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RESEARCH ARTICLE

INVESTIGATION of the EFFECTS of PREPARED PVA/NANO LA_2O_3 MIXTURE on ALIZARIN DYE REMOVAL: KINETIC, ISOTHERM and THERMODYNAMIC STUDIES

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ABSTRACT

With the increasing industrialization, the use of dyestuffs increases. This increasing use causes serious dangers to the environment as waste. For this reason, studies on the removal of dyestuffs have increased. In this study, an adsorbent was prepared by adding nano-sized Lanthanum Oxide (La_2O_3) to Polyvinyl Alcohol for Alizarin Red S removal. The chemical structures of this adsorbent were confirmed by FT-IR analysis. The effects of adsorbent masses, pH, contact time on Alizarin Red S removal were investigated in adsorption studies. Accordingly, the highest 94.5% removal was achieved in 1 gram adsorbent mass, pH 7, 60 minutes. In addition, thermodynamic, isotherm and kinetic studies were carried out in the study. In isotherm studies, it was determined that the most suitable model was Freundlich and the qmax value was found to be 5.06 mg/g. However, the pseudo second order kinetic model was found to be suitable.

Keywords: *Polyvinyl Alcohol, Lantanium Oxide, Alizarin, Adsorption*

1. INTRODUCTION

Dyes are used to color products in a variety of industries, including the textile, pharmaceutical, chemical, and petrochemical industries. These industries discharge a lot of toxic, colored wastewater into bodies of water. Resistant wastewater, particularly textile dyes and derivatives, contains physiologically resistant chemicals that are difficult to decrease or destroy using standard methods such as biological oxidative pathways. Colored organic compounds produce a coating on the water's surface, keeping deep sunlight out of bodies of water. As a result, adequate light cannot be delivered for water flora and fauna's photosynthetic processes. As a result, the dye reduces the total oxygen required to maintain the chemical oxidation of the biological entities in need of chemical oxygen and biological oxygen. On the paint market, 700000 tons are manufactured annually, and 10% of these totals are industrially processed and released into the environment [1].

Anthraquinone dye group member Alizarin Red S (ARS) is a long-lasting anionic dye. In the textile industries, it is frequently used as a coloring agent. Additionally, this dye is used to stain biological material including small invertebrate embryos and the calcified bones of vertebrate species. Due to its

chemical stability and lack of biodegradability, ARS cannot be fully mineralized using standard refining techniques. Due to its great thermal, optical, and physicochemical stability, it resists deterioration. As a result, numerous studies have concentrated on creating quick, easy, and effective procedures for their secure removal [2].

For the overall removal of dyes, numerous methods have been tried. The most widely employed of these are physical ways like adsorption, biological methods, and chemical methods. One of these investigations, which is also economical and efficient, is adsorption. Various adsorbent compounds were utilized. Ion exchange resins, silica, clay, synthetic and natural polymers, composite adsorbents, and biomass are examples of adsorbents. Synthetic polymers have received extra attention since they have several unique features. Poly(vinyl alcohol, or PVA), which has recently caught the interest of researchers among the various synthetic polymers, is notable for its compatibility, non-toxicity, biodegradability, availability, low cost, and good film formation[3].

Therefore, in this study, PVA was used for the removal of alizarin red s dye in water. To make PVA functional, specially prepared nano-sized La2O3 is doped. Adsorption studies were carried out with the help of this prepared adsorbent. The effectiveness of the adsorbent was determined by kinetic, thermodynamic and isotherm studies.

2. MATERIAL AND METHOD

2.1. Materials

Polyvinyl Alcohol and glutaraldhyde were commercially purchased from Merck, La_2O_3 nanography.

2.2. Preparation of Adsorbent

We employed an immersion sonicator to perform mechanical delamination (75W). La_2O_3 was sonicated in DMF for 12 hours to achieve this. The finished product was then collected by allowing the solution to evaporate under normal conditions. The precipitated materials were then dried at 40°C after being centrifuged five times with distilled water. The synthesized nano La_2O_3 was shown to be nano in size via TEM analysis. In addition, XRD analysis was performed to understand the crystal structure of the prepared n-La particles.

At 90^0C with stirring, 5 grams of PVA were dissolved in 100 mL of distilled water. 0.25 grams of nano La_2O_3 (nLa) were then added after it had been cooled to room temperature. This mixture was held on a magnetic stirrer for three hours after being sonicated for one hour. The solution was then adjusted with 1M HCl to pH 2-3. 3 mL of glutaraldehyde was then added and combined. After that, it was put in glass bottles and stored at –12 °C for three days. It was taken out of the cooler and given a distilled water wash. The obtained adsorbent's chemical structures were verified by FT-IR analysis after it had dried.

2.3. Adsorption Studies

To study Alizarin Red S adsorption in produced adsorbents, a number of batch studies using various experimental parameters were conducted. These parameters include the amount of dye present (10, 25, 50, or 100 mg/L), the pH range (2–12), and the mass of the adsorbent (PVA-nLa) (0.1–2.0 g).

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To diluted the determined concentrations, a stock solution of Alizarin Red S at 1000 mg/L was prepared. Adsorption was performed using the IKA KS 3000i Control model shaker by adding the amount of adsorbents to 50 ml of Alizarin Red S (ARS) solution and shaking it at 150 rpm for the predetermined period of time. The pH of the ARS solution was changed to the required level using 0.1 M NaOH and 0.1 M HCl solutions. To remove the adsorbents from the solution after the adsorption procedure, it was centrifuged at 5000 rpm for 30 min. The adsorbents were taken out after centrifugation, and the solution's ARS concentration was calculated. The remaining dye concentration in the solution was evaluated by colorimetry after centrifugation using a UV spectrophotometer (Shimadzu UV-3600 Plus) with a maximum wavelength of 421 nm. The calibration curve between the concentration and absorbance of the dye solution was plotted to obtain an absorbance-concentration profile. The formulae below were used to compute the amount of ARS that was removed as well as the adsorbent's capacity [4].

$$q_e = (c_0 - C_e) \times \frac{V}{W} \quad (1)$$

$$q_t = (c_0 - C_t) \times \frac{V}{W} \quad (2)$$

$$Giderim, \% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

C_0, C_e, and C_t represent the initial ARS concentration, equilibrium concentration, concentration at time t, adsorption capacities qe and qt at equilibrium and t, V ARS solution volume, and W adsorbent mass.

2.4. Thermodynamic, Isotherm and Kinetic Studies

Adsorption experiments were conducted thermodynamically at 3 different temperatures (298, 308, 318 Kelvin). With the use of the findings from these investigations, the following equations were used to derive Gibss, Enthalpy, and Entropy.

$$K_c = \frac{q_e}{C_e} \quad (4)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

The most popular way to depict the equilibrium state of an adsorption system is using the adsorption isotherm. The amount of substance adsorbed by the adsorbent and the equilibrium concentration are related by an adsorption isotherm, which exists at constant temperature. Studies on equilibrium isotherms were conducted at 25^0C, using 1g of adsorbent and various ARS concentrations at pH 7. Analysis of equilibrium adsorption values was done using the Freundlich and Langmuir isotherm models.

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The first theoretically determined adsorption isotherm is represented by the Langmuir isotherm equation. This equation serves as the foundation for the majority of the following proposed equations that fit a variety of experimental results, or they were created using the Langmuir method. As a result, both chemisorption theories and physical adsorption continue to rely on the Langmuir isotherm model. The Langmuir isotherm's mathematical equation is provided below [5].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_c} + \frac{C_e}{q_{max}} \tag{7}$$

The Freundlich isotherm, another popular experimental equation that uses two parameters and is consistent with a wide range of experimental data, is comparable to the Langmuir isotherm [6]. Below is the Freundlich isotherm equation:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{8}$$

The effective adsorbate-adsorbent contact time can be calculated using adsorption kinetics. There are steps in the analysis of adsorption kinetics that have an impact on the rate of the adsorption process. In order to explore the ARS adsorption mechanism on adsorbent surfaces, two distinct kinetic models were applied. These models are pseudo first order (PF) and pseudo second order (PS) kinetic models, respectively [7].
The PF kinetic model was developed by Lagergren (1898). The PF kinetic model equation is given below:

$$Log(q_e - q_t) = \ln q_e - \frac{K_1 t}{2.303} \tag{9}$$

The PS model equation is given below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

3. RESULT AND DISCUSSION

3.1. nLa TEM Analysis

Bulk La_2O_3 and nano La_2O_3 samples were imaged with TEM device. It is seen in Figure 1a that there are bulk La_2O_3's over 1 micron, and in Figure b the n-La dimensions vary between 30-50 nm. In this study, it was observed that the bulk La_2O_3's were reduced to nano size as planned and dispersed in approximately equal sizes.

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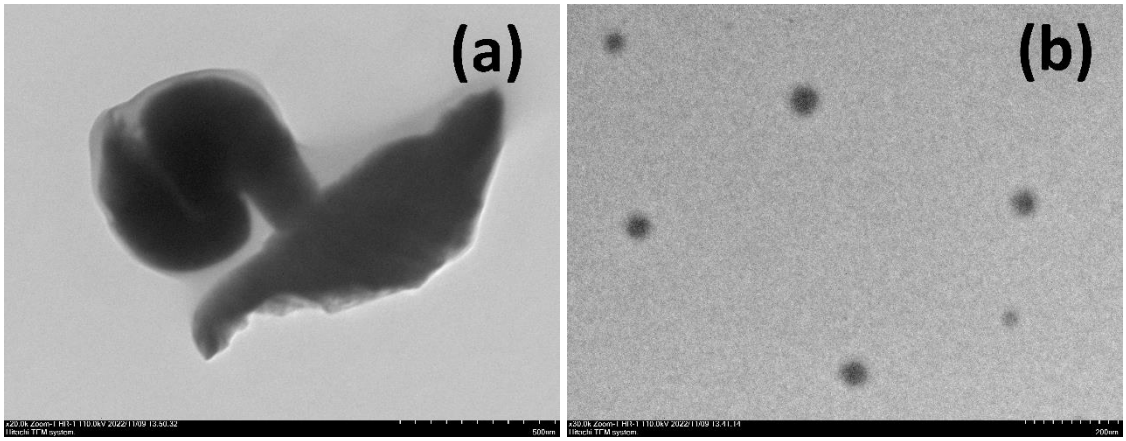

Figure 1. TEM images (a) bulk La_2O_3, (b) nano La_2O_3.

3.2. n-La XRD Analysis

Figure 2 shows the n-La XRD analysis. Accordingly, the peaks seen at 15, 28, 39, 48 and 55 were approximately the same as the xrd peaks of nano La_2O_3 materials prepared in several different studies[8,9]. It has been understood in the literature that n-La has a similar crystal structure to those prepared in the literature.

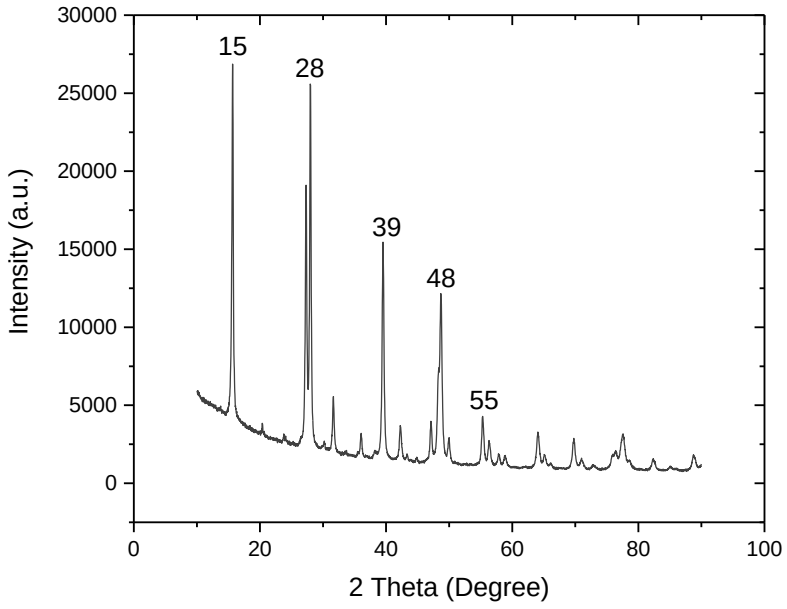

Figure 2. n-La XRD pattern.

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3.3. FT-IR Analysis

Figure 3 shows the FT-IR spectra of PVA, nano La_2O_3, and PVA-nLa. The main peaks of PVA were seen as 3283, 2907, 1700, 1418, 1321, 1086 and 834 cm^{-1} [10]. Nano La_2O_3 main peaks were found to be 3608, 1456 and 628 cm^{-1} [11]. When the PVA-nLa spectra were examined, it was understood that similar peaks appeared. The chemical groups corresponding to the peaks appearing in the FT-IR spectra are shown in Table 1.

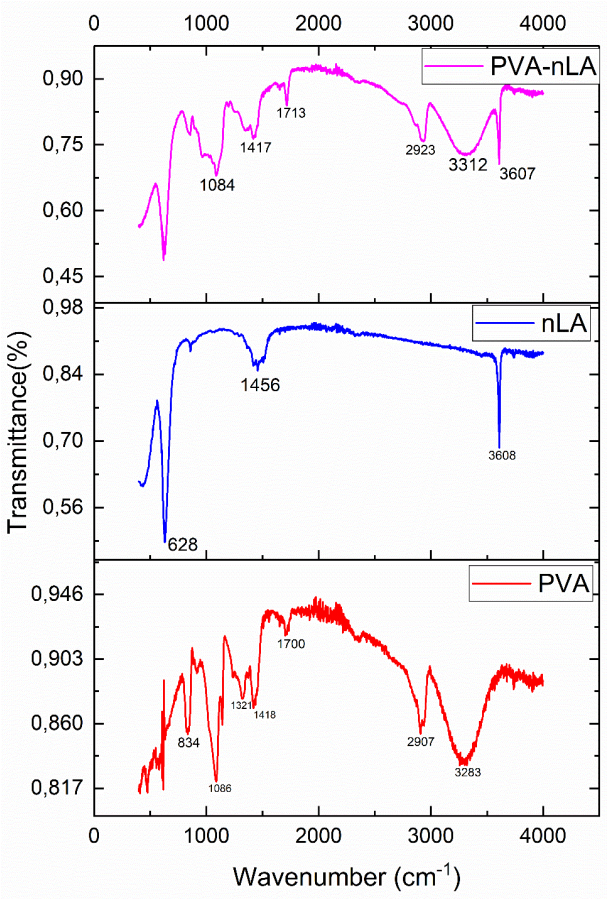

Figure 3. FT-IR spectrum.

Table 1. PVA and nLa_2O_3 FT-IR results.

Chemical Structure	Wavenumber (cm_{-1})
La_2O_3 OH stretching	3608
PVA-GA OH stretching	3283

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PVA-GA CH_2 asymmetric stretching	2907
PVA-GA C=O carbonyl stretching	1700
La_2O_3 CO_2 vibration	1456
PVA-GA CH_2 bending	1418
PVA-GA C-H deformation	1321
PVA-GA C-O stretching	1086
PVA-GA C-C stretching	834
La_2O_3 La-O-C stretching	628

3.4. Effect of Adsorbent Amount

First, the impact of adsorbent masses was assessed in the adsorption trials. As a result, the adsorption was completed in 120 minutes at 25 ^oC, pH 7, and 50 mg/l ARS concentration. According to Figure 4, the greatest amount of ARS that could be removed by adsorption was 94.04%. As seen in Figure 4, as the adsorbent mass is increased, the adsorption increased and remained constant after 1 gram, and the maximum ARS adsorption removal was determined as 94.04%.

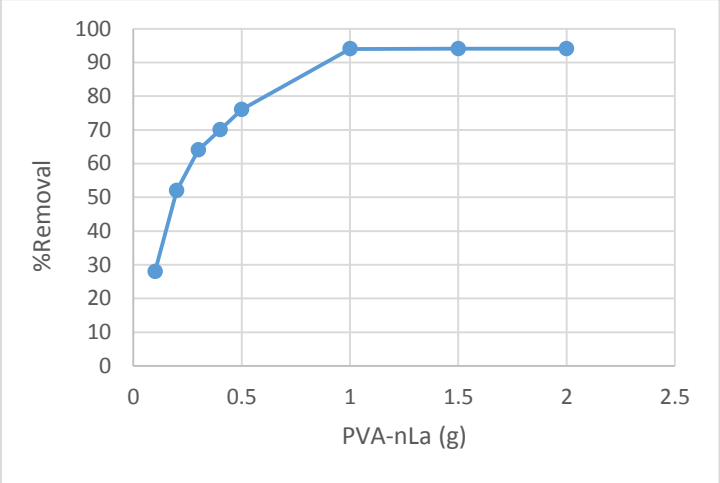

Figure 4. Effect of PVA-nLa amount on adsorption.

3.5. pH's Impact on ASR Removal

The effect of pH change on adsorption was investigated. The adsorption study was carried out at 25^oC, 1 gram of adsorbent, 50 mg/l ARS concentration and 120 min. As seen in Figure 5, the percentage of ARS removed increased until pH 7, but then remained steady. The maximum ARS removal rate was discovered to be 92.5% at pH 7.

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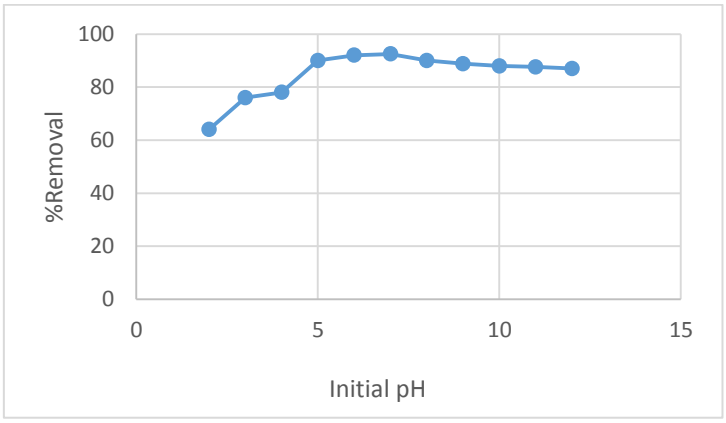

Figure 5. pH's impact on ASR removal.

3.6. Adsorption Effects of Time and Starting Concentrations

Figure 6 depicts the influence of time and initial concentration on adsorption. These tests were conducted out at a temperature of 25°C, with a gram of adsorbent and a pH of 7. As a result, highly quick adsorption was observed for up to 10 minutes. This is due to the adsorbent surface's active sites being filled. At a starting concentration of 10 ppm, the maximum ARS removal was reported to be 94.5%. At an initial concentration of 100 ppm, the greatest adsorption capacity was determined to be 4.6 mg/g.

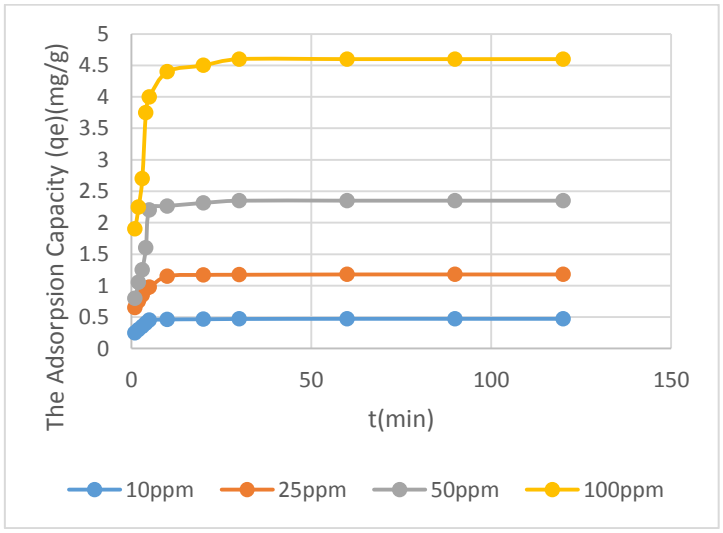

Figure 6. Adsorption effects of time and starting concentrations.

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3.7. Thermodynamic, Isotherm and Kinetic Study Results

Experiments were conducted out at 50 ppm ARS concentration for 60 minutes, pH 7, 1 gram adsorbent quantity to investigate the effect of temperature and thermodynamic investigations. Figure 7 shows that adsorption increased somewhat as temperature increased. Figure 7 was used to derive thermodynamic parameters. Table 2 displays the parameter results. At all temperatures, negative ΔG values (-4.05, -5.04, and -4.51 kJ/mol) suggest that the reaction is spontaneous. Physisorption is generally expressed by G values of -20< ΔG< 0 (kJ/mol). It was also discovered that G decreased with increasing temperature, indicating the possibility of adsorption at higher temperatures. Endothermic adsorption is shown by positive enthalpy (ΔH=2.8 kJ/mol). Positive entropy (ΔS = 0.023 kJ/mol) suggests greater randomness during solid-solution interface adsorption [12].

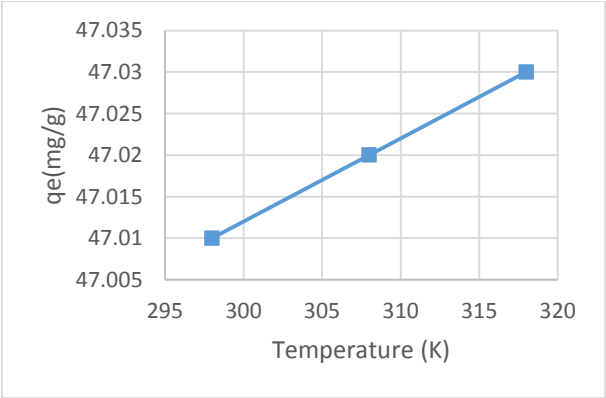

Figure 7. Effect of temprature on adsorption.

Table 2. Thermodynamic parameter values.

T (Kelvin)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol K)
298	2,80	0.023	-4,05
308	2,80	0.023	-5,04
318	2,80	0.023	-4,51

The values of the Langmuir and Freundlich model parameters for ARS adsorption by the produced adsorbent are shown in Table 3 and Figure 8. When these two models were compared, it became clear that the Freundlich model (R^2>0.999) provided a better fit than the Langmuir model (R^2=0.9324). He demonstrated that the adsorption mechanism was consistent with the Freundlich isotherm for this reason. This suggests that the energy and heterogeneity of the ARS adsorption surface are different [13].

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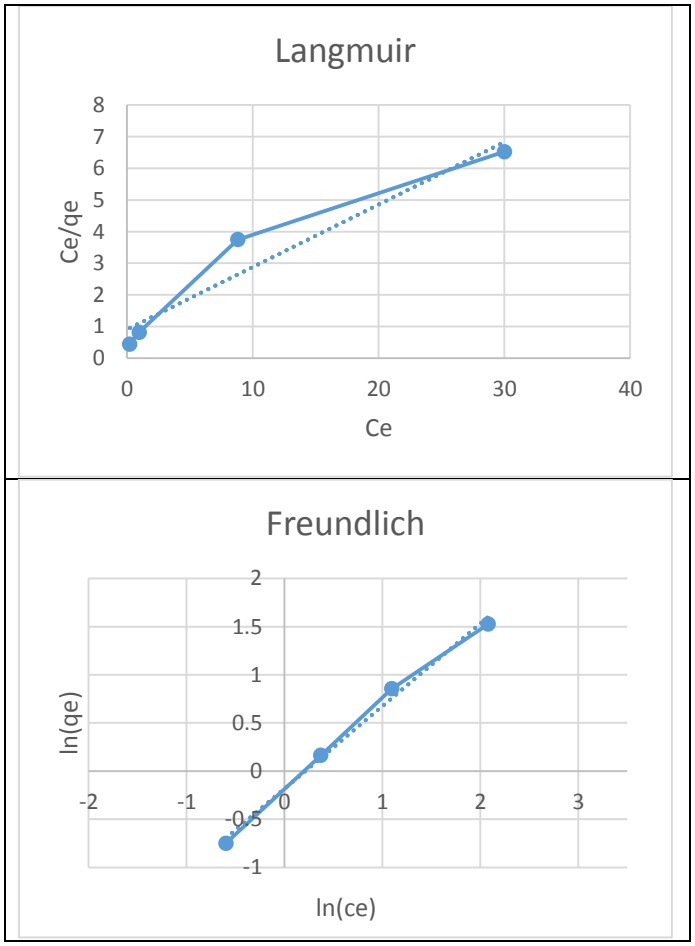

Figure 8. Langmuir and Freundlich plots.

Table 3. Isotherm parameter values.

Isotherm	**Parameters**	**Value**
Langmuir	R^2	0.9324
	q_{max}(mg/g)	5,06
	K_L	0,21
Freundlich	R^2	0.9934
	K_F (L/mg)	0,83
	n	1,16

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The experimentally collected data were used to apply the linear forms of the PF and PS velocity models in order to examine the adsorption control mechanism. Table 4 and Figure 9 contain the data and graphs for the kinetic parameter. Additionally, experimental results and R^2>0.999 demonstrated the compatibility of the PS. Improved and experimental kinetic velocity profiles further supported this. As a result, the rate-controlling step for this adsorbent is probably chemical adsorption[12]. In this study, which was tried for the first time in the literature; When the nano La_2O_3 doped PVA-based adsorbent was compared with many PVA-based studies in the literature, it was seen that similar results were obtained [14]. It has been seen that PVA-La_2O_3 adsorbents, which have never been tried in the literature, can be effective and La_2O_3 additive accelerates the adsorbtion much more than the literature [15]. For this reason, we think that this study can shed light on future studies.

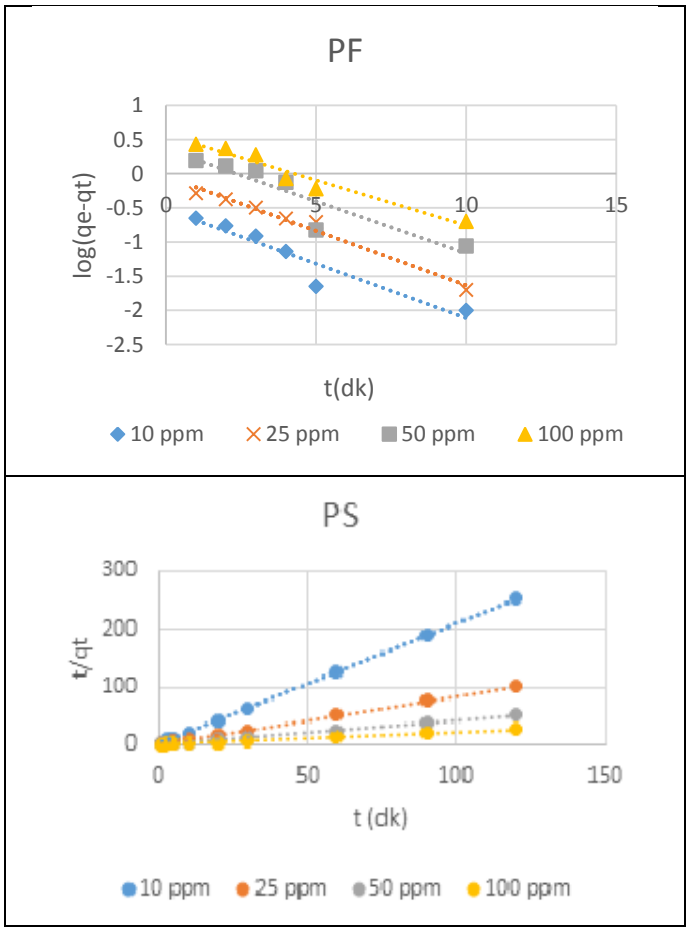

Figure 9. PFO and PSO kinetic model plots.

Table 4. Parameter values of PFO and PSO kinetic models.

		PF			PS		
Co (mg/l)	**q_{exp}(mg/g)**	**q_e (mg/g)**	**K_1**	**R^2**	**q_e (mg/g)**	**K_2**	**R^2**
10	0,47	0,59	0,3654	0.9036	0,476	3,13	0,9999
25	1,17	0,96	0,3668	0.9782	1,18	1,06	0,9999
50	2,35	1,429	0,3505	0,8379	2,39	0,288	0,9996
100	4,6	1,76	0,3056	0,9494	4,66	0,182	0.9998

4. CONCLUSION

As a result, La_2O_3 doped PVA was utilized for the first time in the literature to remove ARS. By using FT-IR analysis, the produced adsorbent's chemical structures were verified. Adsorption tests have shown that 1 g of adsorbent, pH 7, and 60 minutes of adsorption time are the best conditions. It was discovered that the Freundlich isotherm model was appropriate for this adsorption. The qmax value was also discovered to be 5.06 mg/g. The kinetic studies led to the conclusion that the PSO model was appropriate.

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