FULL PAPER

Removing some alizarin dyes from an aqueous solution using a polyacrylic acid hydrogel

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The present work utilizes polyacrylic acid beads (PAA) to remove Alizarin yellow R (AYR)] and Alizarin Red S (ARS) from its solution. The isotherms of adsorption were investigated and the factors that impact them, such as temperature, ionic strength effect, shaking effect, and wet PAA. The isotherms of adsorption of (ARS) were found obeys the Freundlich equation. The isotherms of adsorption of (AYR) were found obeys the Langmuir equation. At various temperatures, the adsorption process on (PAA) was investigated. According to our data, there is a positive correlation between the (ARS and AYR) adsorption on the PAA and temperature (Endothermic process). The computation of the thermodynamic functions (ΔH, ΔG, and ΔS) is based on the foregoing findings, and the ionic strength influence on the dyes adsorption was determined at (20 °C). It was discovered that adsorption decreases in the presence of different salt concentrations and tap water. The adsorption kinetics were investigated, and the data were examined by the Lagergren Equation and the second-order equation model. Based on the experimental data, the adsorption was pseudo first-ordered kinetics changed in response to changing conditions.

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KEYWORDS

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Introduction

Dyes which are organic compounds could pollute water, and as a result, they are widely used in various industries [1], including petroleum, textiles, dyeing, photographic coloring, paper, rubber, leather, pharmaceuticals, plastics, and various other areas [2]. These industries release dye-contaminated wastewater large amounts every year, most of these dyes irritate the skin, and the water-polluted dye reduces photosynthesis, and thus prevents light penetration [3]. Each year, about 80,000 tons of manufactured and consumed dyes are used because they are inexpensive and come in various colors [4], and thus, their existence in wastewater concerns environmentalists [5]. The dyes are commonly utilized but polluting

and dangerous, and the Alizarin Red S dye (ARS) causes malignant disorders of the lungs and respiratory system [6]. Because the Alizarin Yellow R dye (AYS) is used in large quantities in the production of textiles, paper printing, and cosmetics, and because this process leads to wastewater pollution, it poses serious health and environmental risks. It has been classified as an azo dye, the least biodegradable, toxic, carcinogenic, and mutagenic [7]. A lot of research works have been conducted for the removal of these colors from water in various ways [8,9]. Over the past decade, a lot of work has been done to develop better techniques for removing pigments from water [4]. In addition to the surface adsorption, methods such as silica [1] and silica gel [10] have been used. In this work, polyacrylic acid hydrogel (PAA) granules have

been used, which are flexible polymer chains that make it easy for solute molecules with water to penetrate the hydrogel. They were colorless and [11] and were used to remove
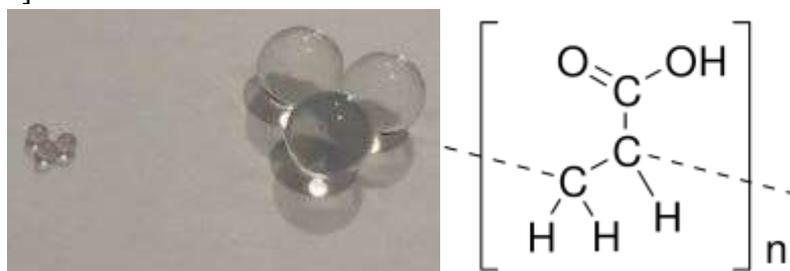

FIGURE 1 Polyacrylic acid hydrogel beads

Experimental

(BDH) provided the materials (ARS, AYR, NaCl, and PAA) and distilled water was used. Figure 2 illustrates the architecture of (ARS and AYR).
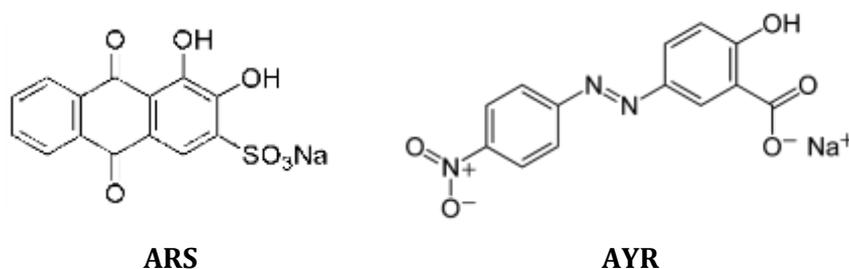

ARS   **AYR**

FIGURE 2 AYR and ARS structures [12,13]

Methods

1. The absorbance as a concentration function was decided by the UV-Vis technique. Absorption wavelengths for Alizarin Red S and Alizarin Yellow R were (425 and 360) nm, respectively.
2. The determination of the required time of equilibrium between adsorbate and adsorbent, some of their concentrations were mixed with (0.1 g) of polyacrylic acid hydrogel beads and put in a water bath shaker at 20 °C. We took the samples from the solution at different times to determine the change in concentration over time.
3. Adsorption isotherms: The measurement of the adsorption isotherms for dye solutions, we weighed (0.1 g) of the surface six round flasks, and then put to each (50 mL) dyes flask (ARS, AYR).We submerged these flasks in a water

ARS and AYR dyes from aqueous solutions. Figure 1 shows the polymer before and after the adsorption process.

bath at (20 °C) for (ARS=210 minutes and AYR=60 minutes). When the mixture was separated, we determined the adsorption by the UV-Vis spectrophotometer.

The determination of the adsorption quantities is based on the following equation [14]:

$$Qe = \frac{(Co - Ce)Vs}{m} \quad (1)$$

Q_e= the adsorbate (mg/g) quantity.
C_o= initial concentration (mg/L).
V_s= solution volume (L).
m= the surfaces (g) mass
C_e= equilibrium concentration (mg/L).

We repeated the preceding procedure at various temperatures to track the adsorption of dyes on the surface as the temperatures varied.

Results and discussion

Contact time effects

The equilibrium time for (ARS and AYR) dyes is (210 min and 60 min), respectively of the adsorption rise as a function of time, as displayed in Figures 3 and 4.
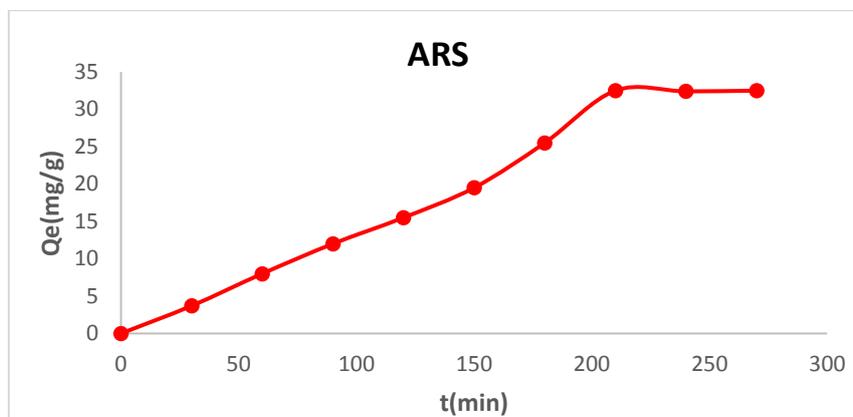

FIGURE 3 The equilibrium time of the (ARS) dye on the (PAA) surface was estimated by using the following parameters: temperature=20 °C, rotations per minute=90, dye concentration=200 ppm, and equilibrium time=210 minutes
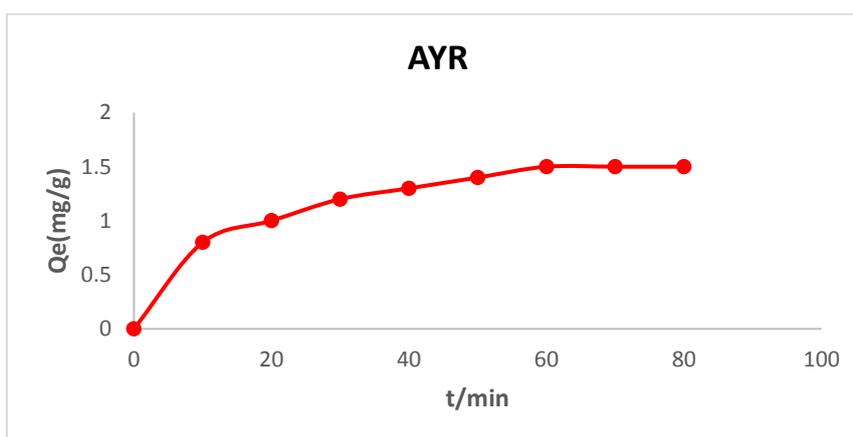

FIGURE 4 The equilibrium time of the (AYR) dye on the (PAA) surface was estimated by using the following parameters: temperature=20 °C, rotations per minute=90, dye concentration=20 ppm, and equilibrium time=60 minutes

Adsorption isotherms

For each equilibrium concentration, the adsorbed amount (Q_e) was computed. Figure 5 illustrates Q_e vs. C_e plotted to demonstrate the general adsorption isotherm scheme.

The overall scheme of the adsorption isotherm of ARS and AYR on the PAA surface highlights these wares as belonging to the (S3) class according to Giles classification, in which

the surface adsorbate particles are bevel vertical [15].

Here, the Temkin's equation is based on:

$$Qe=b_TLnK_T+b_TLnCe \qquad (2)$$

Where, b_T and k_T are the Temkin constants. Figure 6a, b demonstrates the graph of Qe vs. LnCe. The Temkin constants for (ARS and AYR) dyes were calculated, as represented in Table 1.
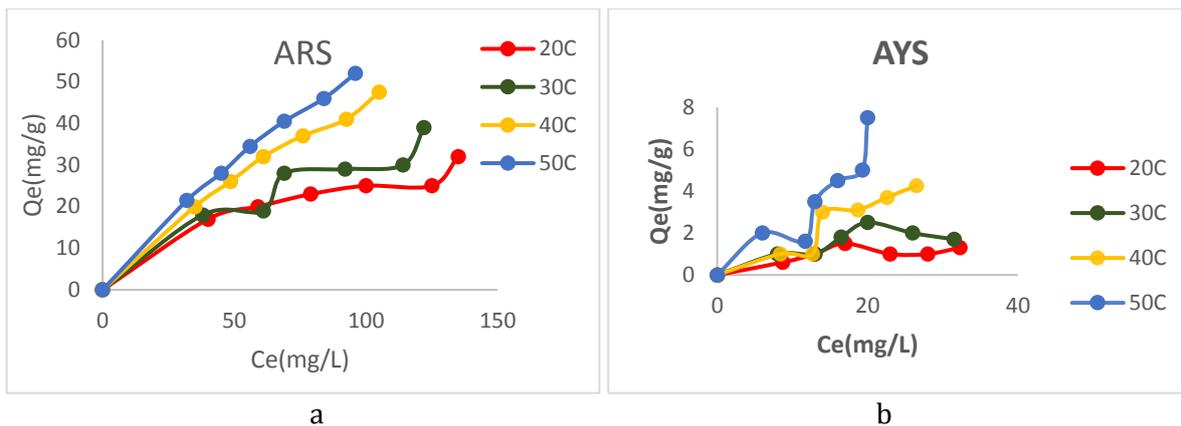
a   b

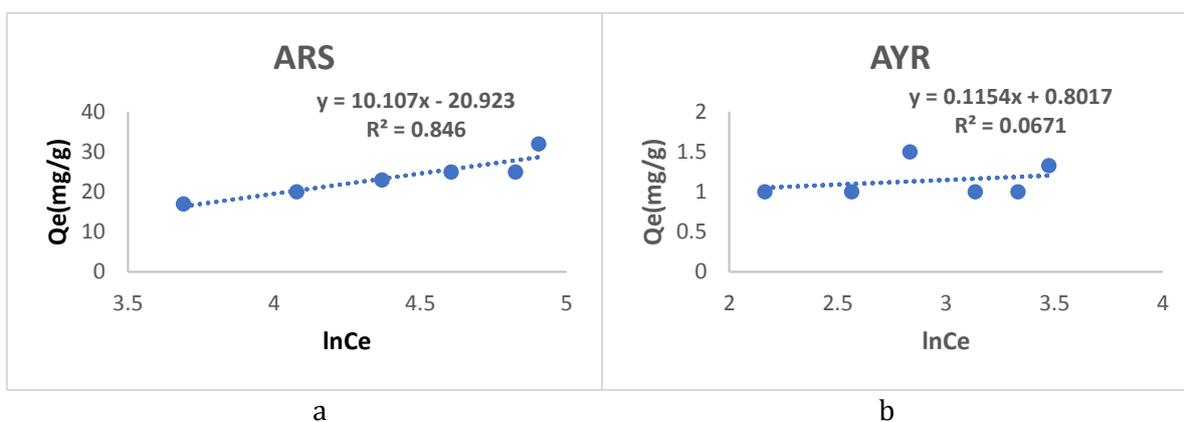**FIGURE 5** (a,b) Adsorption isotherms of (AYR and ARS) dyes on (PAA) at various temperatures

a   b

FIGURE 6 (a,b) Temkin equation linear applications

TABLE 1 Temkin constants (b_T and k_T) for (ARS and AYR) dyes adsorption on PAA

	293K		
Dyes	**b_T**	**K_T**	**R^2**
ARS	10.107	0.126	0.864

Depending on Freundlich Equation:

$$lnQe = lnK_f + \frac{1}{n}lnCe ....Freundlich's\ equatio \quad (3)$$

Where, K_F and n refer to the Freundlich constants.

Figure 7a, b displays the plot of LnQe vs LnCe. These constants for (ARS and AYR) dyes were calculated, as listed in Table 2.
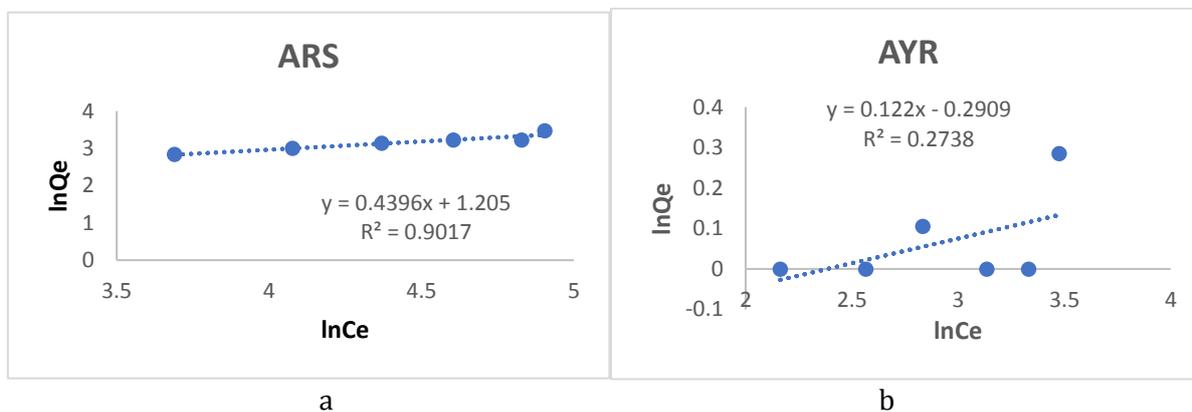

a   b

FIGURE 7 (a, b) Linear applications of the Freundlich equation

TABLE 2 Freundlich constants (k_f and n) for (ARS and AYR) dyes adsorption on PAA

293K			
Dyes	**K_f**	**n**	**R^2**
ARS	3.337	2.275	0.9017

Depending on Langmuir Equation:

$$\frac{Ce}{Qe} = \frac{1}{aK} + \frac{Ce}{a} \quad \text{Langmuir Equation} \quad (4)$$

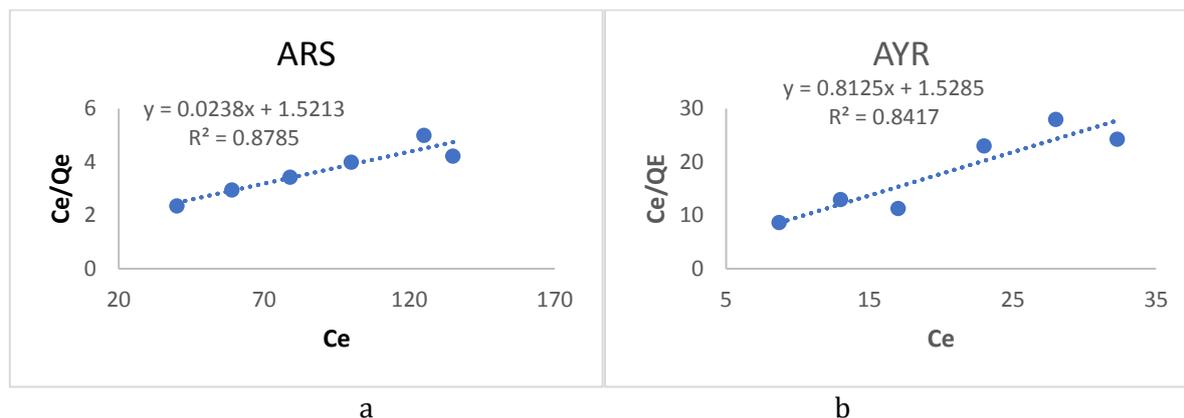Where, K and a are the Langmuir constants. Figure 8a, b shows the plot of Ce/Qe vs. Ce. These constants for (ARS and AYR) dyes were calculated, as reported in Table 3.

FIGURE 8 (a, b) Linear application of the Langmuir Equation

TABLE 3 Langmuir constants (k and a) for (ARS and AYR) dyes adsorption on PAA

293K			
Dyes	**K**	**a**	**R^2**
ARS	0.534	42.017	0.8785
AYR	0.805	1.231	0.8417

The isotherms of adsorption of (ARS) were found obeys the Freundlich equation. The isotherms of (AYR) adsorption were found obeys the Langmuir equation.

Effect of temperature

With rising temperature (Endothermic process), the adsorption amount at (ARS and AYR) dyes rises.

By using the Vant Hoff-Arrhenius equation, the (ΔH) value is as follows:

$$lnXm = \frac{-\Delta H}{RT} + Constant \quad (5)$$

Xm: stands for the maximum amount of adsorbed quantity.

R: stands for gas constant.

T: stands for temperature.

Figure 9 is the plotted LnXm vs. inverted temperature (1/T).

Table 4 represents how to get the (ΔG and ΔS) value by using the following equations:

$$\Delta G = -\frac{nRTlnQe}{lnCe} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

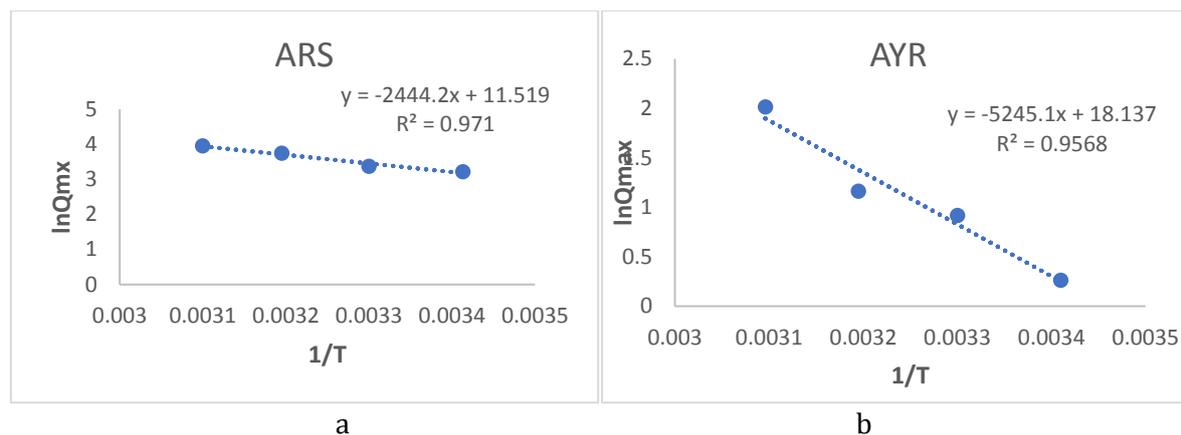**FIGURE 9** (a, b) Vent Hoff curves for (ARS and AYR) the surface dye adsorption

TABLE 4 Thermodynamic functions of dyes at temperature (293 K)

Dyes	T(K)	Δ H (K$J\backslash mole$)	Δ G (K$J\backslash mole$)	Δ S ($J\backslash mole.K$)
ARS	293		+3.277	+58.17
	303	+20.32	+3.015	+57.114
	313		+2.151	+58.050
	323		+1.646	+57.816
AYR	293		+6.658	+126.1
	303	+43.61	+5.238	+126.6
	313		+4.768	+124
	323		+2.633	+126.9

The experimental results indicate that the adsorption (ARS and AYR) increases with the rise of temperature, and this is consistent with the thermodynamic properties. The positive values of (ΔH and ΔG) indicate an endothermic process. When the process is endothermic, this is evidence of an absorption process in addition to the adsorption process (sorption). With increasing temperature, surface-adsorbed molecules diffuse into the pores and the speed of their diffusion increases, which is in agreement with some studies [16,21,22]. The positive (ΔS) value indicates that the molecules arrangement in the solution was more regular than their arrangement on the surface [17].

Effect of ionic strength

The absorption of different concentration of NaCl (3.42x10^{-3}M and 17.1x10^{-3} M) of (ARS and AYR) dyes was studied. It was found that when the salt concentration increases, the absorption decreases, as demonstrated in Figure 10.

The salt molecules crowded the dye molecules to be present on the surface, and this indicates that the salt took some sites on the PAA surface, so the adsorption decreased in the presence of salt.
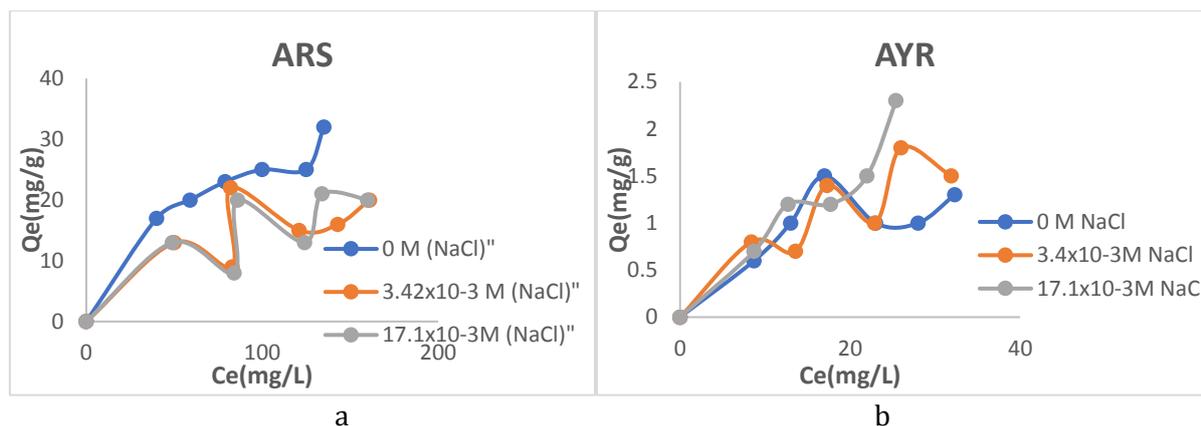
a

b

FIGURE 10 (a, b) At T = 293 K, the effects of salt on the adsorption of (ARS and AYR) dyes on PAA

Shaking effect

The vibration rate is an important component that affects the dye adsorption process because it is related to the diffusion or movement of dye molecules towards the absorbent (PAA) surface [18]. The shaking effect was studied, as demonstrated in Figure 11.
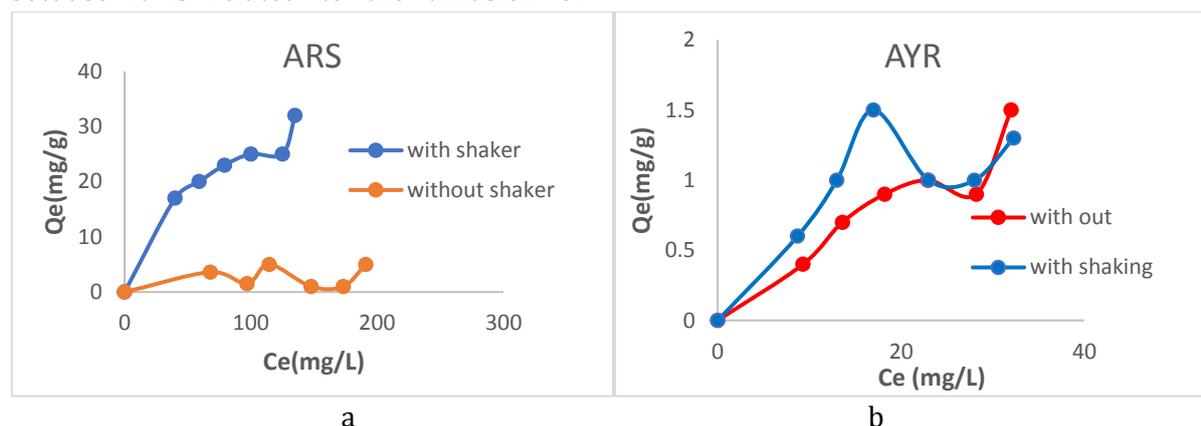

a

b

FIGURE 11 (a, b) Shaking effect on absorption at T=293K

Effect of using wet PAA

The percentage of dyes removal increases when using wet PAA instead of dry, as shown in Figure 12.
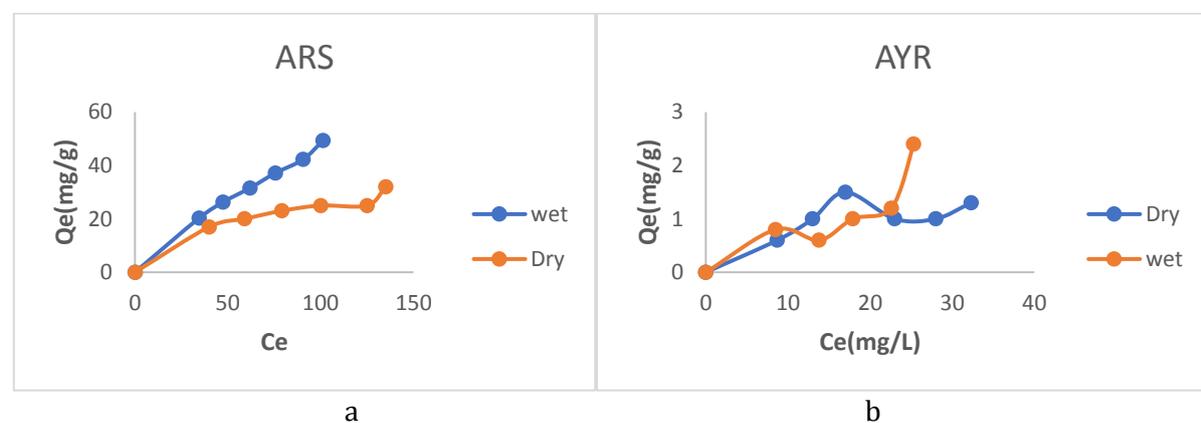

a

b

FIGURE 12 Effect of using wet PPA and dry at T=293K

Effect of initial dyes concentration

The proportion of dye removed was determined by altering the dye concentration at (T = 293K). A 50 mL solution of (ARS and AYR) was employed. After allowing the solution to reach equilibrium, the residual

(ARS and AYR) concentration was calculated. The findings in Figure 13 indicate that the percentage of removed dyes is greater at the low concentrations than at the high concentrations. The removal percentage was examined as follow:
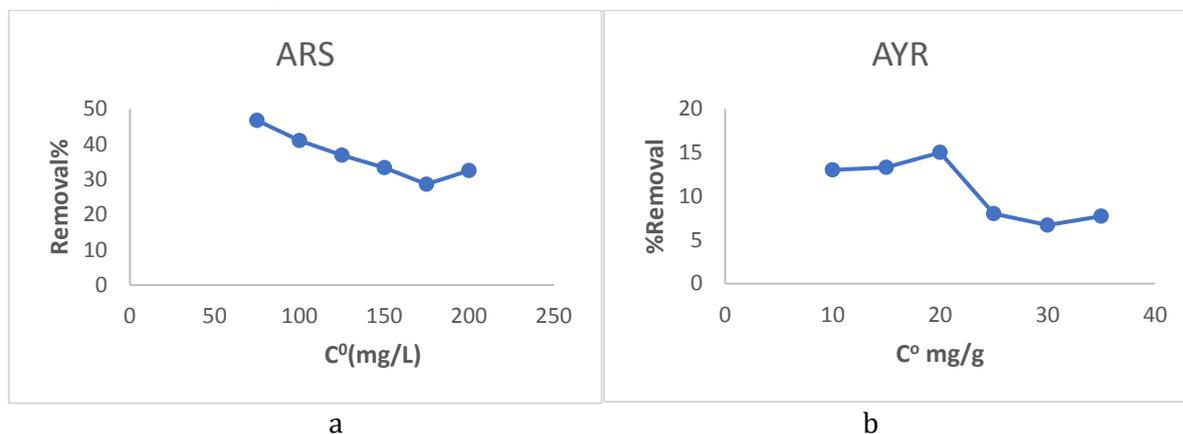

a   b

FIGURE 13 (a, b) The percentage of removal at (T=293K)

Adsorption kinetic

By using (Lagrange Equation) kinetic investigations for dyes (ARS and AYR):

$Ln(q_e - q_t) = lnq_e - K_{ad}$ (8)

Where, q_e and qt are the capacities (mg/L) of adsorption at equilibrium and time (t).

K_{ad} is the pseudo first-order kinetic adsorption rate constant (min^{-1}) [19].

The adsorption kinetics seems to follow a pseudo first-order kinetics models, as illustrated Figure 14 and the adsorption rate constant was calculated in Table 5.
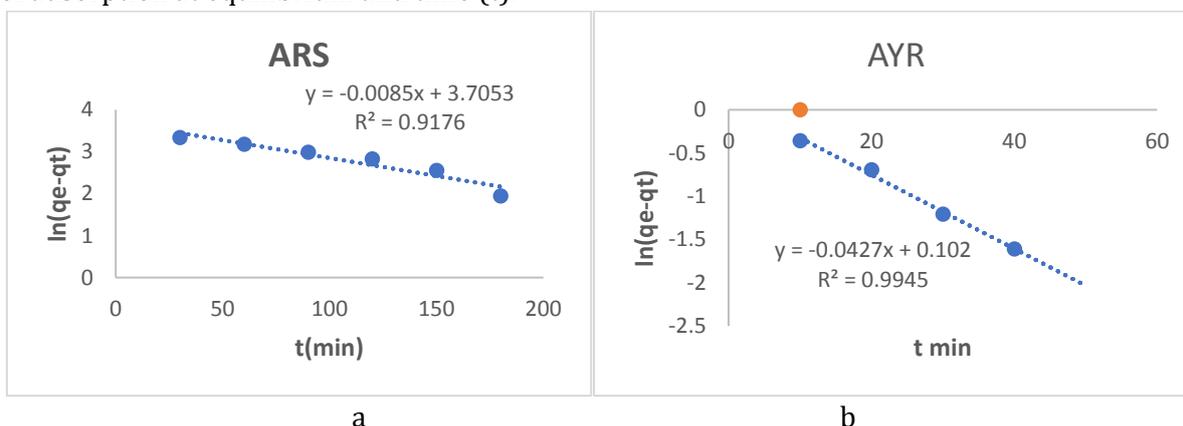

a   b

FIGURE 14 (a, b) Adsorption kinetics of the (ARS and AYR) dyes on the surface

TABLE 5 The adsorption rate constant for (ARS and AYR) dyes on the surface

Dyes	K_{ad}(min^{-1})
ARS	0.0085
AYR	0.0427

And the second-order kinetic study for dyes (ARS and AYR):

$$\frac{t}{qt} = \frac{1}{K_{ad2}qe_2} + \frac{t}{qe}$$ (9)

Where, qe and qt denote the equilibrium adsorption capacities (mg/L) and time (t), respectively.

K_{ad2}: pseudo second-order kinetic adsorption rate constant (mg/L)$^{-1}$min^{-1}[20].

The adsorption kinetics seems to follow the pseudo second-order kinetics models, as indicated in Figure15, and the rate constant of adsorption was calculated in Table 6.
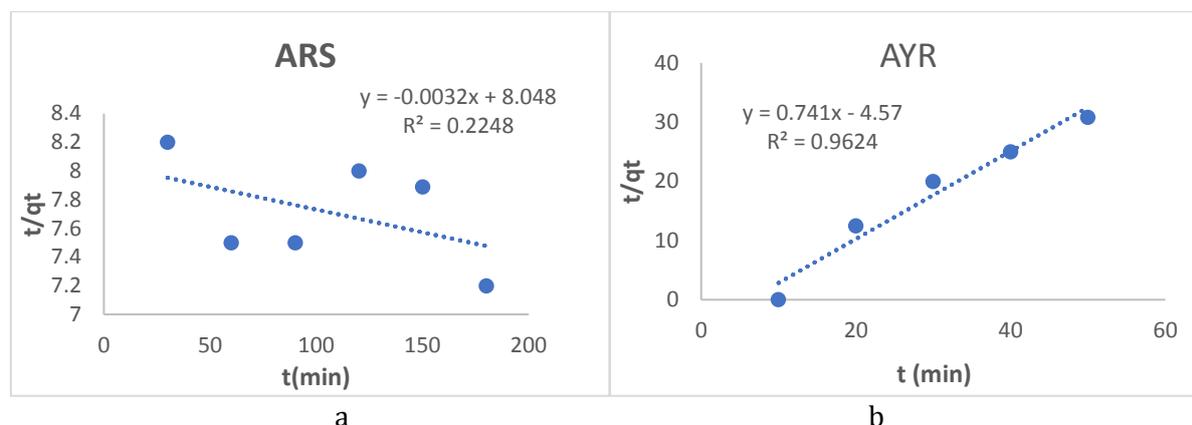

FIGURE 15 (a, b) The ARS and AYR dyes adsorption kinetics on the PAA

TABLE 6 The adsorption rate constants of the dyes on the PAA

Dyes	kad2(mg/L)$^{-1}$.min^{-1}
ARS	0.124
AYR	0.219

The result showed that the removal of (ARS) dye by (PAA) obeys the first-order reaction and the removal of (AYR) dye by (PAA) obeys the first-order and second-order reaction.

Conclusion

Polyacrylic acid (PAA) (Beads form) available in local markets can be used to treat polluted water with high efficiency and low economic cost in the case of low concentrations. The adsorption pattern according to Giles classification for the three alizarin dyes (ARS, AYR, AGG) was (S3) at temperatures (20C^{o}, 30C^{o}, 40C^{o}, 50C^{o}) where the molecules were arranged perpendicularly or obliquely on the surface. The results of adsorption isotherms were interpreted according to the (Langmuir, Freundlich, Temkin) equation for adsorption of the three alizarin dyes on the surface of (APP), whereby (AYR) dye is more compatible with Langmuir's model than other dyes, while the dyes (ARS, AGG) are in great agreement with Freundlich's model. The study showed that the enthalpy value (ΔH) of the three dyes is positive (that is, the adsorption process is endothermic). The value of (ΔG) was positive for all dyes where the adsorption process is accompanied by the absorption process of any process (sorption). Adsorption follows the illusory first-order law for the three dyes (ARS, AYR, and AGG).

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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