# Application of Box-Behnken Design and Response Surface Methodology of Acid Red 18 Adsorption onto PAC (Synthesized Carrot Waste) Coated with Fe<sub>3</sub>O<sub>4</sub> Nanoparticles from Aquatic Solution: Kinetic and Isotherm Studies

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#### A-R-T-I-C-L-EI-N-F-O

Article Notes: Received: Sep 20, 2020 Received in revised form: Nov 07, 2020 Accepted: Nov 07, 2020 Available Online: Dec 30, 2020

Keywords: Adsorption Isotherm Kinetics Ponceau 4R Solutions Synthetic activated carbon

#### A-B-S-T-R-A-C-T

**Background & Aims of the Study:** The dyes present in the effluent from the textile industry are among the most polluted and hazardous wastewater discharged, causing severe changes in water quality and the environment. The use of agricultural residues as inexpensive organic adsorbents is very suitable for removing industrial dyes from aquatic solutions, especially in developing countries. This study aimed to investigate the effectiveness of activated carbon synthesized from carrot waste as an inexpensive and available organic adsorbent in the removal of Acid Red 18 (AR18) dye.

**Materials and Methods:** In this study, response surface methodology (RSM) was discussed as an efficient method for the optimization of AR18 adsorption onto PAC (obtained from waste carrot) coated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles. ANOVA analysis based on the Box-Behnken design-RSM was applied to investigate the correlation coefficient of PAC (Synthesized Carrot Waste). Adsorbent dose, initial dye concentration, and pH were optimized and evaluated using RSM with respect to contact time on adsorption of AR18. Moreover, X-ray diffraction, transmission electron microscopy, Brunauer–Emmett–Teller, Fourier-transform infrared, and field emission scanning electron microscopy techniques were used to study the adsorbent properties and characteristics of PAC. Isotherm data were modeled with both Langmuir and Freundlich isotherm.

**Results:** The results obtained from Langmuir isotherm showed the best fit to experimental data proposing homogeneous dispersion of adsorption sites. Moreover, the compatibility of the adsorbent was examined by fitting the adsorption data with a pseudo-second-order kinetic model. The results of ANOVA analysis showed a good fit between quadratic model predictions with experimental values, resulting in R<sup>2</sup> of 0.997 for PAC. The results showed 99.7% of dye AR18 was removed after 80 min, pH at 3, and the adsorbent dose of 1.5 g.

**Conclusion:** It can be concluded that PAC (Synthesized Carrot Waste) has great potential applications for the removal of AR18 dye from the textile industry. Large-scale applications of adsorbent and adsorbate, due to their recuperation and reusability characteristics, are proposed by observations and experimental results of this study.

**Please cite this article as:** Moradi R, Kashefi Alasl M, Marandi R, Salahi E, Moradi Dehahhi S. Application of Box-Behnken Design and Response Surface Methodology of Acid Red 18 Adsorption onto PAC (Synthesized Carrot Waste) Coated with  $Fe_3O_4$  Nanoparticles from Aquatic Solution: Kinetic and Isotherm Studies. Arch Hyg Sci 2021;10(1):30-48

Archives of Hygiene Sciences

Volume 10, Number 1, Winter 2021

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# Background

Dyes are considered the main pollutants in textile industries. The dyeing process is applicable both for natural and artificial fibers (1). Dyes are among the most used raw materials in textile industries. The number of synthetic dyes exceeds 100,000, which are used in similar industries. Dyes are mainly made up of petroleum intermediates and coal tar with high-volume production exceeding  $7 \times \times 10^5$ tons per year (2). Dyes are widely used in such industries as textile, pharmaceutical, and plastics (3). Organic dyes originated from textile productions utilize a large volume of water during the dying process. More than 200,000 tons of dyes pollute the environment every year; the pollution caused by dyeing processes due to the inefficiency of the treatment (4). Acid red18 (AR18) is one of the azo dyes that are currently used in the textile industries (5). There are some methods, such as advanced oxidation process, filtration, electrodeposition, adsorption, chemical coagulation, and biological treatment, that have been used for textile wastewater treatment. Most of the mentioned methods are efficient only when they are used together (6). Physical and chemical processes are used most of the times for the treatment of effluent water containing dye. The extent of operation total costs and potential for removing dye are not the same for these methods.

Adsorption, among all these methods and techniques, has been revealed to have the highest potential to remove dye effectively from wastewater. The reason for such capacity is related to adsorption's low cost of production, unambiguous design, easy operational procedure, and unresponsiveness to substances that are toxic in nature. Activated carbons (ACs), due to their high capability of adsorption, are considered the most widely used adsorbing agent with a very high level of success (7). In this regard, since AC can remove dyes effectively, it can be considered one of the best options for this process. Activated carbon, as an adsorbent, has important and vital applications. This substance is produced from the pyrolysis of plant substances containing carbon and is subjected to activation operations. Activated carbon has different pores and shapes, depending on the type of used raw materials, showing a wide range of specific applications regarding the distribution of pores. Carbon can be extracted from such sources as corn stalks, wheat husks, reeds, sesame, and fruit kernels, as well as the skin of some seeds, such as hazelnuts, almonds, and coconuts (8).

Today, more attention is focused on getting cheaper and more available adsorbents. Pectin is the main form of soluble fiber in carrots, which is a strong bonding agent. Carrot has a high adsorption capacity due to the presence of such components as polysaccharides, oligosaccharides, and lignin (9). The adsorption techniques on powders or granular materials, especially AC, are among the most used and easiest ones to implement. However, the applicability of this method is limited by the production costs and regeneration of the aforementioned materials. Therefore, in recent years, interest has focused on finding low-cost adsorbent materials (e.g., bio adsorbents, biochar, and AC) through recycling and turning them into by-products or industrial wastes (10). Response surface methodology (RSM) is a combination of methods in math and statistics to analyze the effects of several independent factors on the dependent factor, which provides functions and data to code and decode factor levels (11). This method is highly used in the adsorption process design and its optimization, which has been used in this study as well.

## Materials & Methods

#### **Materials**

To synthesis waste carrot, 1.4 Tesla magnet,

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	Table 1)	Acid Red18 dye char	acteristics		
Chemical structure	Color index name	Molecular Formula	Molecular Structure	$M_w(g/mol^{-1})$	$\lambda_{max} (nm)$
HO <sub>3</sub> S N <sup>-N</sup> -H	Acid Red 18	$C_{20}H_{11}N_2Na_3O_{10}S_3\\$	Single azo class	604.47	506

ethanol 98%, Sodium hydrogen carbonate (NaHCO<sub>3</sub>), Fe<sub>3</sub>O<sub>4</sub> (ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride (FeCl<sub>2</sub> 4H<sub>2</sub>O), ammonium persulfate  $(S_2O_8 (NH_4)_2)$ , sulfuric acid  $(H_2SO_4)$ were purchased from Merck Company, Germany. Acid red18 dye was also purchased from Merck (Table 1). The pH was adjusted with NaOH and HCl solution (0.1 mol  $L^{-1}$ ). The reagents used in this research all had an analytical grade. The determination of AR18 dye in solutions was performed with the aid of a Cary 100 Bio Spectrophotometer device (Varian, USA). Powder X-ray diffractometer (Philips PW-3710) was used for X-ray diffraction (XRD) patterns recording with Cu as a source of X-ray ( $\lambda_{k\alpha l}$  1.5406 Å). The energy dispersion and synthesized PAC (Synthesized Carrot Waste) morphology were investigated emission field scanning electron using microscopy (FESEM) device (VEGA\\TESCAN-LMU, TESCAN, Brno, Czech Republic). The images created by high-resolution transmission electron microscopy (TEM) were recorded using a microscope (Tungsten Hairpin EM208S, FEI, USA) at 100 kV operational mode. Fouriertransform infrared (FTIR) spectroscopy of the PAC (synthesis Waste carrot) was recorded both before and after dye adsorption. The applied range on an FTIR spectrometer (Spectrum 400, Perkin Elmer, USA) was 4000-400 cm<sup>-1</sup>. The adsorption rate and adsorption porosity were measured using Brunauer–Emmett–Teller (BET) analysis (BELSORP-mini II, BEL Japan Inc., Japan).

## Activated carbon preparation

The AC was prepared by physical activation

in a single step. To prepare and synthesize nano-adsorbent, after that 1 kg carrot waste was washed with distilled water for 2 h, it was placed in an oven at 105°C to reach 0.0% of humidity. Subsequently, it was mixed with concentrated sulfuric acid 0.5 Μ and Ammonium persulfate 0.1 M with a ratio of 1:1 (weight: volume) to obtain activate carbon and placed in an oven at 250°C for 5 h (12). At the next stage, NaHCO<sub>3</sub> was added up to 1% to remove the acid vapor from the carbon pores. The AC was washed with distilled water several times to remove the bicarbonate and neutralize the carbon from the alkaline state. Afterward, the AC was put into an oven at 105°C for 24 h (13). To remove other impurities, the product was dissolved in 18% hydrochloric acid solution at room temperature for 16 h. Finally, the product was dried in an oven at 105°C, and 200 g of AC was obtained from carrot waste (14).

In order to produce porous nanocarbon, 100 g of AC was milled with a mortar and put in a 37-µm sieve. During this process, 150 g of AC passed and 50 g of it was milled for 60 min (Planetary Ball Mill, Retsch, Germany) (15). About 0.5 g of AC from carrot waste was dissolved in 70 mL of water by ultrasonic irradiation for 20 min. The mixture was further stirred vigorously for 30 min at 60°C. Subsequently, 177 mg of  $FeCl_3^+/FeCl_2^+$  salts in the mass ratio of 2:1 was added under stirring. The mixture was stirred vigorously for 30 min under N<sub>2</sub> atmosphere, followed by the highly slow addition of 30 mL of NH<sub>4</sub>OH 6% solution into the mixture at 60°C within 1 h and extended for another 2 h. To prevent oxidation,

the  $N_2$  atmosphere was applied during the experiment. The mixture was then centrifuged, washed with double distilled water, and dried. The obtained black precipitate was Fe<sub>3</sub>O<sub>4</sub>/AC from carrot waste nanoparticles ready for use (16). The particles were then placed in a nitrogen furnace at 800°C for 3 h to be carbonized and charged under the nitrogen gas of iron nanoparticles on carbon since the 1.4 Tesla magnet absorbed them easily. The induction of magnetic nanoparticles in the adsorbent tissue was essential. The following formula shows the steps of construction and separation of the adsorbent:

Activated catbon production friuting rate% =  $\frac{\text{The wieght of producted carbon}}{\text{Carrot vaste applie}} \times 100 \text{ (Eq.1)}$ 

### Experimental design and statistical analysis

In this study, the optimization of effective parameters was provided by Box-Behnken, which is one of the RSM designs performed with Design-Expert software (version 7.0.0). Removal percentage was used as a response indicator, and four factors were included and limited to pH (A), contact time (B), adsorbent dose (C), and AR18 dye concentration (D) as constituents of the design. Both interactions between the parameters and function of significant variables can be predicted by a polynomial equation in RSM (Eq.2).

$$\begin{split} Y &= \beta_{\circ} + \ \sum_{i=1}^{K} \beta_{i} \ X_{i} + \sum_{i=1}^{K} \beta_{ii} \ X_{i}^{2} \ + \sum_{i=1}^{K-1} \ \sum_{j=2}^{K} \beta_{ij} \ X_{i} \ X_{j} + \\ \sum_{i=1}^{K-1} \ \sum_{j=2}^{K} \beta_{ij} \ X_{i}^{2} X_{j} \qquad (Eq.2) \end{split}$$

In this formula, Y stands for a predicted response,  $\beta$  is the constant regression coefficient, and independent variables values are coded to Xj and Xi, respectively. Analysis of variance (ANOVA) was used to validate equations. The design included 29 experimental runs in total, 4 center points, and 1 block. The changes among independent variables were compared with respect to responses using ANOVA (17). Levels and ranges of the independent variables in the experiments are summarized in Table 3. The range of variables was between the minimum and maximum levels of -1 and +1, respectively.

## Dye adsorption and removal study

Removal of AR18 dye in the adsorption process on the PAC (Synthesized Carrot Waste) was performed using column and batch run techniques by spectrophotometry. The first technique is one of the most usual and at the same time, effective approaches for wastewater treatment giving value to adsorbent materials practically. The second one is a quite simple technique that is useful in adsorption process designs which generate results from parameters affecting each other, such as contact time, dye concentration, adsorbent dose, temperature, and pH related to the adsorption process. To prepare a stock solution, distilled water was selected as a solvent to dissolve AR18 dye. Afterward, the prepared stock solution was diluted to prepare other dye solutions. A constant amount (1.5 g/L)of magnetite PAC (Synthesized Carrot Waste) was applied for all adsorption experiments and added to stock samples of 200 mL diluted AR18 dye solutions (25 mg/L to 150 mg/L). The adsorption was specified at a maximum wavelength of AR18 dye where  $\lambda_{max} = 512$  nm.

A set of equations used to compute the percentage of adsorption efficiency are provided as follows. In the equation, m (g) stands for the amount of adsorbent added to 200 mL of AR18 dye solution where,  $C_0$  (mg/L) was the initial concentration,  $C_e$  (mg/L) was the remaining concentration of AR18 dye at equilibrium, and finally,  $Q_e$  (mg/g) was the adsorbed amount of AR18 dye at equilibrium (Eq 3, 4).

Dye Removal% = 
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (Eq.3)

$$Q_e = \frac{(C_0 - C_e)v}{m}$$
(Eq. 4)

The same procedure was applied for the kinetic study. The measurement of dye concentrations  $C_t$  (mg/L) was conducted after

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specified time intervals and the adsorbed amount of dye was calculated at time t,  $Q_t$  (mg/g), (Eq.5).

$$Q_t = \frac{(C_0 - C_t)v}{m}$$
(Eq.5)

## Contact time and dye concentration effect

The amount of 1.5 g adsorbent PAC (Synthesized Carrot Waste) was applied to all 200 mL AR18 dye samples with initial concentrations of 10, 25, 50, 75, 100, and 150 mg/L. The dye concentration was observed in the determined times of 20 min, 40 min, 60 min, 80 min, 100 min, 120 min, and 140 min all with 200 rpm on a shaker. After separating the adsorbent from the solution by 1.4 Tesla magnet, the adsorption rate was read by spectrophotometer and the optimum concentration was obtained in optimum time.

## Adsorbent dose Effect

The effect of adsorbent dose on adsorption process was investigated by preparing, 0.5, 0.7, 1 and, 1.5 g of mixed PAC (Synthesized Carrot Waste) applied to 200 mL of AR18 dye solution with 100 mg/L of initial concentration for 140 min all with 200 rpm on a shaker. After separating the adsorbent from the solution by 1.4 Tesla magnet, the adsorption rate was read by the spectrophotometer, and the optimum dose of adsorbent was obtained in optimum time.

## pH Effect

The solution pH effect was measured at pH 3, 5, 7, 9, and 11 containing 1.5 g of adsorbent in 5 samples (each 200 mL) with dye concentration of 100 mg/L for a maximum time of 140 min all with 200 rpm on a shaker. Intervals of sampling were performed every 20 min. to keep the pH of dye samples at the desired level, HCl 0.1 N and NaOH 0.1 N solutions were applied. After separating the adsorbent from the solution by 1.4 Tesla magnet, the adsorption rate was read by the

spectrophotometer and the optimum pH was obtained in optimum time.

## Applied adsorption study technique

Using the column technique, a glass column was filled with 0.5 g amount of the adsorbent to achieve a height of 1 cm and a cross-sectional area of 0.5 cm<sup>2</sup>. The dimensions of the column were 20 cm in length and 0.5 cm inner diameter. The flow rate of the sample collection part was 5 mL/min, taking a 10-min time interval for adding 50 mL of effluent. The reactions of the column are explained by a normalized concentration graph, dye concentration ratio at time (t) to initial concentration of dye ( $C_t/C_o$ ), against time (18).To calculate the volume of effluent,  $V_{ef}$  (Eq.6) (Eq.6), the following formula is used:

In this formula, t (min) is the flow time and v (mL/min) is the rate of flow. The adsorbed amount of dye is  $Q_{total}$  (mg) at the time t, which can be computed from the below space curve (Eq.7):

$$Q_{\text{total}} = v \int_{t=0}^{t=t} (C_0 - C_t) dt$$
 (Eq.7)

The dye flow amount  $(m_{total})$  at time t can be measured by (Eq.8):

$$m_{total} = C_0 vt$$
 (Eq.8)

Removal of dye R (%) can be computed by (Eq.9):

$$R = \frac{Q_{total} \times 100}{m_{total}}$$
(Eq.9)

The adsorbent adsorption capacity  $q_t$  (mg/g) at time t can be calculated by (Eq.10):

$$q_t = \frac{Q_{\text{total}}}{m}$$
(Eq.10)

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In these formulas, m (g) stands for the amount of used adsorbent.

# Adsorbed Acid Red 18 dye desorption and reusability of PAC (Synthesized Carrot Waste)

After adsorption, doped PAC (Synthesized Carrot Waste) was cleaned with ethanol, placed in the oven for 15 min at 40°C. The adsorbent was used seven times to remove AR18 dye over 24 h. Moreover, AR18 dye concentration was specified using UV-visible spectroscopy after each run.

## Results

#### Determining characteristics of activated carbon

Pore volume and BET line of the AC powder are illustrated in Figure 1. This shows that one-fifth of the carrot wastes can be converted into AC powder.

The measurement of special levels and porosity of adsorption method with BET analysis at a constant temperature of liquid nitrogen (77K) (19), showed that the special level of AC 1163.05 m<sup>2</sup>/g after magnetic exposure to nanoparticles decreased to 993 (mg/g). Therefore, approximately 70% of the cavities in AC is related to the medium volume cavities that are suitable for absorbing molecules with a size of 24 nm and smaller. The pH at the point of zero charge  $(pH_{PZC})$ values and the higher concentration of basic than acidic groups indicated that it had a basic chemical nature (20) (Table 2). The presence of surface functions may be the site for specific adsorption and can promote the fixation of some pollutants, such as AR18.

Fourier transform infrared spectroscopy analysis peak existing on the surface of porous absorbent nanocarbon shows the maximum wavelength of 3429.25 cm<sup>-1</sup>, which is related to the OH factor group (21). The wavelength of 2923.51 cm<sup>-1</sup> related to C-H grafting, wavelength of 61.1746 related to the carbonyl C=O, wavelength of 61.1628 cm<sup>-1</sup> related to N-H groups, and magnetic particle characterization in the wavelength of 569 cm<sup>-1</sup> that indicate the link between the Fe-O groups in the face, are the most extreme forms which are synthesized in the final adsorbent.

With the application of FESEM, the high capacity of absorption and the size of cavities is well visible (Figure 2a). Porosity and pores in the adsorbent surface with different sizes and the distribution of almost uniformity show that this increased level and high porosity leads to increased absorption efficiency. The surface morphology of AC powder can be studied from the SEM image. Figure 2b shows the SEM images of the magnetite adsorbent loaded with Fe<sub>3</sub>O<sub>4</sub> NPs. The images showed objects in which some of them were found to be in five-angel shape, overlapping. The existence of bright spots is the sign of pore filling of AR18



Figure 1) Adsorption of Acid Red 18 onto activated carbon (Synthesized Carrot Waste) using the Brunauer–Emmett–Teller Model

	Table 2	) Characteristics	of activated carbo	n (Synthesiz	ed Carrot Waste)	
$S_{BET}$ (m <sup>2</sup> /g)	$S_{mic} \left( m^2/g \right)$	Total acidity (meq/g)	Total basicity (meq./g)	pH <sub>pzc</sub>	Acid Red 18 adsorption (mg/g)	I <sub>2</sub> adsorption (mg/g)
1163.05	730	0.47	1.67	7.79	460	993

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Figure 2) Field emission scanning electron microscopy images of PAC (Synthesized Carrot Waste)-Fe<sub>3</sub>O<sub>4</sub>

dye molecules. Moreover, the details of the PAC structure were investigated at several magnifications using SEM (Figure 2a). It was revealed that the AC powder is in different physical dimensions; however, further observations showed the existence of Fe<sub>3</sub>O<sub>4</sub> NPs thickness of average 24 nm.

The morphology and structure of the adsorbent were determined by the TEM technique. As shown in Figure 3, the crystal



Figure 3) Transmission electron microscopy images of PAC (Synthesized Carrot Waste)-Fe<sub>3</sub>O<sub>4</sub>

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structures, symmetry and orientation of the nanoparticles, and the adsorbent on each other are well visible in bright shadow points.

The results of the X-ray study showed a diffraction pattern for adsorbent nanoparticles. The peaks of the locations were 30.1, 37.36, 44.4, 54, 57, and finally 71.3 degrees, respectively with frequencies of 220, 311, 400, 422, 511, and 440, which are related to the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles crystals (Figure 4a) (22). This result confirmed the presence of magnetite nanoparticles in nano-absorbent structure and its accreditation of the



Figure 4) X-ray diffraction pattern of spectra PAC (Synthesized Carrot Waste)-Fe<sub>3</sub>O<sub>4</sub> (a).without Fe<sub>3</sub>O<sub>4</sub> (b)

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Figure 5) Energy dispersive X-Ray spectra PAC (Synthesized Carrot Waste) of Acid Red 18 adsorption

Fe<sub>3</sub>O<sub>4</sub>, which confirms the presence of magnetite nanoparticles in nano-absorbent structure and the starch of Fe<sub>3</sub>O<sub>4</sub>. Due to particle depletion, the oxides of surface ions may occur as a result of the goethite phase formation, which is the main peak of the oxide phase with Fe<sub>3</sub>O<sub>4</sub> (Figure 4a). Diffraction peaks at positions  $2\theta$  for  $44^{\circ}$  (in common with magnetite) and  $28^{\circ}$  are also characteristic of the nano-sorbent. The recent low peak intensity is due to the coating of carbon extracted from carrot waste with magnetite nanoparticles (Figure 4b).

Energy dispersive X-Ray (EDX) analysis was used to determine the composition of the elements present in the synthesized adsorbent structure (23). The three major constituents of the magnetized adsorbent are iron, carbon, and oxygen. In the adsorbent structure, in addition to the weight percent of the elements present, the contributions of hydrogen, iron, oxygen, and carbon are equal to 11.3, 48.2, 39.5, and 49.8 (Figure 5).

## Optimizing effective parameter on Acid Red 18 adsorption (ANOVA)

Removal percentage, as a dependent variable, and its relationship with independent factors were interpreted in the following calculation of regression coefficients (Eq.3).

 $\begin{aligned} Removal\% &= +55.51 - 43.31A + 1.99B + 56.44C + 3.98D \\ + & 4.08AB - & 3.33AC - & 2.88AD + & 8.06BC - & 20.99BD - \\ & 3.94CD + & 7.09A^2 - & 6.08B^2 - & 8.92C^2 - & 1.66D^2 \end{aligned} \tag{Eq.3}$ 

The independent variables are A, B, C, and D, standing for pH of a solution, time, AR18 dye concentration, and a dose of adsorbent (Table 3).

According to the ANOVA calculation (Table 4), the regressions obtained for the adsorption of AR18 were significant since the F values were significant and P values were less than 0.0001 (P<0.0001). The removal percentage was affected by pH more than all other factors. However, pH was most influential when two other variables (i.e., time and dosage) were used. It was shown that the AR18 adsorption's response to pH was very sensitive. The next effective factors for AR18 adsorption onto the adsorbents were adsorbent dose and time. The effects of factors on AR18 dye removal was

 Table 3) Experimental ranges and levels of the independent test variables

vel (-1)	Level (+1)
3	11
20	140
10	150
0.5	1.5
	<b>vel (-1)</b> 3 20 10 0.5

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depicted using three-dimensional response surfaces.

### Response surface methodology plots

According to three-dimensional plots, pH is a highly significant factor since, with the range of 3-11, the mean removal efficiency ranged from 2-98% by using PAC (Synthesized Carrot Waste), respectively. The adsorbent dose was also found to be a determinant factor in the adsorption process. The scarcity of sites due to low adsorbent dosage caused low efficiency, while a high amount of adsorbent dose caused occupancy of the adsorption sites due to overlapping adsorbent particles (24). The increase in the adsorbent dose led to increased removal efficiencies until they reached a constant state. Therefore, as the number of active sites was increasing due to the more use of adsorbent dose, adsorption efficiency started to increase. The effect of adsorbent dose with other variables is also presented in ANOVA. The p-value for this factor was between 0.0005 and 0.0001.

Figure 6 illustrates the AR18 percentage of adsorption efficiency versus optimal values of other factors. The changes in these plots revealed that there were interactions and effects between the factors. According to figures 6A-D, pH interaction with initial adsorbent dosage. It was observed that the adsorption efficiency of AR18 was increasing by the decreasing value of pH. As the pH decreased and the medium was saturated with H<sup>+</sup> with the increase in the amount of adsorbent, a repulsive force was created between the medium and the AR18; as a result of which the dye ions absorbed the positive charges on the adsorbent Therefore, with increasing surface. the absorbent dose while pH is at the optimum point (pH: 3), the adsorption increases alongside.

According to figures 6A-C, lower pH also increases the adsorption efficiency, while interacts with dye concentration. This might be related to the low pH values since the ionization of the functional groups causes the positive charge of the surface and as a result creates

Source	Sum of Squares	df	Mean Square	(F) Value	P-value Prob > F	
Model	27890.11	14	2019.34	25.99	0<0001	Significant
A-pH	22145.76	1	2456.24	308.06	0<0001	Significant
<b>B-time</b>	55.59	1	59.01	9.73	0<0001	Significant
C-dosage	509.85	1	517.77	15.89	0<0002	Significant
<b>D</b> -concentration	197.88	1	198.01	21.53	0<0099	Significant
AB	59.09	1	59.54	43.76	0<0079	Significant
AC	42.43	1	42.31	14.53	0<0046	Significant
AD	28.65	1	27.13	18.34	0<0001	Significant
BC	230.09	1	227.99	25.99	0<0033	Significant
BD	2336.12	1	2201.29	26.69	0<0001	Significant
CD	63.99	1	66.12	0.87	0<0002	Significant
A2	286.59	1	279.70	31.57	0<0046	Significant
B2	0.63	1	0.62	0.31	0<7012	Not significant
C2	599.01	1	597.59	71/45	0<0039	Significant
D2	16.90	1	27.18	6.21	0<0005	Significant
Residual	1064.99	14	74.66	-	-	
Lack of fit	820.01	10	79.99	1.24	0<4188	Not significant
Pure error	246.63	5	61.89	-	-	
Core total	28989.63	28	-	-	-	-
R <sup>2</sup> 99.70		R <sup>2</sup> adjus	sted 98.88		R <sup>2</sup> predicted 9	4.76

Table 4) Regression model ANOVA results for Acid Red 18 adsorption optimization (determination coefficient  $(R^2)=99.70$ ; adjusted determination coefficient  $(R^2adi)=0.98.88$ )

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powerful repulsive forces between AR18 anionic dye and the surface of the adsorbent, which in turn leads to a significant increase in the adsorption efficiency of AR18. When pH decreases, the protonation of sites on the adsorption (OH and  $H^+$ ) leads to the AR18 adsorption via hydrogen bonding beside electrostatic interaction. Figures 6B and 6C depict the maximum AR18 adsorption, which is obtained at upper contact time. The quick adsorption of AR18 confirms the efficiency of the prepared PAC on the industrial scale for wastewater treatment. The rapid adsorption rate is related to the plenty of vacant sites available on the adsorbent surface area. It is found that in the first 60 min of the interaction more than 88.31% of AR18 is adsorbed, and finally, the equilibrium was obtained after 80 min.



Figure 6) Three-dimensional plots of Acid Red 18 removal onto PAC (Synthesized Carrot Waste)

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Referring to figures 6B and 6D, the adsorption efficiency improves with an increase in the adsorbent dose, the reason of which is regarded to the increase in active site availability; however, at high ratios of AR18 molecule to the vacant sites, the efficiency of adsorption decreases significantly. The interaction between AR18 concentration and the adsorbent dose is presented in figures 6C and 6D. It was also found that adsorption efficiency had an indirect and significant relationship with AR18 concentration. Furthermore, an increase in the dye concentration led to a decrease in adsorption efficiency due to the adsorption site saturation.

# Optimization and Statistical Analysis based on the response surface methodology

Table 5 tabulates the RSM results obtained for optimum values of the factors performed by Design-Expert software (version 7.0.0). To achieve maximum adsorption efficiency, the final results were obtained accordingly: initial pH of 3, an adsorbent dosage of 1.5 g, initial AR18 concentration of 100 mg L<sup>-1</sup>, and contact time of 80 min. According to Table 5, the adsorption efficiency of 99.7% is obtained considering the optimized condition. The validity of the optimization was confirmed through performing experiments under optimum conditions. In this regard, the predicted and

Table 5) Experimental design matrix along with actual removal percentage of Acid Red 18 by PAC (Synthesized
Carrot Waste)

TI	Time	Adsorbent	Acid Red 18 concentration	Actual response	Predicte	d response
рн	(min)	dose (mg/L)	( <b>mg/L</b> )	(PAC)	( <b>P</b> .	AC)
					ANN	RSM
3	80	1.5	100	99.77	99.70	98.81
5	60	1.5	75	95.34	95.91	95.67
7	60	1	50	88.41	88.50	88.48
7	80	1	100	78.06	79.11	78.09
9	80	1	100	68.99	70.04	69.81
11	20	1	50	63.51	65.24	64.33
11	80	1.5	100	63.01	64.82	63.59
3	20	1	100	90.12	91.55	91.01
3	60	0.7	75	94.76	95.21	95.00
3	80	1.5	100	98.31	99.89	99.64
3	80	1.5	10	99.99	99.99	99.97
9	20	1.5	100	71/4	73.13	72.91
9	60	0.7	50	60.59	62.04	61.53
7	20	1.5	75	74.98	76.00	75.45
7	80	1.5	50	86.09	88.02	87.79
11	60	0.7	75	60.03	61.07	60.09
5	80	1	100	93.61	95.00	94.80
5	20	0.7	50	91.10	94.01	93.22
9	80	1.5	75	83.50	86.40	86.52
3	20	1	50	98.81	98.89	97.99
3	20	1.5	100	94.13	96.00	95.17
11	80	0.7	50	61.03	62.09	60.86
5	60	1.5	50	92.54	93.06	92.77
5	80	1.5	10	97.98	98.90	98.63
9	20	1	10	77.90	79.08	77.39
3	80	0.7	10	99.98	99.98	100
9	80	1.5	75	79.03	82.53	82.18
9	60	1.5	100	76.92	79.24	79.16
7	80	0.7	10	60.44	60.15	60.10

ANN: artificial neural network, RSM: response surface methodology

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observed values of response were recorded and compared under the optimum conditions. The predicted value was computed using Eq. 3, and the data collected from the experiments were considered the basis of observed value measurement. Comparison between the observed values of factors and predicted values showed that the performance of the model was validated with an observed value of 99.7% and the predicted value of 98.81%.

The obtained values of R2 = 0.9970 and Adj-R2 = 0.986 (Table 6) indicate a good correlation between the experimental and predicted data. An adequate precision (also known as the signal to noise ratio S/N) of greater than 4 shows the desirability of RSM model. Thus, the adequate precision value of 43.6231 shows an adequate signal for the model that can be used to navigate the design space.

#### Adsorption kinetics

The equilibrium kinetic profiles were studied to specify the elements involved in the process of adsorption and to approach the appropriate performance of the adsorption of AR18 on AC. The Equations (11) and (12) representing the linearized forms of two kinetic models, namely Lagergren pseudo-first-order (25) and pseudosecond-order (26), can be written as:

$$\log(q_e - q_t) = \log q_e - K_1 \times \frac{k_1}{2.303} t$$
 (Eq.11)

$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{1}{q_{e}}t$$
(Eq.12)

where qe (mg/g) is the adsorption capacity at equilibrium and qt (mg/g) is the amount of solute adsorbed at any time t,  $k_1$  (min<sup>-1</sup>) and  $k_2$ (g/mg min) are the constants adsorption kinetics representing the pseudo-first-order and pseudosecond-order adsorption rates, respectively. When the adsorption step is governed by diffusion in the pores, the kinetics in most systems comply with the model of the pseudofirst-order. In this case, the adsorption mechanism is controlled by the adsorption step. This model suggests that the occupancy rate of sites is proportional to the number of unoccupied sites. The pseudo-second-order model suggests that the rate of adsorption is controlled by chemical adsorption involving the interexchange or sharing of electrons between the adsorbate and the adsorbent (Table 7) (27).

The validity of the two models was tested by representing the experimental results by (t/q)versus t and linear fitting of  $\log (q_e-q_t)$  versus t (Figure 7). According to Figure 7, the adsorption of AR18 to an initial concentration (100 mg/L) vs. time indicates that the time required to reach the pseudo-equilibrium state is approximately 80 min. To examine the adsorption isotherms, the researchers of this study have adopted an upper contact time, which is 140 min. Table 6 summarizes the obtained calculations of the value of pseudo-first and second-order rate constants (k1) and (k2), regression coefficient  $(R^2)$ , and equilibrium capacity  $(q_e)$ . The comparison of the regression coefficient  $(\mathbb{R}^2)$ with the obtained q<sub>e,cal</sub> (i.e., adsorption

		]	<b>Fable 6) statis</b>	tical results o	of the Model		
Std. Dev.	Mean	C.V. %	PRESS	R2	Adj-R2	Pred-R2	Adequate precision
1.4	89.92	0.961	70.11	0.9970	0.9888	0.9476	43.6231
	C	1 1 1					

RSM: Response surface methodology

Table 7	) (	Constant rate	decompositio	n reaction in	different	adsorbent	concentrations
Lable /	<i>,</i> ~	Joinstant Late	uccompositio	n reaction m	uniterent	augor bene	concentrations

	Pseud	lo-first- reorder	•			Pseudo-secon	d-order	
Bio-absorbent (gr/L)	qe (mg/g)	$q_{e(cal)}\left(mg/g\right)$	$k_1 \ 10^{-2} \ (min^{-1})$	R <sup>2</sup>	q <sub>e</sub> (mg/g)	$q_{e(cal)} \left( mg/g \right)$	k <sub>1</sub> 10 <sup>-</sup> <sup>2</sup> (min <sup>-1</sup> )	$\mathbb{R}^2$
0.5	22.30	26.01	0.2	0.64	28.90	30.65	0.3	0.79
0.7	28.05	30.11	0.7	0.73	31.03	34.98	0.9	0.85
1	34.99	35.06	0.9	0.86	36.87	39.04	1	0.91
1.5	36.90	38.01	1.01	0.94	38.90	40.01	1.40	0.99

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capacity predicted by the models) revealed that the pseudo-second-order model fitted the kinetics data better than the pseudo-first-order model for AR18 (Figure 7b). The theoretical value (q<sub>e,cal</sub>) computed from the pseudo-firstorder model indicated a remarkable difference, compared to the experimental values (22.9%) illustrated in Figure 7a. Considering the pseudosecond-order model, the theoretical values were very close to the experimental values (about 3.99<5% of difference), indicating that the adsorption process followed the pseudo-secondorder kinetic equation. Similar findings have been reported in AR18 adsorption onto ACs derived from Arundo donax Linn (28), agriculture waste materials (29), and wheatresidue-derived black carbon (30).

### Adsorption Isotherm

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The adsorption process is described by means of adsorption isotherms that can give the relationship between adsorbate and adsorbent at equilibrium and a fixed temperature. These

isotherms help to provide important information on the efficiency of the material (i.e., the maximum sorption capacity of adsorbent). Various models have been proposed for the study of AC adsorption phenomena. However, these models differ in hypotheses of their applicability and parameters obtained from their use. In this study, two models were adopted, namely Freundlich and Langmuir to investigate the AR18 adsorption on AC (Table 8).

### Langmuir model

The adsorption model of Langmuir is defined by a maximum adsorption capacity which is related to the coverage of the surface with a monolayer. Indeed, the Langmuir isotherm indicates homogeneity of the adsorbent surface, as well as considering that all of the adsorption sites are equivalent in energy and there is no interaction between adsorbed species (Eq13) and (Eq.14). The Langmuir adsorption isotherm equation is expressed as a non-linear function (31):



Figure 7) Kinetic study of the adsorption of Acid Red 18 onto activated carbon, pH: 3; Acid Red 18: 100 mg/L; speed: 200 rpm; T: 25±2°C; time: 80 (min); M<sub>0</sub>:1.5 g

Iso	therm models Fe	rundlich	Isotherm mo	dels Longmuir	
n	K <sub>f</sub> (mg/g)	$\mathbf{R}^2$	K <sub>L</sub> (l/mg)	q <sub>max</sub> (mg/g)	$\mathbf{R}^2$
0.85	0.24	95.01	0.013	41	99.70

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$$q_e = \frac{q_{max}k_LC_e}{1+k_LC_e}$$
(Eq.13)

(Eq.14)

$$\frac{c_e}{q_e} = \frac{1}{q_{max}k_L} \times \frac{c_e}{q_{max}}$$

Where  $C_e$  (mg/L) is the concentration equilibrium,  $q_e$  (mg/g) the amount of solute adsorbed per gram of adsorbent at equilibrium,  $q_{max}$  (mg/g) the amount of solute adsorbed per gram of adsorbent in forming a complete monolayer, and  $K_L$  (L/mg) the Langmuir constant related to the adsorption energy. It was revealed that Langmuir adsorption isotherm found a better model fitting with the adsorption process (Figure 8a) compared with Freundlich isotherm (Figure 8b).

#### Freundlich model

The Freundlich isotherm is used to describe adsorption to heterogeneous surfaces, with sites of varied affinities, by multilayer adsorption (32). It is an indication of the heterogeneity of the adsorbent's surface, responsible for the multilayer formation caused by the presence of different energy distribution of adsorption sites (Eq.15).(Eq.15) It is assumed that the stronger binding sites are occupied first and that binding strength decreases as the degree of site occupation increases. The Freundlich equation is as follows:

$$q_e = k_f C_e^{\frac{1}{2}}$$
(Eq.15)

The linear form of the Freundlich isotherm is given by this equation:

$$\log(q_e) = \log(k_f) + \frac{1}{n}\log(C_e)$$
 (Eq.16)

Where  $C_e$  (mg/L) is the concentration at equilibrium,  $q_e$  (mg/g) is the equilibrium amount adsorbed,  $K_f$  ((mg/g) (L/mg)<sup>1/n</sup>) represents the capacity of the adsorption related to the Freundlich isotherm, and n is the Freundlich constant which characterizes the efficiency of the adsorbent or the adsorption's intensity (Eq.16). The value of 1/n fell in the range of 0-1 indicates favorable adsorption (33).



Figure 8) Adsorption isotherm of Acid Red 18 onto activated carbon at pH: 3; [AR]: 100 mg/L; speed: 200 rpm; T: 25±2°C; time: 80 (min); M<sub>0</sub>:1.5 g

## Discussion

Based on the analysis of variance, the effects of the main variables, including initial pH,

adsorbent dose, dye concentration, and interaction between adsorbent dose factors to the initial pH, are significant (P<0.0001) Moreover, the F-value of the RSM model was 25.99 and the obtained p-value was less than

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0.0001 considering the parameters mentioned in the model. Therefore, the model and the results were significant (34).

 $R^2$ , which stands for regression square, was also used to measure the dependent variable (adsorption percentage). Regression equations were found significant since less than 0.01% of variance analysis obtained were not significant and could not be explained. Both predicted and adjusted regression coefficients were high and indicated that the model was very compatible with the findings and could anticipate the desired response properly (percentage of AR18 removal). Additionally, the obtained coefficient of variation was relatively small and equaled to 4.26% for the dependent variable showing both the reliability of the experiments and the precision of the measurements. Variance analysis also was used to measure the goodness of fit in the model. Statistical cross-validation was performed to measure the fit of the model to observations. The values of predicted residual error sum of squares were 70.11 and 1.4 obtained for standard deviation, confirming the good correlation between the experimental and predicted data. Based on the results of the regression equation, the most significant variables were reported to be in an array of pH > adsorbent dose > time > dye concentration.

Contact time is one of the most important parameters affecting practical applications in the adsorption process. The results of studying the effect of this parameter showed that with an increase in the contact time, the color removal efficiency increased (35). The amount of dye removal was fast at the beginning of the process; however, it gradually decreased with a further increase of contact time and continued with less slope until it reached equilibrium at 60 min of contact time. The reason for the occurrence of this phenomenon is the fact that at the beginning and early stages of absorption, available active sites for the adsorption process were plenty; however, with the increase of contact time, the number of these sites decreased and adsorption occurred at a slower rate. In general, it can be stated that the adsorption capacity increases with increasing the contact time, and at a certain time, the amount of adsorbed dye is in equilibrium with the amount of desorption (36).

In the adsorption process, the pH of the solution is one of the most influential parameters due to its effect on the surface charge of adsorbent particles. The results and statistical analyses of this study showed that with increasing the reaction time and the amount of adsorbent, the adsorption process efficiency increased, while with increasing the initial dye concentration and pH, the adsorption efficiency decreased significantly. The pH scale is one of the effective parameters on the chemical activity of dye ions and one of the most important factors affecting the adsorbent capacity. Adsorption efficiency depends on the pH of the solution since changes in the pH lead to changes in the degree of ionization of the adsorbed molecule and the properties of the adsorbent surface. Acid red 18 belongs to the category of anionic dyes due to its R-SO3 functional group. Removal of AR18 under acidic pH conditions indicates that the adsorbent binding sites closely relate to H<sup>+</sup> ions, which act as interface ligands (i.e., bridges) between the adsorbent surface and the dye molecule. Acid red 18 dye removal decreases with increasing pH with pH 12 having the lowest dye removal efficiency. The decrease in removal at high pH attributes to the frequency of OH, as well as the increase in ion repulsion between OH<sup>-</sup> and anionic dye molecules. Therefore, the adsorption process is better at acidic pH than in an alkaline one, which is consistent with the results of a study using ash prepared from the almond shell and palm ash to remove dye from aqueous media at pH 2 (37). Removal of AR18 from aqueous media using adsorption on natural Turkish clay at pH 2 resulted in maximum adsorption (38).

The study of the effect of initial dye

concentration on the removal efficiency showed that with increasing the initial dye concentration the dye removal efficiency decreased and qe increased (39). The decrease of adsorption can be related to the decrease in the level of adsorption due to saturation. The examination of the changes in dye concentration revealed that the highest removal rate occurred at lower concentrations and higher concentrations, the removal rate decreased due to the constant amount of adsorbent sites and adsorption capacity (40). According to the results of other studies, the excessive increase of the dye substance with specific absorption levels has increased the competition for adsorption on the surfaces and the collisions, as well as rising the possibility of desorption (41). In the surface adsorption process, with increasing the amount of dye removal, the driving force of the pollutant from the solution to the adsorbent will increase, which will increase the adsorption on the adsorbent. This has been observed in most adsorption processes and has been reported by various researchers. The main reason for the decrease in removal rate with increasing concentration can be related to the occupancy of active sites on the adsorbent surface (42).

The increase in the absorbent dose led to a significant increase in color removal efficiency. In the examination of different amounts of adsorbent, it was found out that with increasing the amount of adsorbent, the adsorption of dye AR18 on the adsorbent was very high (43); therefore, in the first 20 min, destruction of the red agent arm was achieved and in 30 min later, color degradation and 99% dye removal was observed. The reason for this increase can be related to the fact that with increasing particles of the adsorbent, the number of vacant active sites on the nanoparticles and consequently on the contact surface has increased (44). In the present study, the rate of decomposition of acid-18 dye increases with the increase of loading adsorbent from 0.5 to 1.5 g/L. In other words, with the increasing active surface of the adsorbent, the number of decolonization increases. Absorbent concentration is an important and determinant factor in the adsorption process. The absorption rate in all doses accelerates initially, while it decreases subsequently. In fact, at initial moments, the number of available adsorbent sites is very high; however, they gradually, over time, become saturated, and the adsorption rate decreases (45).

The determination of pollutant adsorption isotherms by different adsorbents is one of the main and important parameters in adsorption studies. Adsorption isotherms are models that describe how contaminants react with adsorbents and play an essential role in the practical applications of adsorbents. It is crucial to establish the right relationship for the equilibrium curve and optimize the design of a surface adsorption system for dye removal. Adsorption equilibrium occurs when the amount of dye adsorbed on the adsorbent surface is equal to the amount of dye desorbed (46). The adsorption of AR18 dye on AC prepared from carrot waste (i.e., Fe<sub>3</sub>O<sub>4</sub>) matched with Langmuir and Freundlich adsorption isotherms. Based on the results obtained from the adsorption balance study, the Langmuir isotherm model has a stronger correlation with the laboratory data, compared with the Freundlich isotherm in this study  $(R^2=0.997)$ , indicating the uniform distribution of active sites on the adsorbent surface. Moreover,  $q_{max}$  Value describes the monolayer between adsorbed molecules. Those Freundlich isotherms which are higher than 0.95 are indicative of a good agreement with the data. The constant 'n' in the Freundlich model is 0.950, which is close to one, indicating the appropriate conditions for dye adsorption by the studied adsorbent. A similar study reported the removal of azo dyes by an adsorbent using protein-rich solution following the Langmuir isotherm model (47). The correlation coefficients  $(R^2)$  of the Langmuir and Freundlich

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isotherms for agricultural residues adsorbent adsorption data showed that the adsorption process follows the Langmuir isotherm. Moreover, the best fitting for experimental data of AR18 adsorption is achieved by Langmuir isotherm (Figure 8a). The high correlation coefficient ( $R^2$ >0.997) and the low values of error show the fitness and agreement of the Langmuir model for the interpretation of the experimental data, reflecting the monolayer adsorption of AR18 on AC (48). In addition, the color absorption kinetics follows the quasiquadratic kinetic model better than the quasifirst-order model.

# Conclusion

In this study, the adsorbent made up of AC powder was obtained from carrot waste and magnetized with Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Characteristics and effectiveness of adsorbent confirmed using EDX, BET, TEM, XRD, FTIR, and FESEM techniques. Structural examination of the XRD from magnetite adsorbent and its comparison with the standard sample pattern indicates that the magnetic phase was synthesized correctly. In the XRD pattern, the presence of the characteristic and peak of the magnetite phase indicates the synthesis of Fe<sub>3</sub>O<sub>4</sub> crystals in the structure of AC powder and the successful production of the adsorbent. The present investigation showed that AC prepared from waste carrot and magnetized by Fe<sub>3</sub>O<sub>4</sub> in a one-step physical activation was an effective adsorbent for the removal of AR18 from aqueous solutions. Moreover, it was revealed that a one-step physical activation could produce a good quality of AC from waste carrot rather than of the usual two-step process (i.e., carbonization followed by activation). The produced AC had a large specific surface area of 1163.05 m<sup>2</sup> g<sup>-1</sup> and good adsorption capacities for AR18, suggesting that it had a structure consisting

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essentially of microporous and mesopores. The adsorption of AR18 was strongly influenced by the pH of the medium. It was noted that the maximum of adsorption was obtained at pH 3 for AR18. Kinetics studies revealed that AR18 adsorption was highly fast at the beginning which started to decrease while achieving equilibrium. The optimum time required to reach the pseudo-equilibrium state was approximately 80 min, and it was found out that the pseudo-second-order model fitted the kinetics data for AR18 better than the pseudofirst-order model. Experimental results were compatible highly with the Langmuir adsorption isotherm model and showed a better fitting to the theoretical data. Desorption tests in distilled water, in solutions of HCl, NaOH, indicated that the maximum removal efficiency of AR18was estimated at 99.7%. According to the experimental results, the main mechanism of AR18 adsorption on the AC is through interactions. electrostatic The adsorption capacities of AC, prepared from waste carrot and magnetized by Fe<sub>3</sub>O<sub>4</sub> for AR18removal, in the same experimental conditions, were higher or comparable to ACs obtained from different by-products cited in the literature.

# Footnotes

# Acknowledgements

This work has been financially supported by the Materials and Energy Research Center, Karaj, Iran.

# Funding

The project is funded by Islamic Azad University, North Tehran Branch, Tehran, Iran.

# **Conflict of Interest**

The writers announce that they have no conflicts of interest concerning the publication of the study.

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Archives of Hygiene Sciences

Volume 10, Number 1, Winter 2021