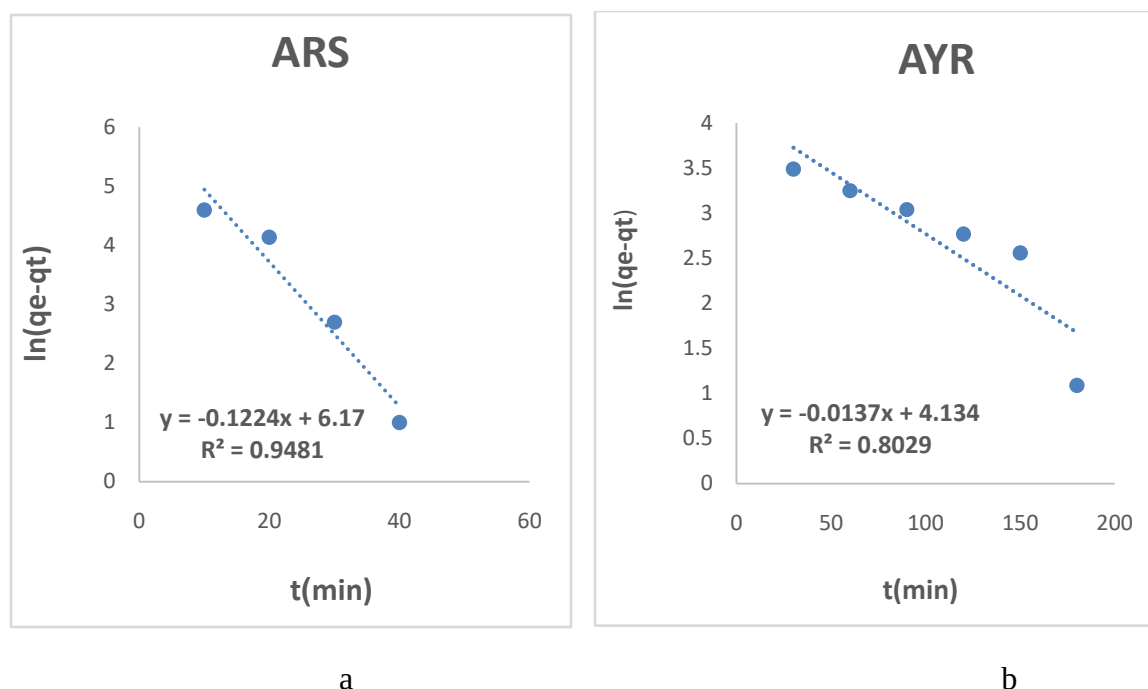


Fig.10: (a,b)The adsorption kinetics of the(ARS,AYR) dyes on the surface

Table.6: value the rate constant of adsorption for dyes on the surface

Dyes	$k_{ad} \text{ (min}^{-1}\text{)}$
ARS	0.1224
AYR	0.0137

And kinetic studies for dyes (ARS,AYR), by used second – order:

$$\frac{t}{qt} = \frac{1}{k_{ad} 2q_e^2} + \frac{t}{q_e}$$

where q_e and q_t : are the adsorption capacity at equilibrium and time (t) respectively (mg/L),

K_{ad2} : the rate constant of pseudo second- order kinetic adsorption $(\text{mg/L})^{-1} \cdot \text{min}^{-1}$

The adsorption results that the adsorption kinetics followed pseudo second- order kinetics model , as shown in figure (11), table(7) shown value the rate constant of adsorption.

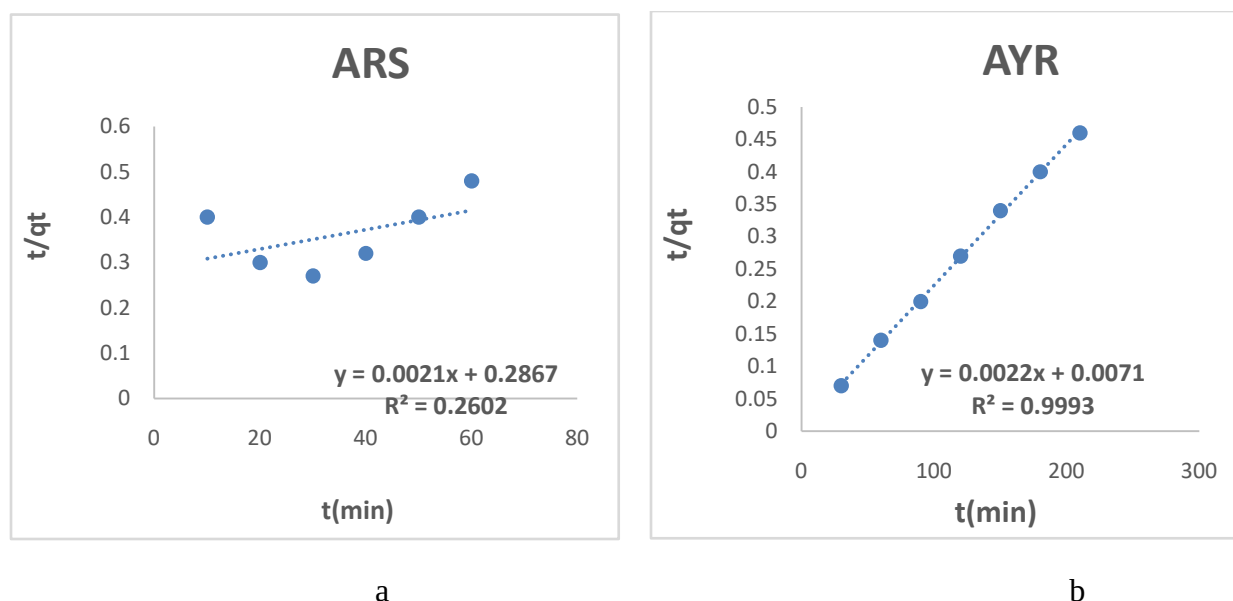


Fig.11: (a,b)The adsorption kinetics of the(ARS,AYR) dyes on the surface

Table.7: value the rate constant of adsorption for dyes on the surface

Dyes	$k_{ad2}(\text{mg/L})^{-1}.\text{min}^{-1}$
ARS	3.3879
AYR	140.845

References

- Baruah, M., Supong, A., Bhomick, P. C., Karmaker, R., Pongener, C., & Sinha, D. (2020), Batch sorption–photodegradation of Alizarin Red S using synthesized TiO_2 /activated carbon nanocomposite.
- Gupta, S., Mittal, Y., Tamta, P., Srivastava, P., & Yadav, A. K. (2020), "Textile wastewater treatment using microbial fuel cell and coupled technology: a green approach for detoxification and bioelectricity generation" , In Integrated Microbial Fuel Cells for Wastewater Treatment, (pp. 73-92).
- Khapre, M. A., & Jugade, R. M. (2020), "Hierarchical approach towards adsorptive removal of Alizarin Red S dye using native chitosan and its successively modified versions" Water Science and Technology, 82(4), 715-731.
- Malakhova, I., Privar, Y., Parotkina, Y., Eliseikina, M., Golikov, A., Skatova, A., & Bratskaya, S. (2020),"Supermacroporous monoliths based on polyethyleneimine: Fabrication and sorption properties under static and dynamic conditions", Journal of Environmental Chemical Engineering, 8(6), 104395.
- Ali, Nisar, et al. (2020), "Characterization and deployment of surface-engineered cobalt ferrite nanospheres as photocatalyst for highly efficient remediation of alizarin red S dye

- from aqueous solution." *Journal of Inorganic and Organometallic Polymers and Materials*, 30,12,5063-5073.
6. Liu, M., Zhang, X., Li, Z., Qu, L., & Han, R. (2020)," Fabrication of zirconium (IV)-loaded chitosan/Fe₃O₄/graphene oxide for efficient removal of alizarin red from aqueous solution", *Carbohydrate Polymers*, 248, 116792.
7. Tiwari, D., Lee, S. M., & Kim, D. J. (2020),"New insights in photocatalytic removal of Alizarin Yellow using reduced Ce³⁺/TiO₂ catalyst", *Environmental Science and Pollution Research*, 1-11.
8. Mahmoudi, F., Amini, M. M., & Sillanp., M. (2020), "Hydrothermal synthesis of novel MIL-100 (Fe)@ SBA-15 composite material with high adsorption efficiency towards dye pollutants for wastewater remediation", *Journal of the Taiwan Institute of Chemical Engineers*, 116, 303-313.
9. Tiwari, D., Tiwari, A., Shukla, A., Kim, D. J., Yoon, Y. Y., & Lee, S. M. (2020),"Facile synthesis and characterization of nanocomposite Au⁰ (NPs)/titanium dioxide: Photocatalytic degradation of Alizarin Yellow", *Journal of Industrial and Engineering Chemistry*, 82, 153-163.
10. Yu, F., Chen, Y., Pan, Y., Yang, Y., & Ma, H. (2020), "A cost-effective production of hydrogen peroxide via improved mass transfer of oxygen for electro-Fenton process using the vertical flow reactor", *Separation and Purification Technology*, 241, 116695.
11. G.MchKay, M.S.Otterburn and A.G.Sweeny,(1980)." *Water Research*, 14,pp21-27.
12. V. Ponec, Z. Knor and S. (1947), *Adsorption of Solids*, 1st, Butterworth, London.
13. Dickson, J. A. D. (1966),"Carbonate identification and genesis as revealed by staining", *Journal of Sedimentary Research*, 36 (4), 491– 5058
14. Lide, David R. (2008), *CRC Handbook of Chemistry and Physics*, 89thed, CRC Press.
15. R. H. Ali , (2009). " A Study of Adsorption of some Metals Cations from their Aqueous solution on some Iraqi Mineral Surfaces and their Modifications" A Thesis Ph.D , College of Science for Women-University of Baghdad.
16. H.I. Tarkih, (1973). " Liquid- Solid Adsorption Studies : an experimental study and A Mathematical Modulation of Multi stage adsorption Apparatus ", Victoria University of Manchester .
17. F. J. Hesselink, (1977). " On the theory of polyelectrolyte adsorption: The effect on adsorption behavior of the electrostatic contribution to the adsorption free energy" *Colloid Interface Sci.*, 60, 448-.664.
18. K.K.Panday, Gup.presad N.V. Singh, (1985), ,*Water Research* .,19(7),pp.869 -873.
19. E.H.M.Wright and N.C. Partt, (1961)."Current chemical Papars", *J. Chem. Soc. Faraday Trans.*, 70 , 1461
20. D.Hillel , (1980). "Fundamentals of Soil Physics", Academic Press, New York.