



## Basic dyes Removal by Natural *Salvadora Persica* Adsorbent

A. Hamidi, K. Seifpanahi-Shabani\*, M. Karamoozian

Faculty of Mining, Petroleum and Geophysics Engineering, Shahrood of University Technology, P. O. Box: 361995161, Shahrood, Iran.

### ARTICLE INFO

#### Article history:

Received: 10 Dec 2016

Final Revised: 4 Mar 2017

Accepted: 6 Mar 2017

Available online: 10 Apr 2017

#### Keywords:

*Salvadora persica*

Basic dyes

Adsorption

Wastewater treatment

### ABSTRACT

**I**n this paper, the sorption activity of *Salvadora Persica* fine particles provided from internal natural resources in Iran with respect to Crystal Violet, Basic Violet-16 and Basic Blue-41 dyes is investigated. *Salvadora Persica* particles were modified and prepared via particle size reduction and they were characterized by CHNS, XRD, SEM and FT-IR analysis. In the batch system, the influence of pH, adsorbent dosages and dye initial concentration was investigated. The results of isotherm and kinetics studies show that the Langmuir isotherm and pseudo-second order kinetic have better correlation with the experimental data. Calculations of thermodynamic parameters show negative Gibbs free energy ( $\Delta G$ ) values or spontaneous reaction, the enthalpy ( $\Delta H$ ) changes shows the exothermic process and values of entropy ( $\Delta S$ ) indicate low randomness at the solid/solution interface during the uptake of dyes. So, these locally available cheap adsorbents for the removal of basic dyes from the aqueous solution have high efficiency and can also be utilized for other water pollutants such as toxic elements. Prog. Color Colorants Coat. 10 (2017), 115-128 © Institute for Color Science and Technology.

### 1. Introduction

Since the discovery of first synthetic dye in 1856, more than 100,000 dyes have been synthesized worldwide, with over 700,000 tons per annual production [1]. Dyes usually present in the effluent water from many industries, such as textile, leather, rubber, plastic and paper printing [2-4]. The dye contamination in aqueous phase reduced the sunlight penetration and deplete the dissolved oxygen in the water environment [5]. In addition, some toxic, mutagenic and carcinogenic intermediates were produced by different reaction such as hydrolysis and oxidation of dye [6, 7]. Being a protein dye, Crystal Violet (CV) is used as an enhancer for bloody fingerprints. The dye is also used on most types of adhesive tapes, because conventional powders

adhere to the entire sticky side of the tape and are not selective to the latent prints [8, 9]. Basic Violet-16 (BV-16) has been widely employed in human as well as veterinary medicine as a biological stain. It is also used in textile, printing, papermaking, leather, food and cosmetic industries [1]. Basic Blue-41 (BB-41) is a monoazo-basic dye of bright blue hue. It is particularly suitable for dyeing acrylic substrates and can also be applied to some polyamide and polyester type, viscose, cotton and wool [10]. The dye BB-41 can cause eye burns, which may be responsible for permanent injury to the eyes of human and animals, irritation to gastrointestinal tract with symptoms of nausea, vomiting and diarrhea as well as methemoglobinemia, cyanosis, convulsion, tachycardia and dyspnea. Contact

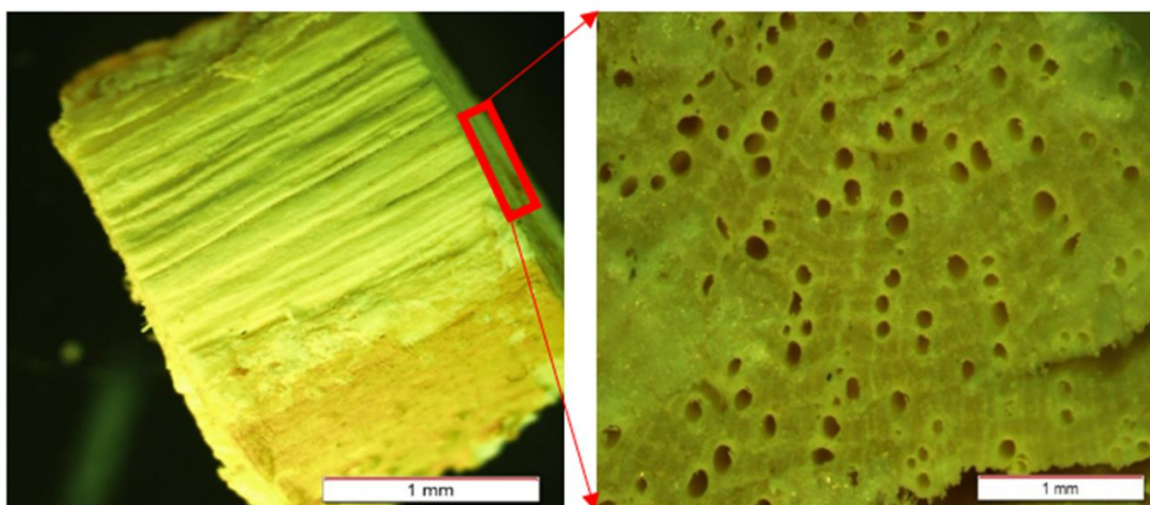
\*Corresponding author: [seifpanahi@shahroodut.ac.ir](mailto:seifpanahi@shahroodut.ac.ir)

with skin causes irritation [11]. Therefore, dyes present in wastewater generates high toxicity following possible accumulation in the various ecosystem and environment. CV, BV-16 and BB-41 dyes typical example of industrially relevant toxic dyes with known harmful effects on humans [12, 13]. Adsorption has been recognized as an attractive separation technique for the removal of dyes from wastewater because of its low cost, simple design and high efficiency [14, 15]. One of the most widely used adsorbents is activated carbon because of its large surface area and high adsorption capacity [16]. However, the relatively high cost and difficult regeneration of activated carbon restrict its use in industrial wastewater treatment. This limitation has encouraged the search for inexpensive and readily available adsorbents for the removal of dyes. Such as natural materials, bio-sorbents and waste materials from industrial and agricultural process [17, 18]. Stems and roots of the *Salvadora Persica* (SP) plant in the past markable for oral hygiene and a tubular structure is very super porous and fibrous component (Figure 1). SP plant contains various ingredients including: flavonoids, saponins, tannins, sulfur compounds, benzyl isothiocyanate, chloride, fluoride, calcium and organic silicon [19-21].

The application of SP plants for mouth cleaning

returns to 7000 BC. Using SP plant for oral hygiene is recommended by the World Health Organization (WHO) [22]. Different parts of SP plant due to existence of tannins, sulfur compounds and benzyl isothiocyanate have strong and broad anti-microbial activity [20]. Sulfur compound has antibacterial effect [23, 24]. Tannin is a substance found in many plant extracts and usually get it from oak bark these are the plants that have been used in the leather industry. Also, tannins combined with proteins that cause the precipitation of gelatin, made of organism's skin to prevent it established and the corruption [23]. According to the literature review, SP plant has not been used by now for wastewater treatment as a fine adsorbent and was only used as row for removal of pollutant on limited basis [25, 26].

In this paper, SP plant stem was utilized as a high efficiency adsorbent, spatially. So, SP plant was used for removal of basic dyes consisted of CV, BV-16 and BB-41 dyes in the simulated wastewater in the batch system. These three basic dyes have more application in the textile industries and also more volume of them entered to the environment that others dyes. Their color intensity has been widely compared with other dyes and these basic dyes have intense toxicity.



**Figure 1:** Tubular, porous and fibrous structure of SP plant in natural size.

## 2. Materials and methods

### 2.1. Preparation and activation of SP fine particles

SP plant was collected from the local area and was thoroughly washed with 3 molar hydrochloric acid for removing impurities and volatile components. After drying under sunlight, they were oven dried at  $333 \pm 1$  K for 12h and then crushed using ball mill grinding (Laboratory Denver model) without any water for 3h. The SP plant micro-powder was re-crushed by Planetary Ball Mill (Narva-MPM-H model) for further particle size reduction to nanoscale. After wet milling, SP plant particles were spray dried (B-290 model). The procedure of producing SP plant particles is shown

in Figure 2.

### 2.2. Characterization of SP plant adsorbent

For characterization of SP plant adsorbent CHNS, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) analysis were performed. The results of CHNS analysis are reported in Table 1.

According to Table 1, carbon is the major element of SP plant. To consider the natural functions of SP plant particle, the FT-IR spectra analysis is done in Figure 3. The interpretation of major peaks of SP-1, SP-2, SP-3, SP-4 and SP-5 is presented in Table 2.

Table 1: CHNS analysis of SP plant particles.

| Element | Element Percentage (Wt. %) |
|---------|----------------------------|
| C       | 33.25                      |
| H       | 5.01                       |
| N       | 2.63                       |
| S       | 4.84                       |

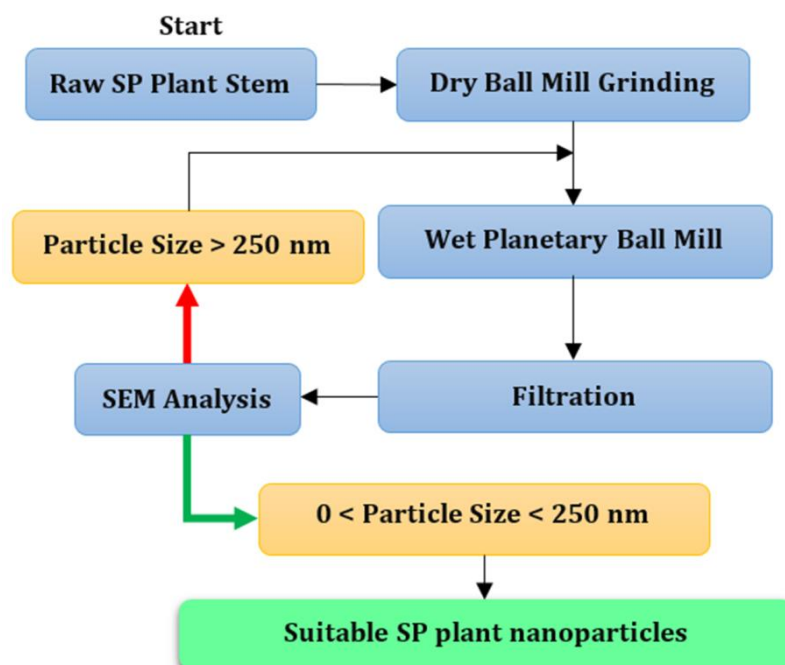
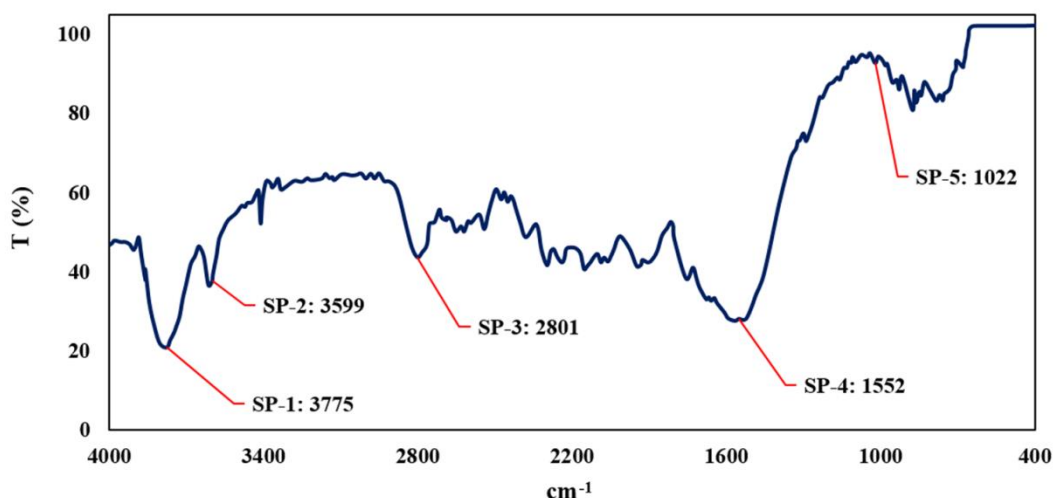


Figure 2: SP plant particles producing procedure.

**Table 2:** FT-IR spectra analysis of SP plant particles.

| Functional group           | Band position in FT-IR spectra ( $\text{cm}^{-1}$ ) |               |
|----------------------------|---|---------------|
| -OH and $-\text{NH}_2$     | 3775 and 3599                                       | SP-1 and SP-2 |
| -CH aliphatic              | 2926.8  | SP-3          |
| C=O, C=C and $-\text{NH}$  | 1676.3, 1624.7 and 1524.7, respectively             | SP-4          |
| C-O-C ( $\text{cm}^{-1}$ ) | 1022  | SP-5          |

**Figure 3:** The FT-IR spectra analysis of SP plant particles.

The XRD Spectrum of SP particles was plotted by XRD Unisantis model and show in Figure 4. Based on XRD analysis, the main peak (002) refers to the glucan bio-structure. Also, the Miller indices of the XRD curve were shown and the SP adsorbent has an amorphous non-crystalline structure. For further characterization of SP plant particles, the SEM image was prepared as shown in Figure 5. It is obvious that SP plant particles are smoothness and coagulated tissue and their size is smaller than 250 nm. So, this fine adsorbent can be used for wastewater treatment.

### 3. Results and discussion

#### 3.1. Experimental studies

Batch adsorption experiments were carried out in Erlenmeyer flasks with 25 mL of working volume, with a concentration of CV, BV-16 and BB-41 dyes (10, 20 and 50 mg/L), respectively. A weighted amount

of adsorbent for CV, BV-16 and BB-41 dyes (0.05, 0.025 and 0.025g, respectively) was added to the synthetic wastewater solution. The stock solution (150  $\text{mg L}^{-1}$ ) was prepared by dissolving accurately weighed quantity of the dye (0.150 g) in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water. The initial solution pH was adjusted using 1.0 M HCl and 1.0 M NaOH solutions. The chemical structure of CV, BV-16 and BB-41 are illustrated in Figure 6.

Contact time (10, 20, 40, 60, 80, 100 and 120 min) was evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration on the solution phase. The residual amount of dye in each flask was determined by using UV-Vis spectrophotometer (UV-Visible/2100, UnicoUSA), the amount of dye adsorbed per unit (mg dye per g adsorbent) was calculated according to a mass balance

on the dye concentration using Equation 1 [27]:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \times 100 \quad (1)$$

where  $q_e$  (mg/g) is amount of adsorption at equilibrium,  $C_0$  and  $C_e$  are the initial and the equilibrium concentrations (mg/L), respectively,  $V$  is the volume of solution (l) and  $m$  is the weight of SP (g)

adsorbent. The removal percent of dye was calculated using Equation 2 [28, 29]:

$$Removal(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

The flasks were agitated at a constant speed of 150 rpm for 2 h in a magnetic stirrer at 294K with 2.0, 4.0, 5.5, 7.0, 9.0 pH values (Figure 7).

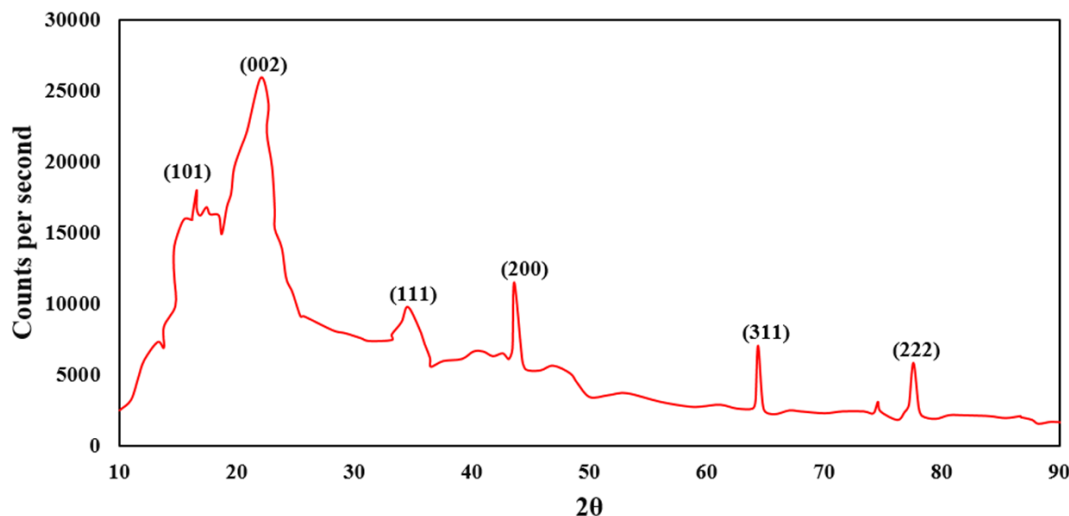


Figure 4: The XRD Spectrum of SP particles.

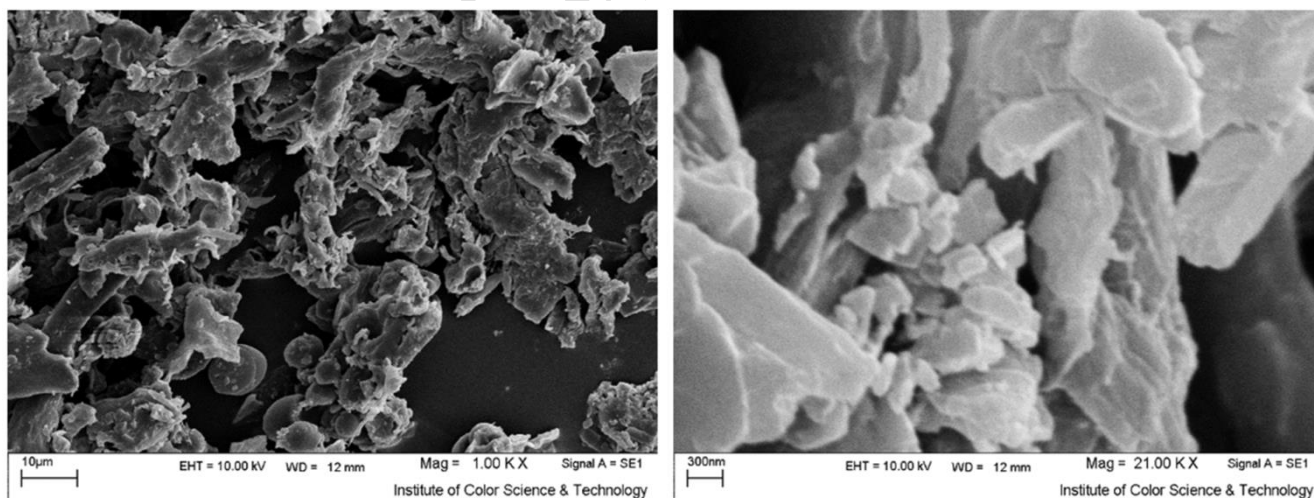
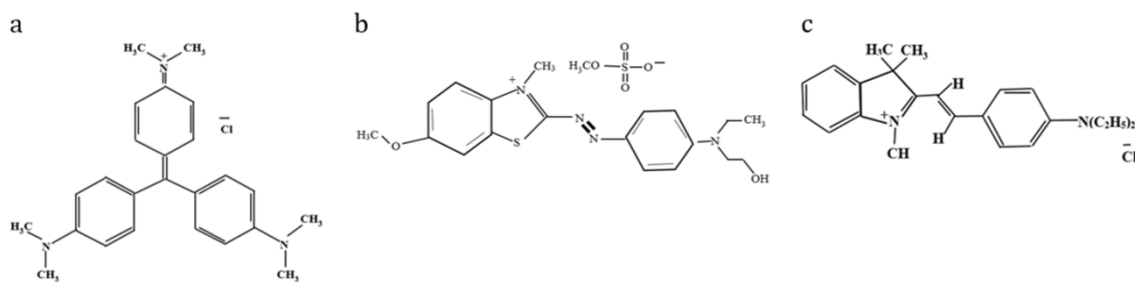
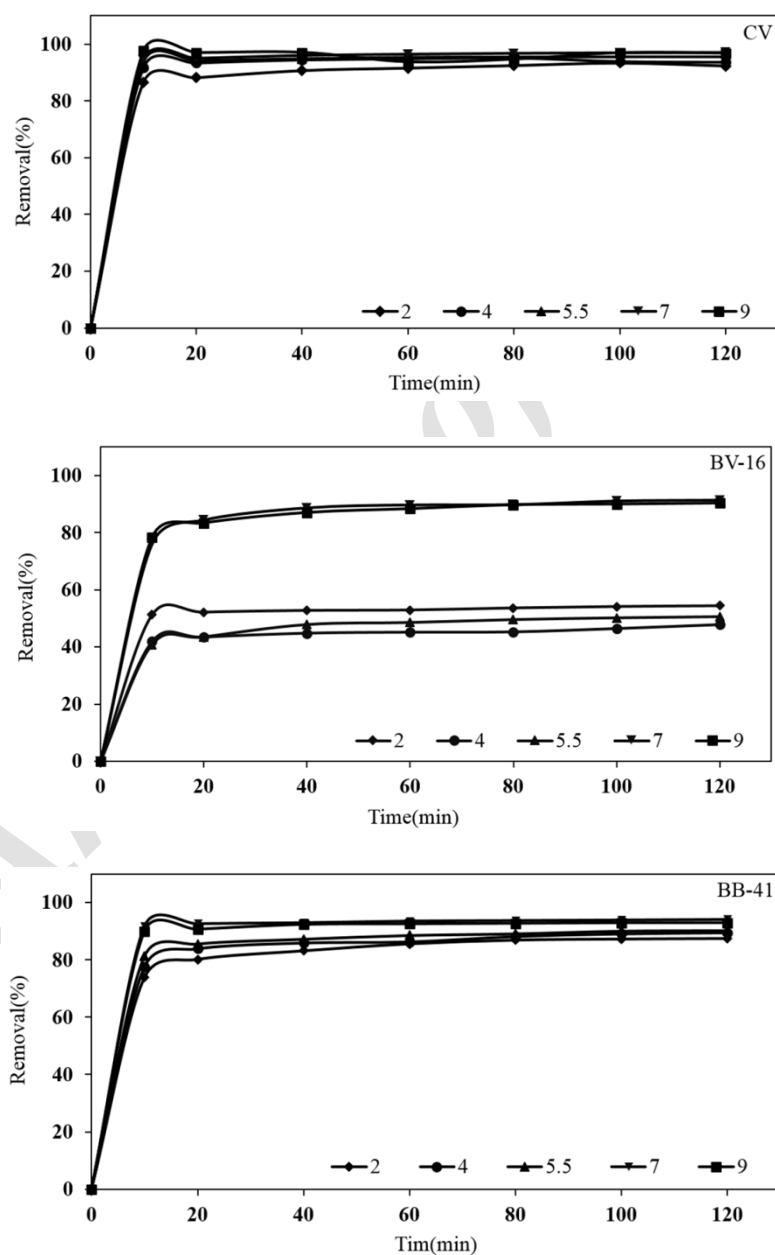


Figure 5: SEM image of SP plant particles.



**Figure6:** Chemical structure of a) CV, b) BV-16 and c) BB-41.



**Figure7:** Effect of pH on adsorption of CV, BV-16 and BB-41 dyes by SP adsorbent (Experimental conditions:  $C_0=10, 20, 50$  mg/L, adsorbent dosage = 0.05, 0.025, 0.025 g/25mL, respectively and agitation speed = 150rpm,  $T = 293$  K and time = 2 h).

According to Figure 7,  $\text{pH} = 7$  showed better adsorption efficiency for the removal of the three dyes. The  $\text{pH}_{\text{pzc}}$  of the adsorbent was determined using a procedure similar to the one described previously by Khormaei: 50 mL of 0.05 M NaCl solutions were transferred to a series of 100 mL Erlenmeyer flasks. The initial pH of each solution was adjusted from  $\text{pH}=2$  to  $\text{pH}=12$  by adding either 0.1 M HCl or NaOH. Then, 0.1 g of adsorbent was added to each flask and the final pH was measured after 48 h under agitation at ambient temperature ( $20\text{ }^\circ\text{C}$ ). The  $\text{pH}_{\text{pzc}}$  is the point where the plot of  $\text{pH}_{\text{final}}$  versus  $\text{pH}_{\text{initial}}$  (Figure 8) crosses the line  $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$  [30].

Reaction pH is a significant control on most dye sorption from aqueous solution. This is because pH dictates the adsorbent surface properties, the ionic state of functional groups, and aqueous dye speciation. Surface charge and therefore electrostatic attraction is a function of pH. The pH with which net total surface charges is zero is called the point of zero charge ( $\text{pH}_{\text{pzc}}$ ). Below  $\text{pH}_{\text{pzc}}$  the surface of the adsorbent is positively charged and vice versa. In this work, the SP displays a zero surface charge at  $\text{pH}_{\text{pzc}}$  7.1 (Figure 8).

After optimization of pH, CV, BV-16 and BB-41 dyes initial concentration were considered in optimal

pH value. The initial concentration of CV, BV-16 and BB-41 dyes were varied in the range of 2, 5, 10, 20, 50, 100  $\text{mg L}^{-1}$ , 20, 30, 40, 50, 60  $\text{mg L}^{-1}$  and 50, 60, 70, 80, 90, 100  $\text{mg L}^{-1}$ , respectively. The results are shown in Figure 9.

According to Figure 9, the dependence of adsorbent efficiency to dyes initial concentration as  $\text{CV} > \text{BV-16} > \text{BB-41}$ . So, for example BB-41 in 100  $\text{mg/L}$  will be adsorbed better than BV-16 and CV. For adsorbent dosage considering the governing parameters set as:  $\text{pH} = 7$ , CV, BV-16 and BB-41 dyes initial concentration = 10, 20, 50  $\text{mg/L}$ , respectively, agitation speed = 150 rpm and  $T = 293\text{ K}$ . Thus, the results for adsorbent dosage variation are shown in Figure 10.

According to Figure 10, for CV, BV-16 and BB-41 dyes and the variation in adsorbent dosage 0.1, 0.2 and 0.2 g, respectively. By decreasing the adsorbent dosage, the value of dye removal was changes and decreased by 3, 52 and 31%, respectively. According to CV, BV-16 and BB-41 dyes concentration changes (10, 20 and 50  $\text{mg/L}$ ), this is obvious that dyes removal order with increasing the adsorbent dosage is as:  $\text{BB-41} > \text{BV-16} > \text{CV}$ . The FT-IR analysis of SP particles after and before adsorption of CV, BV-16 and BB-41 dyes are shown in Figure 11.

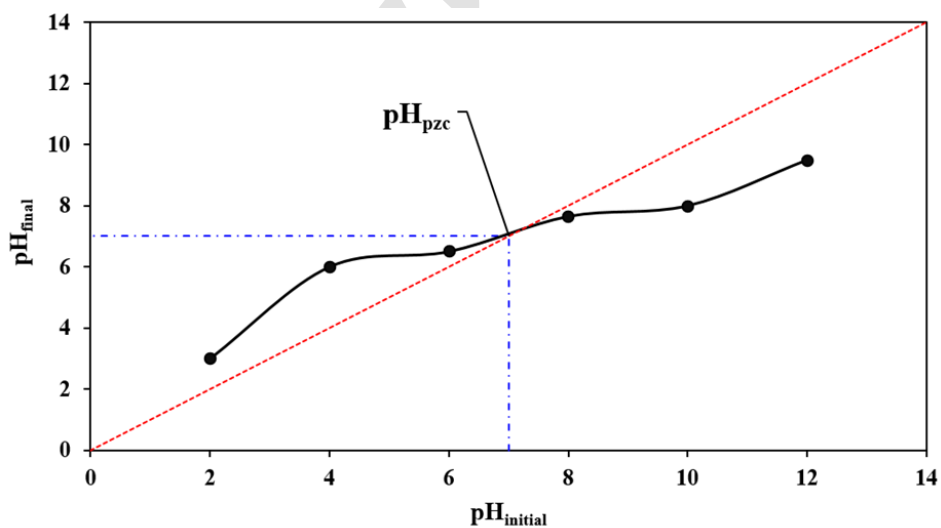
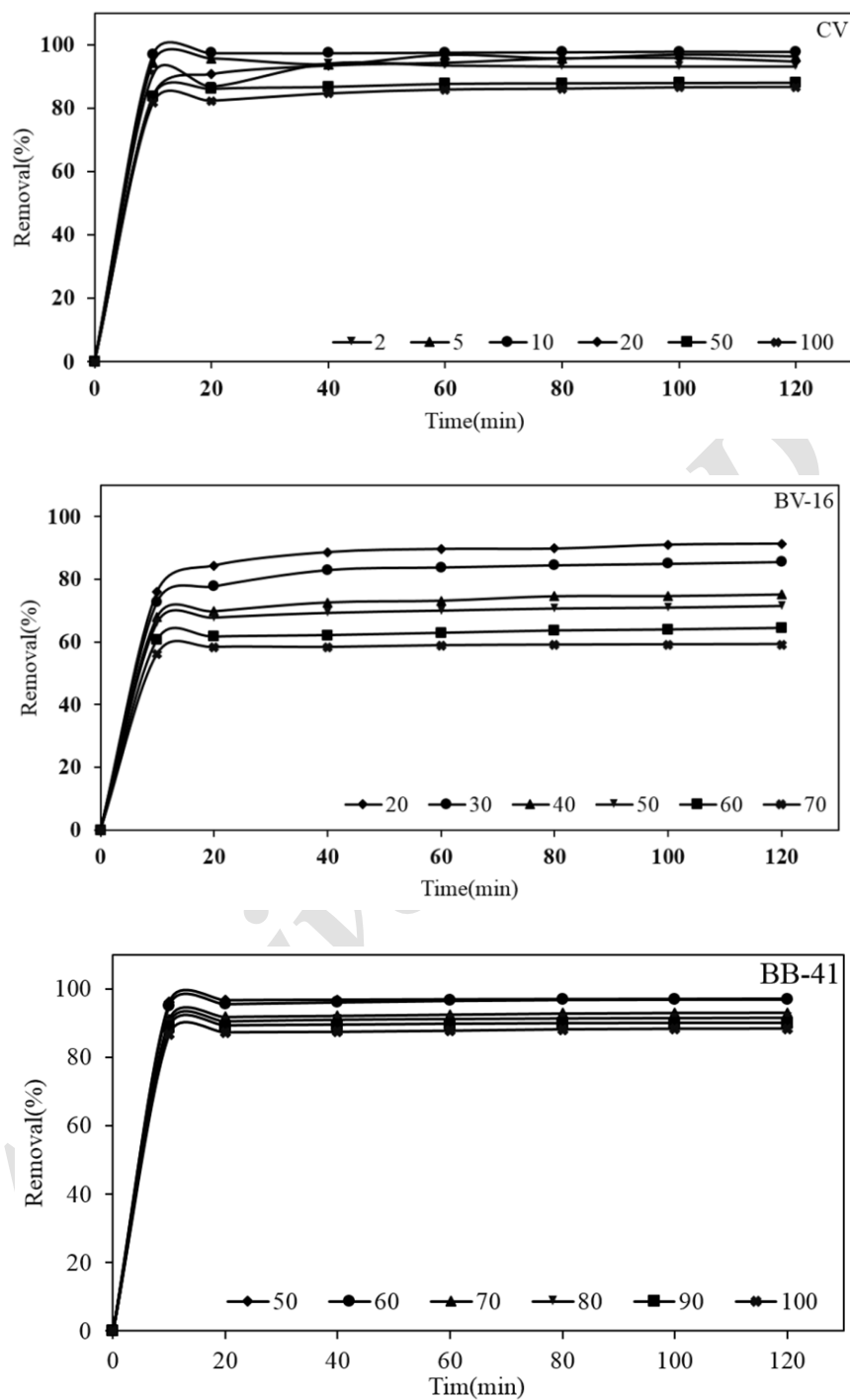
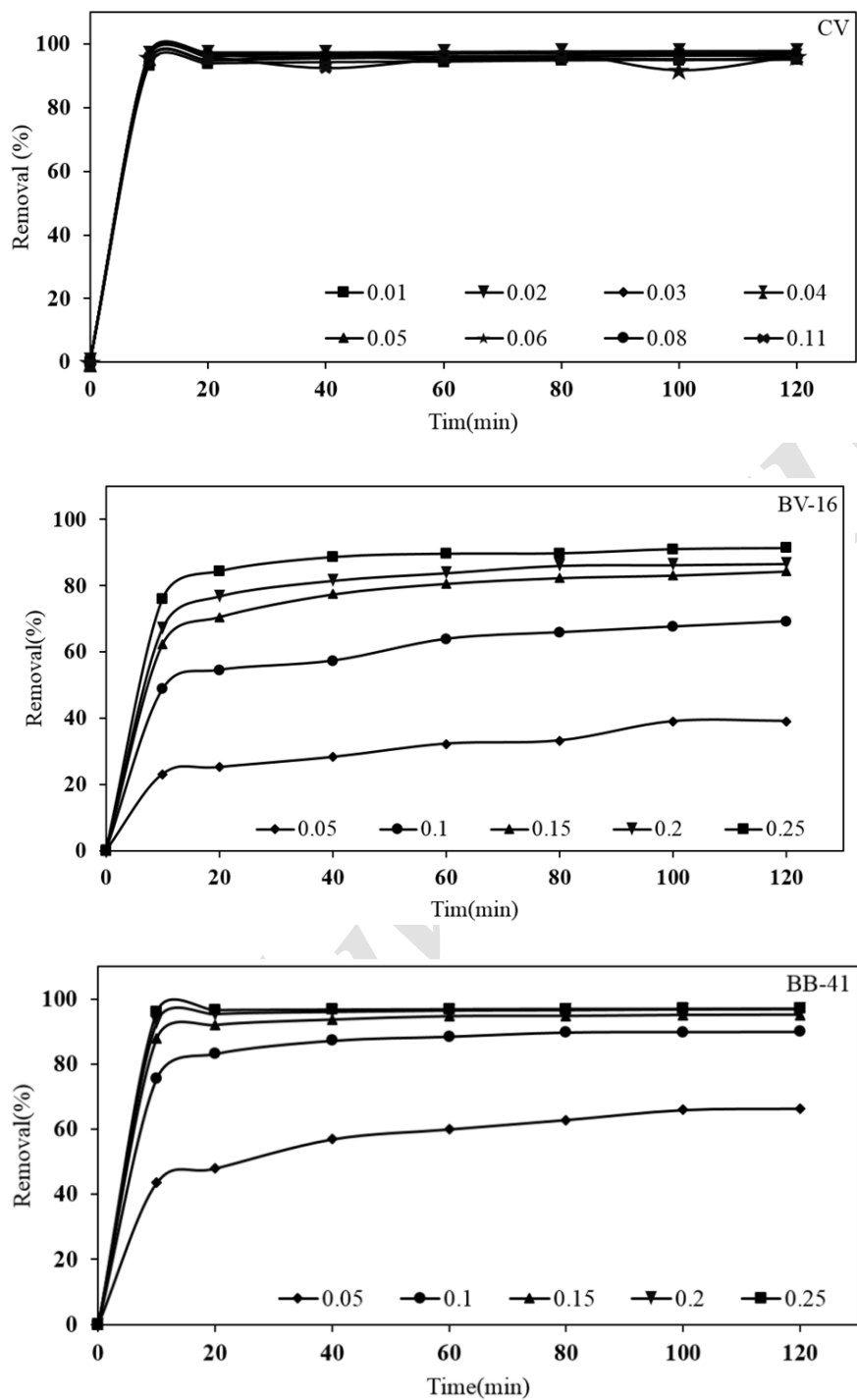


Figure 8: Determination of the point of zero charge pH ( $\text{pH}_{\text{pzc}}$ ).

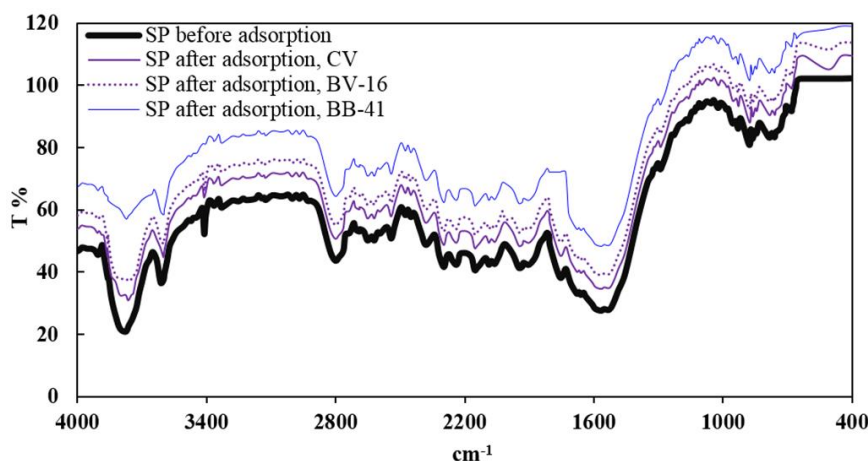


**Figure 9:** Effect of initial concentration on adsorption of CV, BV-16 and BB-41 dyes by SP adsorbent, experimental conditions: pH = 7, adsorbent dosage = 0.05, 0.025, 0.025 g / 25 mL, respectively and agitation speed = 150rpm, T = 293 K and time = 2 h.





**Figure10:** Effect of adsorbent dosage on the adsorption of CV,BV-16 and BB-41dyes by SP particles in pH = 7, initial concentration = 10, 20, 50 mg/L, respectively, and solution volume = 25 mL and time = 2 h.



**Figure11:** The FT-IR analysis of SP particles after and before adsorption process of different dyes.

As it is obvious, the adsorption sites were filled by dyes after adsorption process that is due to the reduction in SP-1 band ( $3775\text{ cm}^{-1}$ ). The intensity of chemical functional groups (OH<sup>-</sup> group, especially) after adsorption process will be decreased because the OH<sup>-</sup> band or adsorption sites was joint with pollutions from aqueous solution. Also, this factor can be used as an evidence and confirmation of the adsorption of dyes well done.

### 3.2. Kinetic and Equilibrium Models

#### 3.2.1. Adsorption Isotherm

Several equations can be used to express the equilibrium elimination of an adsorption process. In this investigation, the Langmuir, Freundlich and Temkin isotherm functions were used to evaluate the elimination of the dyes from aqueous solution. Adsorption isotherm provides vital information on optimizing the use of adsorbents. Descriptions on the affinity between sorbates and sorbents, bond energy and adsorption capacity, to mention a few, can be extracted from isotherm equilibrium model applicable to adsorption processes [31, 32]. The equilibrium data were analyzed in accordance with the Langmuir, Freundlich and Temkin isotherms model. All of the models are listed in Equation 3-5, respectively [9, 33, 34]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (5)$$

In the Langmuir isotherm,  $q_m$  is a constant related to the area occupied by a monolayer of the adsorbate, reflecting the maximum adsorption capacity (mg/g),  $C_e$  is the equilibrium concentration of solution (mg/L),  $K_L$  is a direct measure of the intensity of adsorption (L/mg) and  $q_e$  is the amount adsorbed at equilibrium (mg/g). In the Freundlich isotherm,  $K_F$  ((mg/g) (L/mg)<sup>1/n</sup>) and  $n$  (dimensionless) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. In the Temkin isotherm,  $R$  is the gas constant (8.314 J/Mol K),  $T$  is the absolute temperature (K) and  $b$  is the Temkin constant related to the heat of sorption (J/Mol). Isotherm parameters for the adsorption of dye onto SP adsorbent at 294 K are shown in Table 3.

It was found that the Freundlich isotherm for CV dye and Langmuir isotherm for BV-16 and BB-41 dyes showed better correlation with the experimental data than other isotherms. Adsorption isotherms constants ( $R^2$ ) showed that the uptake of dye onto SP adsorbent could be described by the Freundlich model for CV dye and Langmuir isotherm for BV-16 and BB-41 dyes. The Langmuir model assumes monolayer adsorption onto a homogenous surface where the binding sites have equal affinities and energy, and there is no molecular interaction. Whereas, the Freundlich model assumes adsorption of dyes occurs on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with increasing concentration. For three basic dyes, the comparison of maximum capacity of adsorption is as follow: CV = 11.587 mg/g < BV-16 = 48.309 mg/g < BB-41 = 208.333 mg/g for wastewater volume of 1 liter.

### 3.2.2. Sorption Kinetic

In the present study, the adsorption kinetics of CV, BV-16 and BB-41 dyes on SP adsorbent were modeled using three common models including pseudo-first-order, pseudo-second-order and intra-particle diffusion. The three kinetics models are listed in Equation 6-8, respectively [35, 36]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (6)$$

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (7)$$

$$q_t = \frac{K_i}{m} t^{0.5} \quad (8)$$

where  $q_e$  and  $q_t$  are the amounts of dyes adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively,  $K_1$  is the rate constant of the first-order adsorption in  $\text{min}^{-1}$  and  $K_2$  is the rate constant of second-order adsorption in  $(\text{g mg}^{-1} \text{min}^{-1})$ , also for intra-particle diffusion model,  $m$  is the mass of sorbent ( $\text{g}$ ),  $q_t$  is the amount of solute adsorbed at time  $t$  ( $\text{mg/g}$ ) and  $K_i$  is the initial rate of intra-particle diffusion ( $\text{mg/l s}^{-1/2}$ ). The values of parameters obtained by different kinetic models and intra-particle diffusion model for the adsorption of dyes onto SP adsorbent are shown in Table 4.

The correlation coefficient for the pseudo-second-order kinetic model for CV dye was 0.998, for pseudo-first order kinetic model for BV-16 was above 0.994 and for pseudo-second-order kinetic model for BB-41 was above 0.995. Kinetics data for three dyes adsorption onto SP adsorbent was studied according to mass transfer or intra-particle diffusion model. The adsorption kinetics can be controlled by different steps which are as follow [31]:

- Solute transfer to the sorbent particle surface (film diffusion).
- Transfer from the sorbent surface to the intra-particle active sites (particle diffusion).
- Retention on the active sites via sorption, complexation or intra-particle precipitation phenomena.

The third step is assumed to be very rapid and can be considered negligible. The slowest step in any adsorption process is the rate limiting step. For design purposes, it is necessary to distinguish between film diffusion and particle diffusion in order to identify the

slowest step in the adsorption process.

### 3.3. Thermodynamic studies

The amount of CV, BV-16 and BB-41 uptake at 283.15, 294.15, 303.15 and 318.15 K were calculated to obtain the thermodynamic parameters which were evaluated using the Van't Hoff equation [37, 38]:

$$\text{Log } K_d = \frac{\Delta s}{2.303R} - \frac{\Delta H}{2.303RT} \quad (9)$$

The values of  $\log K_d$  were defined as follows [39]:

$$K_d = \frac{a}{1-a} \quad (10)$$

where  $\Delta s$  and  $\Delta H$  are entropy ( $\text{kJ/Mol K}$ ) and enthalpy ( $\text{kJ/Mol}$ ) change of adsorption, respectively,  $R$  is the universal gas constant ( $8.314 \text{ J/Mol K}$ ) and  $T$  is the absolute temperature ( $\text{K}$ ). The  $K_d$  is the equilibrium constant and “ $a$ ” is the uptake percentage of adsorbate at equilibrium. The values of  $\Delta H$  and  $\Delta s$  were calculated from the slope and intercept of linear regression of  $\text{Ln}(K_d)$  vs.  $(1/T)$ . Values of  $\Delta G$  were estimated by [40]:

$$\Delta G = -RT \text{Ln}(K_d) \quad (11)$$

The calculated thermodynamic parameters including  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  are given in Table 5. The negative values of  $\Delta G$  indicate that the sorption of dyes onto SP adsorbent was spontaneous processes. The negative change of  $\Delta H$  values shows that the sorption of CV and BV-16 dyes is exothermic in nature and positive enthalpy values show that the sorption of BB-41 dye is endothermic in nature.

The positive low values of  $\Delta S$  indicate low adsorption of CV dye onto SP adsorbent. Based on  $\Delta H < 0$  and  $\Delta S > 0$ , it is obvious that enthalpy and entropy are favorable agent for CV and BV-16 dyes. In other words, entropy and enthalpy cause to the adsorption processes was done to more adsorption. So, these adsorption processes are equilibrium and can be occurred spontaneously. Also, at the adsorption reactions that enthalpy and entropy are inversely, the temperature is a determinant agent, i.e. at higher temperatures the entropy is predominant and at lower temperatures the enthalpy is effective.

**Table 3:** Langmuir, Freundlich, Temkin isotherm constants for the adsorption of CV, BV-16 and BB-41 dyes on SP adsorbent.

| Isotherm model | Parameter     | CV     | BV-16  | BB-41   |
|----------------|---------------|--------|--------|---------|
| Langmuir       | $q_m$ (mg/g)  | 11.587 | 48.309 | 208.333 |
|                | $K_L$ (L/mg)  | 1.299  | 0.365  | 0.241   |
|                | $R^2$         | 0.691  | 0.991  | 0.998   |
| Freundlich     | $K_F$ (mg/g)  | 74.210 | 15.749 | 47.899  |
|                | $1/n$ (L/mg)  | 1.865  | 0.393  | 0.467   |
|                | $R^2$         | 0.892  | 0.908  | 0.952   |
| Temkin         | $B_1$ (J/mol) | 21.433 | 10.984 | 46.056  |
|                | $K_t$ (J/mol) | 5.086  | 3.268  | 2.240   |
|                | $R^2$         | 0.785  | 0.946  | 0.990   |

**Table 4:** Values of parameters obtained from different kinetic models for the adsorption of CV, BV-16 and BB-41 dyes onto SP adsorbent.

| Kinetic model                  | Parameter                                    | CV     | BV-16  | BB-41   |
|--------------------------------|--|--------|--------|---------|
| Pseudo first-order             | $K_1$ ( $\text{min}^{-1}$ )                  | 0.027  | 8.980  | 0.043   |
|                                | $q_e$ (mg/g)                                 | 1.655  | 0.013  | 7.452   |
|                                | $R^2$  | 0.967  | 0.994  | 0.972   |
| Pseudo second-order            | $K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ ) | 0.005  | 0.001  | 0.001   |
|                                | $q_e$ (mg/g)                                 | 3.952  | 42.918 | 172.413 |
|                                | $R^2$  | 0.998  | 0.980  | 0.995   |
| Intra-particle diffusion model | $K_i$ ( $\text{mg/L s}^{-1/2}$ )             | 0.032  | 1.308  | 7.598   |
|                                | $R^2$  | 0.976  | 0.973  | 0.968   |
|                                | $q_e$ Exp                                    | 11.714 | 20.880 | 88.141  |

**Table 5:** Values of thermodynamic parameters for the adsorption of CV, BV-16 and BB-41 dyes onto SP adsorbent.

| Dye   | $\Delta H$ ( $\text{kJ mol}^{-1}$ ) | $\Delta s$ ( $\text{J mol}^{-1}\text{K}^{-1}$ ) | $\Delta G$ ( $\text{kJ Mol}^{-1}$ ) |        |        |         |
|-------|-------------------------------------|---|-------------------------------------|--------|--------|---------|
|       |                                     |   | 283K                                | 294K   | 303K   | 318K    |
| CV    | -2.726                              | 0.075   | -24.14                              | -24.97 | -25.65 | -26.78  |
| BV-16 | -2.053                              | 0.085   | -26.05                              | -26.98 | -27.75 | -29.002 |
| BB-41 | +24.025                             | 0.169   | -23.74                              | -25.59 | -27.11 | -29.65  |

#### 4. Conclusion

The surface properties and potential use of SP particles as a sorbent for CV, BV-16 and BB-41 basic dyes removal was studied. SP that was prepared from

internal resources (Iran) was initially modified and then characterized by XRD, CHNS, SEM and FT-IR analysis. XRD and CHNS showed that the main component is carbon as chitin, glucan and cellulose.

The FT-IR showed the positive effect of OH function in cellulose. According to the FT-IR spectra of SP particles before and after adsorption of CV, BV-16 and BB-41 dyes, it is obvious that the SP-1 band has OH weakened after CV, BV-16 and BB-41 dyes adsorption processes than before adsorption due to OH function saturating by CV, BV-16 and BB-41 dyes. According to the equilibrium study, the Freundlich isotherm for CV dye and Langmuir isotherm for BV-16 and BB-41 dyes showed better correlation with the experimental data than other isotherms. Based on the study of adsorption kinetic, the correlation coefficient for the pseudo-second-order kinetic model for CV dye was 0.998, for pseudo-first order kinetic model for BV-16 was above 0.994 and for pseudo- second-order kinetic

model for BB- 41 was above 0.995. Calculations of thermodynamic parameters showed negative Gibbs free energy ( $\Delta G$ ) values or spontaneous reaction, the enthalpy ( $\Delta H$ ) change showed the exothermic process and values of entropy ( $\Delta S$ ) indicated low randomness at the solid/solution interface during the uptake of dyes. With attention to the obtained results, the ability of very fine SP particles can be explored in treatment technologies since SP plant is a cheap, abundant and locally available resource.

### Acknowledgments

The authors appreciate the support of Shahrood University and Mr. Kabirian toward the project.

### 6. References

1. Sh. Nouren, H Nawaz-Bhatti, Mechanistic study of degradation of basic violet 3 by Citrus limon peroxidase and phytotoxicity assessment of its degradation products, *Biochemical. Eng. J.*, 95(2015), 9-19.
2. M. Ghaedi, A. Ansari, M. Habibi, A. Asghari, Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: Kinetics and isotherm study, *J. Eng. Chem.*, 20(2014), 17-28.
3. M. Roosta, M. Ghaedi, A. Daneshfar, S. Daneshfarin, R. Sahraei, M. Purkait, Simultaneous ultrasound-assisted removal of sunset yellow and erythrosine by Zn:Ni nanoparticles loaded on activated carbon: Optimization by central composite design, *Ultrason. Sonochem.*, 21(2014), 1441-1450.
4. M. Roosta, M. Ghaedi, A. Daneshfar, R. Sahraei, A. Asghari, Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology, *Ultrason. Sonochem.*, 21(2014), 242-52.
5. A. Arunarani, P. Chandran, B. Ranganathan, N. Vasanthi, K. Sudheer, Bioremoval of Basic Violet 3 and Acid Blue 93 by *Pseudomonas putida* and its adsorption isotherms and kinetics, *Colloid. Surf. B: Biointer.*, 102(2013), 379-384.
6. K. Alpat, O. Ozbayrak, S. Alpat, H. Akcay, The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite, *J. Hazard. Mater.*, 151(2008), 213-220.
7. A. Shuai, L. Xuevan, Y. Lijun, Z. Lei, Enhancement removal of crystal violet dye using magnetic calcium ferrite nanoparticle: Study in single- and binary-solute systems, *Chem. Eng. Res. Design.*, 94(2015), 726-735.
8. D. Saha, S. Chakraborty, S. Chowdhury, Batch and continuous (fixed-bed column) biosorption of crystal violet by *Artocarpus heterophyllus* (jackfruit) leaf powder, *Colloied. Surf. B: Biointer.*, 92(2012), 262-270.
9. A.T. Khan, A.E. Khan, A. Shahjahan, Removal of basic dyes from aqueous solution by adsorption onto binary iron-manganese oxide coated kaolinite: Non-linear isotherm and kinetics modeling, *Appl. Clay. Sci.*, 107(2015), 70-77.
10. R. Maria, A. Alexandros, P. Vassiliadis, Interactions between C.I. Basic Blue 41 and aluminosilicate sorbents, *J. Colloid. Inter. Sci.*, 291(2005) 37-44.
11. R. Sumanjit, R. Seema, R. Mahajan, Equilibrium, Kinetics and thermodynamic parameters for adsorptive removal of dye Basic Blue 9 by ground nut shells and Eichhornia, *Arab. J. Chem.*, article in press (2012).
12. S. Chowhury, R. Mishra, P. Saha, P. Kushwaha, Adsorption thermodynamics, kinetics and isothermic heat of adsorption of malachite green onto chemically modified rice husk, *Desalination*, 265(2011), 159-168.
13. M. Schoonen, J. Schoonen, Removal of crystal violet from aqueous solutions using coal, *J. Colloid. Inter. Sci.*, 422(2014), 1-8.
14. M. Alkan, M. Dogan, Y. Turhan, O. Demirbas, P. Turan, Adsorption kinetics and mechanism of maxilon blue 5G dye on sepiolite from aqueous solutions, *Chem. Eng. J.*, 139(2008), 213-223.
15. T. Kan, X. Jiang, L. Zhou, M. Yang, M. Duan, P. Liu, X. Jiang, Removal of methyl orange from aqueous solutions using a bentonite modified with a new Gemini surfactant, *Appl. Clay. Sci.*, 54(2011), 184-187.
16. M. Ahmad, R. Alrozi, Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: equilibrium, kinetic and thermodynamic studies, *Chem. Eng. J.*, 171(2011), 510-516.
17. A. Saeed, M. Sharif, M. Lqbal, Application potential of grapefruit peel as dye sorbent: Kinetics, equilibrium and mechanism of crystal violet adsorption, *J. Haz. Mat.*, 179(2010) 564-572.
18. S. Jain, R. Jayaram, Removal of basic dyes from aqueous solution by low-cost adsorbent: Wood apple

- shell, *Desalination*, 250(2010), 921-927.
19. K. Almas, The effects of extracts of chewing sticks (*Salvadora Persica*) on healthy and periodontally involved human dentine: A SEM study, *Indian. J. Dent. Res.*, 12(2001) 127-132.
  20. B. Hanan, G. Basma, H. Al-Sulaiman, The efficacy of *Salvadora Persica* extract in the elimination of the intracanal smear layer: A SEM study, *Saudi. Dental.*, 24(2012), 71-77.
  21. P. Ramoliy, H. Patel, A. Pandey, Effect of salinization of soil on growth and macro- and micro-nutrient accumulation in seedlings of *Salvadora persica* (Savadoraceae), *Forest. Ecology. Manage.*, 202(2004), 181-193.
  22. M. Khatak, S. Khatak, A. Siddqui, N. Vasudeya, P. Aggarwal, *Salvadora persica*, *Pharmacogn Rev.*, 4(2010), 209-214.
  23. S. Halawany, A review on miswak (*Salvadora persica*) and its effect on various aspects of oral health, *Saudi. Dental.*, 24(2012), 63-69.
  24. R. Sanogo, M. Monforte, A. Daquino, A. Rossitto, D. Mauro, E. Galati, Antiulcer activity of *Salvadora persica* structural modification, *Ohytomedicine*, 6(1999), 363-366.
  25. F. Wahid, I. U. Mohammadzai, A. Khan, Z. Shah, W. Hassan, N. Ali, Removal of toxic metals with activated carbon prepared from *Salvadora Persica*, *Arab. J. Chem.*, article in press (2013).
  26. E. A. Moawed, A. B. Abulkibash, Selective separation of Light green and Safranin O from aqueous solution using *Salvadora persica* (Miswak) powder as a new biosorbent, *J. Saudi. Chem. Soci.*, article in press (2012).
  27. Z. Mansoureh, B. Alireza, Highly efficient removal of basic blue 41 with nanoporous silica, *Water. Resour. Indust.*, 5(2014), 49-57.
  28. D. Chahrazed, Z. Rachida, D. Faycal, B. Bachir, L. Abdelaziz, M. Ali, R. Marek, Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon, *J. Taiwan Ins. Chem. Eng.*, 53(2015) 112-121.
  29. J. Yinhua, L. Yingying, Z. Fumei, G. Leiqun, N. Liang, Equilibrium and kinetic studies of C.I. Basic Blue 41 adsorption onto N, F-codoped flower-like TiO<sub>2</sub> microspheres, *Appl. Surface. Sci.*, 273(2013), 448-456.
  30. M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, Copper biosorption from aqueous solutions by sour orange residue, *J. Haz. Mat.*, 149(2007), 269-274.
  31. K. Seifpanahi-Shabani, F. Doulati-Ardejani, K. Badii, M.E. Olya, Preparation and characterization of novel nano-mineral for the removal of several heavy metals from aqueous solution: Batch and continuous systems, *Arab. J. Chem.*, article in press (2013).
  32. T. Mohammad, A. Francesco, F. Ada, R. Giorgio, Use of N-methylformanilide as swelling agent for meta-aramid fibers dyeing: Kinetics and equilibrium adsorption of Basic Blue 41, *Dye. Pigm.*, 113(2015), 554-561.
  33. M. Najafi, Y. Yousefi, A. Rafati, Synthesis, characterization and adsorption studies of several heavy metal ions on amino-functionalized silica nano hollow sphere and silica gel, *Sep. Purif. Technol.*, 85(2012), 193-205.
  34. U. Pal, A. Sandoval, S.I. Uribe Madrid, G. Corro, V. Sharma, P. Mohanty, Mixed titanium, silicon, and aluminum oxide nanostructures as novel adsorbent for removal of rhodamine 6G and methylene blue as cationic dyes from aqueous solution, *Chemosphere*, 163(2016), 70-77.
  35. T. Anirudhan, M. Ramachandr, Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): Kinetic and competitive adsorption isotherm, *Process. Saf. Environ. Prot.*, 95(2015), 215-225.
  36. Ch. O. Ijagbemi, Mi. Baek, K. Dong-Su, Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, *J. Haz. Mat.*, 166(2009), 538-546.
  37. K. Koolia, L. Yan, R. Al-Fazea, A. Al-Sehimia, Removal enhancement of basic blue 41 by brick waste from an aqueous solution, *Arab. J. Chem.*, 8(2015), 333-342.
  38. L. Yonghui, H. Xingbing, H. Guomin, T. Qijian, H. Wenyong, Removal of Crystal Violet from aqueous solution using powdered mycelial biomass of *Ceriporia lacerata* P2, *J. Environl. Sci.*, 23(2011), 2055-2062.
  39. A. Arunagiri, J. Indulekha, P. Kalaichelvi, R. Anantharaj, Removal of crystal violet dye from aqueous solution using triton X-114 surfactant via cloud point extraction, *Eng. Sci. Technol. Inter. J.*, 17(2014), 137-144.
  40. W. Monika, W. Malgorzata, M. Vladimir, Z. Vladimir, Adsorptive removal of acid, reactive and direct dyes from aqueous solutions and wastewater using mixed silica-alumina oxide, *Powder Technol.*, 278(2015), 306-315.

How to cite this article:

A. Hamidi, K. Seifpanahi-Shabani, M. Karamoozian, Basic dyes Removal by Natural *Salvadora Persica* Adsorbent. *Prog. Color Colorants Coat.*, 10 (2017), 115-128.



## حذف مواد رنگزای بازیگ با استفاده از جاذب سالوادورا پرسیکا

علی حمیدی<sup>۱</sup>، کیومرث سیف‌پناهی شعبانی<sup>۲\*</sup>، محمد کارآموزیان<sup>۳</sup>

<sup>۱</sup> فارغ‌التحصیل کارشناسی ارشد، دانشکده مهندسی معدن، نفت و ژئوفیزیک، دانشگاه صنعتی شاهرود، کد پستی: ۳۶۱۹۹۵۱۶۱، شاهرود، ایران.

<sup>۲</sup> استادیار، دانشکده مهندسی معدن، نفت و ژئوفیزیک، دانشگاه صنعتی شاهرود، کد پستی: ۳۶۱۹۹۵۱۶۱، شاهرود، ایران.

<sup>۳</sup> دانشیار، دانشکده مهندسی معدن، نفت و ژئوفیزیک، دانشگاه صنعتی شاهرود، کد پستی: ۳۶۱۹۹۵۱۶۱، شاهرود، ایران.

### چکیده

در این تحقیق، فرآیند جذب سه ماده رنگزای کریستال بنفش، بازیگ بنفش ۱۶ و بازیگ آبی ۴۱ توسط جاذب ریزدانه سالوادورا پرسیکا تهیه شده از منابع داخلی مطالعه و بررسی شده است. بنابراین ذرات سالوادورا پرسیکا با استفاده از کاهش ابعاد اصلاح شده و شناسایی آن با استفاده از آزمون‌های CHNS، XRD، SEM و FT-IR انجام گردید. لذا در سیستم گسسته تاثیر تغییرات عوامل pH، مقدار جاذب، دما و غلظت اولیه مواد رنگزا بررسی شد. نتایج مطالعات آزمایشگاهی نشان می‌دهد که مدل‌های ایزوترم لانگمویر و سینتیک شبه مرتبه دوم تطابق بهتری با داده‌های آزمایشگاهی دارد. محاسبه ویژگی‌های ترمودینامیکی نشان‌دهنده منفی بودن مقادیر انرژی آزاد گیبس و در نتیجه خودبخودی بودن واکنش است. تغییرات آنتاپی حاکی از گرماده بودن واکنش جذب مواد رنگزا و مقادیر آنتروپی هم تایید کننده تأثیر جزئی فصل مشترک بین جاذب و پساب می‌باشد. بنابراین با توجه به نتایج به دست آمده می‌توان گفت که این جاذب ارزان و موجود به صورت بومی برای حذف مواد رنگزای بازیگ از فاز محلول مناسب بوده و می‌تواند برای حذف دیگر مواد رنگزا و یون‌های فلزی سمی هم به کار برود.

### اطلاعات مقاله

#### تاریخچه مقاله:

تاریخ دریافت: ۱۹ خرداد ۱۳۹۵

تاریخ دریافت آخرین اصلاحات: ۱۳ اسفند

۱۳۹۵

تاریخ پذیرش: ۱۵ اسفند ۱۳۹۵

تاریخ در دسترس به صورت الکترونیکی: ۲۱

فروردین ۱۳۹۶

#### واژه‌های کلیدی:

سالوادورا پرسیکا

مواد رنگزای بازیگ

جذب سطحی

تصفیه پساب