Simultaneous removal of basic dyes from binary systems by modified orange peel and modeling the process by an intelligent tool

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**Abstract**

This study presents the consecutive modification of orange peel (OP) by NaOH and sodium dodecyl sulfate (SDS) for simultaneous elimination of basic dyes from the binary system and modeling the adsorption process using an intelligent tool. The natural and modified biosorbents were characterized by a variety of analyses such as: field emission scanning electron microscopy with energy dispersive X-ray, \( \text{N}_2 \) physisorption and Fourier transform infrared spectroscopy techniques. The influence of various variables on dye removal like pH, the quantity of biosorbents, dyes concentration, contact time, and temperature in the binary system were investigated and optimized by an artificial neural network (ANN) model as an intelligent tool. The optimum quantity of the sorbent was found to be 0.30 g for orange peel (OP) and 0.25 g for NaOH-treated OP (NOP) and SDS-decorated NOP (SNOP) at pH = 7. The kinetics and thermodynamics investigations showed that the removal of dyes obeyed the pseudo-second-order kinetic model and were spontaneous and exothermic in nature. Moreover, in order to describe the mechanism of sorption process, desorption studies of dyes were carried out. The desorption percentages of methylene blue (MB) in water and HCl were found to be in the range of 1.93\%–4.76\% and 18.87\%–28.76\%, respectively; in addition, the desorption percentages of crystal violet (CV) in water and HCl were obtained to be in the range of 4.11\%–7.41\% and 32.84\%–43.00\%, respectively; which could be a recommendation ion exchange or electrostatic attachment of dyes onto biosorbents. The ANN predictions matched with the experimental data very well (0.95308 < \( \text{R}^2 \) < 0.99191 and 0.98335 < \( \text{R}^2 \) < 0.99773 for MB and CV, respectively) which indicated high accuracy of the ANN model. In addition, the relative importance of each parameter was calculated by Garson's equation.

**Keywords:** Binary system; Surfactant modification; Orange peel; Artificial neural network modeling.

1. Introduction

Nowadays, an expansion of contaminant disposal is happening due to the quick industrial development, urbanization, and population growth which leads to effect human beings as well as plants and animals [1]. The genotoxic agents are more troublesome due to the possibility of causing heritable disorders. There are different types of pollutants that among them, synthetic dyes are concerning because of their wide application in numerous industries such as pharmaceutical, textile, plastic, cosmetics, tanner, leather, pigments, rubber, and paint. Remarkable amounts
of contaminated wastewaters are discharged into the surrounding areas along with wastewater produced during the industrialized process [2–4]. Recently, the removal of dyes from dissipate effluents becomes a serious environmental challenge. There are different types of dyes according to the ionic charge on dye molecules: cationic, anionic, and non-ionic dyes, that among them cationic dyes are the most toxic ones [5,6]. Previous studies [7–9] concentrated on single adsorption systems using various adsorbents. Recently, by analyzing wastewater containing dyes, it was observed that many dyes coexist simultaneously; therefore, nowadays researches are focused on multicomponent dye adsorption [10–12]. Thus, finding a cost-effective way to eliminate such effluents from wastewaters has attracted a lot of attention these days [13]. There are two types of methods to treat contaminated effluents: physical and chemical processes [14] which include membrane processes, floatation, coagulation, evaporation, photo-catalytic degradation, sedimentation, micellar enhanced ultra-filtration, adsorption, etc. [15,16]. Adsorption has displayed promising results among all of these methods and is considered as a practical way to eliminate dyes from aqueous solutions in order to its easiness of design, low price procedure, insensitivity to poisonous contaminants, simplicity of operation, and a smaller quantity of dangerous substances [17,18]. Various industrial byproducts or natural materials are inexpensive and abundant, for this reason, they are assumed to be low-cost adsorbents. These kinds of wastes need little processing and can be used after some insignificant treatments. As adsorbents, agricultural wastes like orange peel, apple pomace, wheat straw, tea leaves, banana peel, sawdust, bamboo, etc. have gained more attention [7,19–22]. Generally, agricultural residues require physical and chemical modifications because of their low adsorption capacity [23]. Physical modifications are usually supposed as being complex and economical, although they are not commonly used due to their low effectiveness [24,25]. Conversely, chemical treatments are able to improve the properties of adsorbents including larger surface area, higher porosity, and expansion of the number of available active sites, and accordingly, these methods are preferred by most researchers [26,27]. Treatment with aqueous sodium hydroxide (NaOH) solution has a significant impact on molecular, supramolecular, and morphological characteristics of cellulose, causing a change in pore structure, stiffness, ease of access, crystallinity, the direction of fibrils in cellulosic fibers, and unit cell structure [28]. Treatment with NaOH makes the cellulose fiber surface empty of natural fats and waxes that causes revealing functional groups like –OH [29]. On the other hand, in recent years, researchers have focused on the application of surfactants for removing dyes and other toxic substances from industrial wastewaters [30,31]. Surfactants decrease the surface tension of aqueous solutions; they are produced by chemical reactions and do not exist in nature. The surface activity of surfactants originates from the fact that each molecule of surfactants contains both hydrophilic and hydrophobic parts which allow them to adsorb different types of pollutants [32]. The efficiency of the adsorption process can be figured out by various modeling techniques like artificial neural networks (ANNs). As many of complex engineering systems could be solved and modeled by using ANN due to its nonlinearity, reliability, simplicity, and robustness. ANN has an inclusive structure and can build a model from the historical data [33,34]. Moreover, it can be employed for modeling the complex relationships between the sorbent and sorbates in multicomponent aqueous solutions [35].

Present study concentrates on simultaneous removal of basic dyes, Methylene blue (MB) and Crystal violet (CV), on orange peel (OP), sodium hydroxide-treated OP (NOP), and sodium dodecyl sulfate-decorated NOP (SNOP). It should be noted that it is the first time that a plentiful agricultural waste is treated twice and is used as an effective adsorbent in order to simultaneous removal of dyes. Optimization of all the effective parameters such as pH, adsorbent dosage, reaction contact time, and initial dyes concentration were carried out and mechanism of adsorption was proposed. Furthermore, the ANN model has been applied for the prediction of removal efficiency of MB and CV.

2. Experimental

2.1. Materials

The orange peel (OP) was obtained from a local farm in Iran and used for the preparation of the chemically modified biosorbents. These collected materials were cut into small pieces, washed with boiled water to eliminate any adhering dirt, and finally dehydrated in the oven at 80°C for 12 h (the color changed from orange to pale-orange). The dehydrated peels were crushed and sieved to achieve an average particle size range of 100–500 μm and kept in an air tight container for future use. Basic dyes used in this study, namely, methylene blue (MB) (No. 115943) and crystal violet (CV) (No. 115940), were purchased from Merck (Germany). Mixed dyes solution with proposed initial dye concentrations ranged from 20 to 500 mg L\(^{-1}\) were prepared. All solutions were prepared with a dye solution of equal concentrations. The pH of the solutions were set to the wanted value by adding 0.01 mol L\(^{-1}\) NaOH or 0.01 mol L\(^{-1}\) HCl. Methyl orange (MO) was bought from Merck (Germany) (no.101322). Sodium dodecyl sulfate (SDS) solutions were provided from a commercially sample (Merck, Germany, 822050) dissolved in distilled water.

2.2. Preparation of NaOH-treated orange peel

OP was treated with sodium hydroxide solution in order to ameliorate the capacity of adsorption of mixed dyes. For this purpose, 10 g of dried OP was mixed with 200 mL NaOH (0.1 mol L\(^{-1}\)) for 6 h. After filtration, the modified sorbent (NOP) was washed thoroughly with deionized water until neutral pH and after that, the product was dehydrated at 60°C in the oven for 8 h. Finally, the prepared sample was kept in an air tight vessel to perform elimination tests.

2.3. Modification of NOP by SDS

The surface modification is not influential above the critical micellar concentration (CMC). Therefore, the SDS solution was provided below its CMC (CMC = 0.0082 mol L\(^{-1}\)). 5.7 × 10\(^{-3}\) g SDS was dissolved in 100 mL of distilled water and after 10 min of shaking, 10 g of NOP was poured to the solution. The prepared solution was shaken at 180 rpm by...
shaker for 3 h at 303 K. After that, the SDS-decorated NOP (SNOP) was separated and rinsed with distilled water to reach the conductance of filtrate less than 0.05 μS. The SNOP was dehydrated in oven at 80°C for 24 h. The prepared sample then was saved in air tight vessel for further use.

2.4. Characterization

Using an X-ray diffractometer (Siemens, D5000, Germany), the X-ray diffraction (XRD) measurements were collected using CuKα radiation as the X-ray source. The diffractograms were recorded within the 20 range of 20°–80°. Using field emission scanning electron microscopy (FESEM, CamScan MV2300, England) with an energy dispersive X-ray (EDX, BRUKER Xflash6110, USA), the morphology of the prepared biosorbents was investigated. A nitrogen adsorption system (Belsorp mini) was applied to investigate specific surface area based on nitrogen physisorption. The Brunauer–Emmett–Teller (BET) areas were determined by static nitrogen physisorption at −196°C followed by out-gas at 200°C until the pressure was lower than 5 mbar. Fourier transform infrared (FTIR) spectroscope (Perkin Elmer-Spectrum 1, USA) in the range of 4,000–400 cm−1 was measured by a double beam UV-vis spectrophotometer (Rayleigh UV-2601 UV/VIS spectrophotometer, USA) at λmax = 664 nm for MB and λmax = 584 nm for CV.

2.5. Adsorption procedure

Batch elimination tests were determined to make the biosorption equilibrium isotherm data. Each test was carried out in the presence of a fixed mass of OP (0.3 g), NOP, and SNOP (0.25 g) in 250 mL glass Erlenmeyer’s flasks contains 100 mL of a mixture of MB and CV solutions at a temperature of 30°C and pH = 7. The process was carried out for temperatures 40°C and 50°C. The primary pH adjustments were performed by 0.01 mol L⁻¹ NaOH or 0.01 mol L⁻¹ HCl solutions. To prepare the mixed solution, dye solutions were prepared separately in the range of 50–250 mg L⁻¹, mixed in equal volume to obtain dye concentration in the range of 20–500 mg L⁻¹. Adsorption equilibrium was reached after 20 min. After the end of the reaction time, the samples were centrifuged, and then the remaining MB and CV concentrations were recorded within the 2θ range of 20°–80°. Using CuKα radiation as the X-ray source. The diffractometer (Siemens, D5000, Germany), the morphology of the prepared biosorbents was investigated. For this purpose, 100 mL of mixed dyes solution with diverse initial concentrations (100–300 mg L⁻¹) were provided to prepare the mixed solution in the range of 50–250 mg L⁻¹. kinetic studies were carried out by contacting prepared solutions with 0.3 g of OP and 0.25 g of NOP and SNOP at room temperature under constant stirring. At fixed time intervals, the sorbents were extracted from the solution and the absorption measured at the λmax for each dye. The kinetic parameters are widely favorable to predict the sorption rate of the simultaneous MB and CV adsorption onto the adsorbents. Moreover, these parameters give crucial information to progress and model the biosorption processes.

The Lagergren pseudo-first-order kinetic model can be expressed as [36]:

\[
\frac{dq}{dt} = -k_1q
\]

Integrating this equation considering the boundary conditions \( t = 0 \) to \( t = t \) and \( q = 0 \) to \( q = q_t \) gives:

\[
\ln\left(q_t - q_{1,1}\right) = \ln\left(q_{1,1} - k_1t\right)
\]

where \( q_{1,1} \) and \( q_t \) are the quantities of dye (mg g⁻¹) at time \( t \) (min) and at equilibrium, respectively; and \( k_1 \) is the rate constant of pseudo-first-order model (min⁻¹). Using linearized plot of \( \ln\left(q_t - q_{1,1}\right) \) vs. \( t \), the validity of the model can be discovered. Additionally, the rate constant of pseudo-first-order adsorption can be calculated from the slope of the plot.

The pseudo-second-order equation can be represented as:

\[
\frac{d\left(q_{1,1} - q_{1,1}\right)}{(q_{1,1} - q_{1,1})^2} = k_2\frac{dt}{t}
\]

The integrated linear from the above equation, considering the boundary conditions \( t = 0 \) to \( t = t \) and \( q = 0 \) to \( q = q_{1,1}\) can be written as:

\[
\frac{1}{q_{1,1} - q_{1,1}} - \frac{1}{q_{1,1}} = k_2t
\]

Rewriting Eq. (7) gives Eq. (8):

\[
t = k_2\frac{t}{q_{1,1}} = k_2\frac{t}{q_{1,1}}
\]
where \((q_{e})\) is the theoretical equilibrium capacity and \(k_{2,2}D\) is the second-order constant \((g \text{ mg}^{-1} \text{ min}^{-1})\) which can be calculated from the slope and intercept of plot \(t/q_{t}D\) vs. \(t\), respectively.

2.7. Determination point of zero charge pH (pH\(_{\text{pzc}}\))

To determine pH\(_{\text{pzc}}\), 1,000 mL NaCl solution \((0.01 \text{ mol L}^{-1})\) was provided and its pH value was adjusted in the range of 1–10 by adding HCl or NaOH \((0.1 \text{ mol L}^{-1})\). Afterward, 0.1 g of each prepared adsorbent was inserted to 50 mL NaCl \((0.01 \text{ mol L}^{-1})\) and kept for 96 h. Finally, graphs were plotted for pH\(_{\text{final}}\) vs. pH\(_{\text{initial}}\).

3. Results and discussion

3.1. FESEM/EDX analysis

FESEM micrographs of the prepared samples with magnification of 5 μm are presented in Fig. 1A. After treatment of OP with NaOH, the porosity and irregular structure of NOP extended, which may be due to the removal of natural fats and waxes from the cellulose fiber surfaces\([29]\) and leads to a significant increase in the adsorption capacity of this biosorbent. The surface of SNOP is rougher compared to the NOP and it may be due to the surfactant can change the physico-chemical features of the adsorbents\([30]\). Therefore, it can be concluded that after decoration of NOP by SDS, the pores of NOP are occupied with SDS molecules and the SNOP surface appears to be more homogeneity compared to the NOP. The EDX analysis was used to determine the chemical composition of the biosorbents in which the results were presented in Fig. 1B. The EDX analysis data display that C, O, Fe, S, P, K, and Ca elements are presented over the testing area (Fig. 1B). It is obvious that after NOP decoration with SDS, the amount of sulfur atom is increased to 0.33% that indicates the presence of SDS on the surface of NOP.

3.2. N\(_2\) physisorption analysis

In the present work, the BET model was used to obtain the specific surface area, pore volumes, and pore sizes.

![Fig. 1. (A) FESEM images of (a) OP, (b) NOP, and (c) SNOP and (B) EDX patterns of (a) OP, (b) NOP, and (c) SNOP.](image-url)
of the prepared biosorbents based on N$_2$ physisorption (Table I and Fig. S1). Compared to the International Union of Pure and Applied Chemistry (IUPAC) classification [37], the sorption isotherms of the prepared samples are the same as type IV (a). The textural and structural parameters of OP, NOP, and SNOP biosorbents are presented in Fig. S1. It should be mentioned that Barrett–Joyner–Halenda (BJH) model was used to investigate pore diameter. After treatment by NaOH, the value of the BET surface area decreased compared to OP due to entrap of NaOH in the micropore area and causes a significant change in the structure of the biosorbent and reduces its ultimate surface area [38]. Furthermore, it was observed that after treatment with NaOH, the pore size of OP increased from 12.431 to 20.183 nm. On the other hand, it was found out that the surface area of SNOP was 2.814 m$^2$ g$^{-1}$. This enhancement may be due to the general characteristics of micelle formation, solubilization, wetting, and adsorption. Surfactant molecules are able to organize themselves appropriately, thus, naturally being amphipathic, surfactant-modified sorbents possess improved surface area, and wetting (oil or water wet). Additionally, selective adsorption happens facilely due to the electrostatic interactions [30].

### 3.3. FTIR analysis

Fig. S2 shows the FTIR spectra of the prepared sorbents in the range of 400–4,000 cm$^{-1}$. The vibration at 3,400 cm$^{-1}$ is ascribed to vibrational modes of hydroxyl groups (–OH) attend to the different hydrogen bonding (inter and intra) of polymeric compounds including carboxylic acids, alcohols, and phenols as in lignin, cellulose, and pectin [39]. By attending to the FTIR spectra, it is obvious that there are two peaks at 2,920 and 2,850 cm$^{-1}$ that can be ascribed to the C–H stretch vibration which is originated from the surface of the biosorbents [40]. The observed peak at 1,709 cm$^{-1}$ is due to the C=O stretch vibration which is totally obvious in the spectrum of OP (Fig. S2a) [41]. Moreover, the peaks detected at 1,617 and 1,041 cm$^{-1}$ are due to C=C aromatic and C–H, respectively [42]. It should be noted that vibrations at 3,599 and 2,900 cm$^{-1}$ can be allocated to the –CH$_2$ group from SDS and peak at 1,244 cm$^{-1}$ can be attributed to –SO$_2$ stretching vibration [43]. However, regarding to FTIR spectrum of OP (Fig. S2a), intense vibrations are observed at 3,599; 2,900; and 1,244 cm$^{-1}$, hence, using FTIR analysis, the presence of SDS molecules could not be identified. Generally, the presence of these peaks indicates that the prepared samples possess various functional groups that simplify the adsorption of dyes through hydrogen bonds [9,12]. However, the FT-IR spectra of NOP and SNOP after dyes adsorption were found to exhibit similar functional groups due to the domination of the functional groups of OP in this sorbent as the major component in these materials.

### 3.4. Effect of pH on simultaneous removal of MB and CV

One of the effective factors in the dye adsorption process is the pH of solution. The charge of the adsorbent surface, the solution chemistry, and functional groups present on the active sites depend strongly on pH of the solution [44]. Consistent with the obtained results in Fig. 2, by increasing the pH of the mixed dyes solution from 2 to 10, the removal percentages increase. Low sorption at lower pH values could be as a result of the electrostatic repulsion between the cationic adsorbate and adsorbent. The linear range of pH sensitivity, the adsorption capacity, and the type of active centers of the biosorbent can be studied by point of zero charge pH ($pH_{pzc}$) [45]. When the pH of the solution is lower than $pH_{pzc}$ ($pH < pH_{pzc}$), the adsorption becomes positively charged which leads to an electrostatic repulsion between dye cations and the biosorbents which reduces the removal efficiency. Furthermore, the concentration of H$^+$ ions in acidic pH is remarkable which compete with MB and CV cations for active sites onto the prepared biosorbents. Reversely, at pH > $pH_{pzc}$, the presence of –COOH and –OH groups on the adsorbents surface, makes it negative, and, therefore, the MB, and CV cations can be easily adsorbed onto the surface of the sorbents by electrostatic attraction forces [46].

#### Table 1 Textural parameters of the prepared samples

| Sorbent | BET surface area (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Pore size (nm) |
|---------|----------------------------------|------------------------------|---------------|
| OP      | 1.3811                           | 0.0042922                    | 12.431        |
| NOP     | 0.9154                           | 0.0046192                    | 20.183        |
| SNOP    | 2.8140                           | 0.0072586                    | 10.318        |

Fig. 2 shows that the % removal of MB is more than CV on the prepared sorbents and it can be explained according to Duan et al. [47] work. The adsorption behavior of two organic dyes, namely, crystal violet (CV, triphenylmethane dye of symmetric structure) and methylene blue (MB, azo dye of linear structure), were investigated, characterized, and differentiated at the silica/water interface at two range of concentrations using the total internal reflection induction near field evanescent wave (TIR-NFEW) platform. They observed diffusion and absorption processes for MB and CV adsorption on the sorbent. MB dye showed a faster diffusion speed than CV because the symmetric structure of the CV is larger in size than the linear MB structure, which leads to a corresponding larger space hindrance and a slower diffusion speed for CV. For the second adsorption step, CV had nearly the same interaction speed as MB. The two interactions similar to the low concentration stage took place for both CV and MB at the high concentration stage as well. They proposed molecular aligned-mechanism to describe the interfacial interaction process for both CV and MB that includes molecular reactions involving electrostatic attraction and H-bonds of functional groups. In our work, at first, both CV and MB molecules interacted with the accessible functional groups through strong electrostatic attraction and other functional groups on the sorbents were occupied and saturated with dye molecules at high concentrations through H-bonds. Also, we observed higher % removal for MB and CV onto NOP and SNOP due to the presence of more functional groups on OP after treatment by NaOH and SDS. The $pH_{pzc}$ value of OP was found to be 3.7 and this value for NOP and SNOP were found to be 6.8 (Fig. 2d). Thus, due to the neutral pH ranges (6.0–7.0)
of water and wastewaters, the adsorption studies were performed at the optimum pH of 7.0.

3.5. Effect of adsorbent quantity on simultaneous sorption of MB and CV

Adsorbent quantity is a key parameter that significantly affects on the adsorption efficiency by changing the biosorption capacity of the prepared sorbents [48]. Therefore, the impact of adsorbent quantity on MB and CV adsorption by OP, NOP, and SNOP was determined in the range of 0.05–0.40 g/100 mL of an aqueous solution of MB and CV and the obtained data are displayed in Fig. 3. The removal percent of each dye increased by increasing the amount of biosorbents which may be due to the fact that, by increasing the quantity of biosorbents, the number of biosorbents active sites are increased which leads to the elimination of MB and CV [49]. Higher removal of MB may be attributed to smaller chemical structure of MB and the lower initial concentration (129.9 mg L\(^{-1}\)) of it as compared to the initial concentration of CV (152.9 mg L\(^{-1}\)).

It has been discovered that after adding more than 0.30 g of OP and 0.25 g of NOP and SNOP, no remarkable changes have been observed in the removal efficiency of dyes. Thus, these amounts of biosorbents were chosen as optimum dose for further experiments.

3.6. Effect of initial concentration and contact time on simultaneous sorption of MB and CV

The results of the initial concentration effect of MB (52–172 mg L\(^{-1}\)) and CV (71–227 mg L\(^{-1}\)) on the competitive adsorption of these dyes are shown in Fig. 4. It was found that the quantity of MB and CV adsorbed on the sorbents was fast for the first 6 min and after that it proceeds with a lower rate (6–20 min) and after a while reached saturation. It was apparent from Fig. 6, that by increasing the initial dye concentration, the percentage of dye removal reduced which may be due to the saturation of adsorption sites on the adsorbent surface [3]. Moreover, there is an increase in adsorption percent which may be due to an enlargement of the mass transfer driving force, therefore, resulting in more MB and CV adsorption [50]. In addition, contact time has an effective role in adsorption processes. It is specified that the required contact time to reach adsorption equilibrium was 20 min (Fig. 4). This quick elimination of dyes demonstrates that the binding sites of the prepared biosorbents were controlled by diffusion mechanism [16]. However, the experiments were performed at 40 min to be certain that complete adsorption equilibrium were achieved.

3.7. Effect of temperature on simultaneous adsorption of MB and CV

The effect of temperature on the adsorption was investigated at various temperatures (30°C, 40°C, and 50°C). For this reason, different initial concentrations of MB within 21.47–366.87 mg L\(^{-1}\) and different initial concentrations of CV within 28.99–456.32 mg L\(^{-1}\) were provided. These equilibrium experiments were accomplished at optimum pH of 7 for all the used adsorbents, optimum dose of 0.30 g for OP and 0.25 g for NOP and SNOP and agitation time of 20 min. Regarding to Fig. S3, it can be concluded that temperature has no significant influence on equilibrium
capacities of simultaneous sorption of MB and CV. It will be discussed in section 3.10 (Adsorption thermodynamics).

3.8. Mechanism of simultaneous adsorption of MB and CV dyes onto SNOP

Fig. 5 is a schematic of the surface treatment and proposed mechanism of simultaneous adsorption of MB and CV onto SNOP. Generally, surfactant molecules form monolayer namely hemi-micelles on the surface of oxides. In this structure, the surfactant head group facing toward the hydrocarbon tail groups and its surface into solution. A new hydrophobic interaction between hydrocarbons tail groups form if the concentration of surfactant molecules present in the solution is higher, which causes the formation of separated surface aggregates which is called admicelles. The regions on the surface of oxides where these hemimicelle or admicelle are formed have potential to adsorb different contaminants [51]. Other possible mechanism is that the hydrocarbon tails group of surfactants may have interaction with the surface of adsorbent via hydrophobic bonding and the head group intended for the bulk of the solution, therefore, the surface has positive or negative charge. In this work, the head group of SDS molecules with negative charge toward the bulk of the solution and the alkyl tail of SDS might interact with NOP surface via hydrophobic bonding, thus, the surface has negative charge. It is concluded that the surface of SNOP is negative and the mechanism of binary adsorption of MB and CV dyes onto SNOP may be due to ion-exchange or electrostatic interaction. Moreover, some of dyes molecules adsorbed onto SNOP surface via hydrophobic interaction between MB and CV molecules and hydrocarbon tail of surfactant (Fig. 5).

3.9. Adsorption kinetic models in binary dyes system

The dynamics of adsorption data was determined to figure out the kinetics of adsorption process [52,53]. In this work, the pseudo-first-order and pseudo-second-order kinetic models were used to obtain the equilibrium adsorption capacity and rate constants of binary adsorption of MB and CV process. By plotting ln(qe − qt) vs. t, the values of pseudo-first-order rate constants, k1 and qe can be determined from slope and intercept of the plots (Fig. S4). The obtained values and correlation coefficients (R²) are shown in Table 2. The R² reported for the pseudo-first-order kinetic model is in the range of 0.7974–0.9830. Moreover, the experimental and theoretical adsorption capacities attained from this model differed broadly, thus, it can be established that the pseudo-first-order kinetic model cannot illustrate simultaneous removal of MB and CV dyes on the prepared samples well. On the other hand, the kinetic data displayed a desirable agreement with pseudo-second-order kinetic model. By plotting t/qt against t, an excellent linearity can be observed (Fig. 6). Regarding Table 2, the obtained qe values show an agreement with experimental qe values and the R² values of pseudo-second-order model were equal or close to 1, which is higher than the R² values obtained from the pseudo-first-order model. Thus, the adsorption kinetics could be more agreeably defined by pseudo-second-order kinetic model for simultaneous removal of MB and CV dyes on the prepared adsorbents. Better fit to the pseudo-second-order kinetic model proves that the adsorption mechanism relies on the adsorbent and adsorbate, and the rate restrictive step can be chemisorption including valance forces through exchange or sharing electrons [54,55]. In addition, the second-order rate constants were applied to compute initial sorption rate (h) of simultaneous adsorption of MB and CV using the following equation:
The initial rate adsorption of each dye is increased by increasing of solution concentration (Table 2). During the adsorption mechanism, the dyes species move toward the surface of the biosorbent. When equilibrium is reached, the movement of dyes species from the solution reaches the maximum amount, therefore, measuring the quantity of the distribution of dyes species between the solution and the adsorbent is possible and the efficiency of the used adsorbents can be measured. After contacting a solid biosorbent with dyes-containing solutions, in the beginning, the dyes move to the surface of the liquid film from the bulk solution. This surface applies a very or less remarkable diffusion barrier [56]. The association

\[ h_D = k_z D_A L^2 \]  

Fig. 4. Effect of contact time and initial concentration on the binary adsorption of (A) MB and (B) CV onto (a) OP, (b) NOP, and (c) SNOP.
of a remarkable quantum of diffusion barrier shows the principal role continued by the film diffusion during the adsorption process. In addition, the rate of sorption is limited by internal diffusion or external diffusion or by both of them. Internal diffusion controls the transferring of dyes species from the external surface to the internal surface of pores in the biosorbent. External diffusion controls the movement of the dyes species from the solution to the boundary layer of the liquid phase [57]. It is considered that during the biosorption of dyes onto a porous sorbent, three sequential steps are happened [58,59]:

- Transportation of dye molecules over the liquid film surrounding the sorbent particles (film diffusion).
- Adsorption of dyes species onto the pores of the sorbent (particle diffusion).
- Internal diffusion of ingoing dyes species by surface diffusion, pore diffusion, or both.

Among these processes, the third one cannot be considered as the rate-limiting step in the removal of contaminants because it occurs rapidly. Three possibilities exist about the other two steps:

- If internal transport < external transport, the rate is directed by particle diffusion.
- If internal transport > external transport, the rate is directed by film diffusion.
- If internal transport = external transport, the movement of the dyes species to the boundary is taken place. In this situation, the rate is not that much significant and afterward a liquid film surrounded by dyes molecules, with an appropriate concentration gradient, would be formed.

The Boyd model has applied additionally for analyzing the kinetic data to investigate the real slow step of the biosorption mechanism. This model can be expressed as below [60]:

\[ B_{t,D} = -0.4977 - \ln(1 - F) \]  \hspace{1cm} (10)

where \( F \) exhibits the portion of dyes adsorbed at any time, \( t \) (min), which is obtained using Eq. (11):

\[ F = \frac{q_{t,D}}{q_{e,D}} \]  \hspace{1cm} (11)

where \( q_t \) and \( q_e \) are the quantities of dyes removed after time \( t \) and infinite time (80 min), respectively.

As shown in Fig. S5, \( B_t \) values are plotted against time for the used sorbents in this study. These plots distinguish
between the particle and film diffusion-controlled rates of adsorption. The linear lines of each dye for all concentrations did not go through the origin and the points were scattered. Therefore, it can be concluded that the simultaneous adsorption of MB and CV on all used biosorbents was principally controlled by external mass transport where particle diffusion was the rate-controlling step [61].

3.10. Adsorption thermodynamics

Thermodynamic parameters like standard enthalpy ($\Delta H^\circ$), Gibbs free energy ($\Delta G^\circ$), and entropy ($\Delta S^\circ$) of adsorption express the type and nature of adsorption and disarrangement of the system at the liquid–solid interface. $\Delta H^\circ$ amounts smaller than 21 kJ mol$^{-1}$ describe physisorption while greater than this value show chemisorption. If $\Delta G^\circ$ is negative, adsorption processes take place spontaneously [62]. The negative values of $\Delta S^\circ$ demonstrate disorder decreasing at the interface during sorption mechanism. Using following equations, the thermodynamic parameters of $\Delta H^\circ$, $\Delta G^\circ$, and $\Delta S^\circ$ can be calculated [63,64]:

$$\Delta G^\circ = -RT\ln K_D$$

where $K_D$ is the distribution coefficient and is attained by the following equation:

$$K_D = \frac{q_{e,D}}{C_{e,D}}$$

Fig. 6. Pseudo-second-order kinetic model for binary adsorption of (A) MB and (B) CV onto (a) OP, (b) NOP, and (c) SNOP.
\[
\ln K = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]  

(14)

where \( R \) represents universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)) and \( T \) is the absolute temperature in K. The plots of \( \ln K \) were found to be linear. The values of \( \Delta H^o \) and \( \Delta S^o \) were obtained from the slope and intercept of the plots, respectively. As shown in Table 3, the values of \( \Delta H^o \) were negative which expresses that the adsorption reaction is exothermic in nature. Furthermore, the negative values of \( \Delta G^o \) prove that simultaneous adsorption of MB and CV onto the prepared sorbents for both dyes is spontaneous in nature and the process is feasible. The values of \( \Delta G^o \) in the range of 1 to –20 kJ mol\(^{-1}\) represent physical sorption, although higher \( \Delta G^o \) are characteristics for chemical adsorption, which generally falls into the range of –80 to –400 kJ mol\(^{-1}\) [65]. The positive values of \( \Delta S^o \) for both MB and CV, in binary sorption system, onto OP and for adsorption of MB onto NOP, indicates that the freedom of the dyes is not much limited in OP or NOP approving a physical biosorption, which is proved by the approximately low values of \( \Delta G^o \).

Furthermore, these positive values exhibit increased randomness at solid-liquid interface, proving the accumulation of dye(s). Reversely, the values of \( \Delta S^o \) for adsorption of CV onto NOP and for adsorption of both dyes onto SNOP was negative which is indicative of absence of a considerable change in the internal structure of NOP and SNOP through the adsorption process, the formation of stable chemical complexes on the sorbents surface, and the association of dye(s) molecules with NOP or SNOP active sites [66].

The values of sticking probability (\( S^* \)) was calculated from the experimental data in order to support the declaration that physical adsorption is the controlling mechanism. It was determined by the following equation which is a modified Arrhenius type equation [63,68]:

\[
S^* = \left(1 - \frac{C_{D}}{C_{D,0}}\right)^{\frac{-E_a}{RT}}
\]

(15)

where \( C_{D,0} \) is the initial concentration and \( C_{D} \) is the residual concentration of each dye in the solution (mg L\(^{-1}\)).

The values of sticking probability (\( S^* \)) shows the potential of dyes to remain continuously on the sorbent surface is demonstrated by the parameter \( S^* \) which

| Table 2 | Kinetic parameters for the simultaneous adsorption of MB and CV onto the prepared sorbents based on the Lagergren rate equation |

| Sorbent | \( C_0 \) (mg L\(^{-1}\)) | \( q_e \) (mg g\(^{-1}\)) | \( K_1 \) (min\(^{-1}\)) | \( q_e \) (mg g\(^{-1}\)) | \( R^2 \) |
|---------|----------------|----------------|----------------|----------------|---------|
| MB CV   | MB CV          | MB CV          | MB CV          | MB CV          | R^2     |
| OP      | 52.20          | 71.55          | 8.6556         | 15.1000        | 0.1253   |
|         | 125.65         | 159.63         | 31.0337        | 37.4014        | 0.1059   |
|         | 171.83         | 226.96         | 38.9000        | 46.9100        | 0.1472   |
|         | 52.20          | 71.55          | 16.5418        | 20.8073        | 0.1493   |
| NOP     | 125.65         | 159.63         | 44.8000        | 53.4321        | 0.3125   |
|         | 171.83         | 226.96         | 62.8000        | 79.9000        | 0.2209   |
|         | 52.20          | 71.55          | 17.9000        | 22.2500        | 0.1043   |
| SNOP    | 125.65         | 159.63         | 45.6000        | 55.1000        | 0.3125   |
|         | 171.83         | 226.96         | 64.3600        | 83.0000        | 0.2209   |

| Sorbent | \( C_0 \) (mg L\(^{-1}\)) | \( h \) (mg g\(^{-1}\) min\(^{-1}\)) | \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) | \( q_e \) (mg g\(^{-1}\)) | \( R^2 \) |
|---------|----------------|----------------|----------------|----------------|---------|
| MB CV   | MB CV          | MB CV          | MB CV          | MB CV          | R^2     |
| OP      | 52.20          | 71.55          | 33.777         | 13.891          | 0.0405   |
|         | 125.65         | 159.63         | 67.563         | 74.660          | 0.0700   |
|         | 171.83         | 226.96         | 34.093         | 48.543          | 0.0208   |
|         | 52.20          | 71.55          | 30.110         | 34.965          | 0.1066   |
| NOP     | 125.65         | 159.63         | 105.304        | 212.773         | 0.0505   |
|         | 171.83         | 226.96         | 188.684        | 322.600         | 0.0471   |
|         | 52.20          | 71.55          | 30.120         | 34.965          | 0.1066   |
| SNOP    | 125.65         | 159.63         | 105.304        | 212.770         | 0.0505   |
|         | 171.83         | 226.96         | 188.684        | 322.580         | 0.0471   |

\[
\theta = 1 - \frac{C_{D}}{C_{D,0}}
\]

(16)
is reported in Table 3. The impact of temperature on the $S^*$ was calculated over the temperature range from 303 to 323 K by evaluating the surface coverage at different temperatures. The sticking probability ($S^*$) and the activation energy ($E_a$) are determined from the plot with an acceptable fit for binary adsorption of MB and CV on the prepared sorbents. The values of $E_a$ specify the type of adsorption. Low activation energies ($E_a < 40$ kJ mol$^{-1}$) represent physical sorption, although higher activation energies ($E_a > 40$ kJ mol$^{-1}$) are characteristics for chemical adsorption. The given values of $E_a$ in Table 3 represent better simultaneous adsorption of MB and CV onto prepared samples; therefore, it can be concluded that the sorption mechanism is exothermic and diffusion controlled. As shown in Table 3, the probability of simultaneous MB and CV sticking to the OP, NOP, and SNOP surface is $0 < S^* < 1$ for MB and CV which approved that the sorption process is physiosorption [48,68]. The negative values of the activation energy (Table 3) suggested that the rise in the solution temperature did not favor MB and CV adsorption onto OP and NOP. The negative value also indicates an exothermic reaction and the low values of the activation energy indicate that the dyes adsorption onto OP and NOP might be physisorption. It means that the rate-limiting step of dyes adsorption onto these sorbents involved predominantly a physical process [69].

3.12. Selective adsorption

Due to the fact that dyes exist simultaneously in wastewaters and in order to study the performance of the used biosorbents in the industrial situation, the adsorption of ternary system methylene blue, crystal violet, and methyl orange (MO) was checked out. The absorption visible spectrum of each solution is shown in Fig. 7. These experiments were performed at optimum pH value and thus the surface of sorbents was negatively-charged during the adsorption process and the optimum dose of adsorbents was used. As shown in the spectrum of each sorbent, it can be observed that each dye is adsorbed onto the biosorbents, although the sorption of MO, an anionic dye, onto negatively
charged surface sorbents was not expected due to the electrostatic repulsion. It may be attributed to the fact that the MB and CV dye molecules are adsorbed onto the sorbents, make the surface slightly positive and make the sorption of MO onto the sorbent possible.

3.13. ANN modeling

Recently, ANN models have widely been used for simulation, optimization, forecasting, and classification [35]. ANNs are organized based on uncomplicated models of the human brain, like learning, thinking, and problem-solving. ANNs models, which contain weights and neurons, depending on the conjecture that a complicated problem-solving. ANNs models, which contain weights and neurons, depending on the conjecture that a complicated relevance between dependent and independent variables could be learned by a system of simple processing elements [71,72]. Developing an ANN model consists of the following stages:

Selecting data and processing, choosing an appropriate structure for the neural network, training algorithm selection for the network, and using the network for validation and simulation [73].

The ANN is typically organized in layers. It contains an input layer, one or more hidden layers, and an output layer. There are some simple processing elements in each layer which are called neurons. Neurons associate layers by weight adjust signals. Signals from external sources are received by the input layer. In this layer, each input is being weighted separately and the hidden layer receives these data in order to processing [74]. In hidden layers, the preprocessing is performed and using transfer functions and the results are transferred into the output layer or other hidden layers [72]. A back propagation neural network, which is being used extensively has a powerful mathematical basis based on gradient descent learning [75]. Different factors such as training algorithms, number of hidden neurons, and initial weights can influence in training modern deep neural networks and achieve favorable results [76]. Therefore, to optimizing these parameters, the experimental data of simultaneous adsorption of MB and CV were randomly divided into three groups in which 70% of 62% data of both dyes is used for training, 15% for testing, and 15% for validating. In this work, a three-layer perceptron ANN with a back-propagation algorithm was established with tansig and purelin as the transfer functions at the hidden and the output layers, respectively (Fig. 8). The structure of ANN in this study for all biosorbents is 5–n–1 where n is the number of hidden neurons which is different for each dye and sorbent, 5 is the number of input neurons which are the effective parameters on adsorption process that include the solution pH, adsorbent dose, initial concentration, contact time, and temperature and number 1 indicates the desired output of the problem which in this study, it is the removal percentages of MB or CV at various situations. In order to reduce the errors, decline the training time, and avoid any numerical overflow, normalizing all input and output variables between 0.1 and 0.9 will be helpful [77]:

\[
\eta_j = 0.8 \frac{(x_j - \min(x_j))}{(\max(x_j) - \min(x_j))} + 0.1
\]

where \(x_j\) is the original value and \(\eta_j\) is the normalized value of \(x_j\).

The mean square error (MSE) and the determination coefficient \((R^2)\) measures the performance of the model according to the following equations [35]:

\[
\text{MSE} = \frac{1}{N} \sum_{i=1}^{N} (y_{\text{pred},i} - y_{\text{exp},i})^2
\]

\[
R^2 = 1 - \frac{\sum_{i=1}^{N} (y_{\text{pred},i} - y_{\text{exp}})^2}{\sum_{i=1}^{N} (y_{\text{pred},i} - y_{\text{exp}})^2}
\]

where \(N\) is the number of all the training data, \(y_{\text{pred},i}\) is the predicted values, \(y_{\text{exp}}\) is the ith calculated value and \(y_{\text{exp}}\) is the mean value of \(y_{\text{exp}}\).

Lower MSE and higher \(R^2\) indicate a model with a very good prediction performance [35]. Optimization of the number of hidden neurons was performed after many repetitions. The optimal number of hidden neurons and MSE values of each dye are listed in Table 5.

Garson recommended an equation based on the dividing of weights for evaluating the relative importance of each input variable:

\[
I_j = \frac{n_{\text{h}}}{\sum_{m=1}^{n_{\text{h}}}} \left( \frac{|W_{im}^{\text{out}}|}{\sum_{m=1}^{N_{\text{in}}} |W_{im}^{\text{out}}|} \times W_{im}^{\text{in}} \right)
\]

where \(I_j\) is the relative importance of the jth input variable on the output variable; \(N_{\text{in}}\) and \(N_{\text{h}}\) are the number of hidden and input neurons, respectively; \(W\) is connection weights.
weights; the subscripts $k$, $m$, and $n$ indicate input, hidden, and output neurons, respectively; and superscripts $I$, $h$, and $o$ indicate input, hidden, and output layers, respectively [78]. Fig. 9 demonstrates the importance of each input variable on the adsorption of MB and CV, respectively. It can be observed that all variables have an important influence on the simultaneous adsorption of MB and CV. Experimental and predicted values of dye removal efficiency for all 62% data are compared and the results are shown in Fig. 10. The predicted values are found to be relatively similar.

---

**Fig. 8.** Schematic diagram of the three layers ANN model with five input layers and one output layer.

**Fig. 9.** Relative importance of the input variables on binary adsorption of (A) MB and (B) CV onto (a) OP, (b) NOP, and (c) SNOP.
to the experimental values. In addition, the performance of the designed model was evaluated by comparison of the experimental and predicted values in the test data set. The results are presented in Fig. S6. Regarding $R^2$ values on the test data sets and based on Fig. S6 and Table 5, it is obvious that the ANN model is accurate for predicting and modeling the complex behavior of the multi-component adsorption of dyes using modified OP.
Number of neurons and MSE of the used ANN model

| Sorbent | Number of neurons in the hidden layer | MSE MB | MSE CV |
|---------|--------------------------------------|--------|--------|
| OP      | 8                                    | 0.0014 | 9.71e-04 |
| NOP     | 19                                   | 4.03e-04 | 6.77e-04 |
| SNOP    | 15                                   | 5.93e-04 | 6.2e-04 |

4. Conclusions

The efficiency of orange peel (OP), NaOH-treated orange peel (NOP), and SNOP have been investigated for simultaneous removal of methylene blue (MB) and crystal violet (CV) dyes from the binary system. The results of FESEM and FTIR analyses indicated that the functional groups and morphology of OP altered after treatment by NaOH and SDS and higher removal percentage of dyes obtained using modified samples (NOP and SNOP). The obtained thermodynamics parameters showed that the adsorption process of dyes is exothermic in nature and negative values of activation energy ($E_a$) proved that lower solution temperature favors for dye adsorption onto the prepared biosorbents. The pseudo-second-order kinetic model showed the best fitting with the experimental data. Desorption tests were carried out in the presence of H$_2$O and HCl (0.1 mol L$^{-1}$) and the obtained results confirmed that the main mechanism for dyes removal was ion exchange. The effect of different parameters like solution pH, adsorbent dose, initial concentration of dyes, contact time, and the temperature was studied using the ANN model as an intelligent tool. The designed ANN model for simulation of dyes removal in binary system was in good agreement with experimental data.

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**Supplementary information**

**Fig. S1.** N₂ adsorption–desorption isotherms for (a) OP, (b) NOP, and (c) SNOP.
Fig. S2. FTIR spectra of (a) OP, (b) SNOP, (c) NOP, (d) SNOP, and (e) NOP after dyes removal.

Fig. S3. Effect of temperature on the multi-component adsorption of (A) MB and (B) CV at different initial concentrations onto (a) OP, (b) NOP, and (c) SNOP.
Fig. S4. Pseudo-first-order kinetic model for binary adsorption of (A) MB and (B) CV onto (a) OP, (b) NOP, and (c) SNOP.
Fig. S5. Plots of $B_t$ vs. time for different initial concentrations of mixed solutions of (A) MB and (B) CV onto (a) OP, (b) NOP, and (c) SNOP.
Fig. S6. Predicted normalized results vs. experimental normalized results for the test data sets for multi-component adsorption of (A) MB and (B) CV onto (a) OP, (b) NOP, and (c) SNOP for the optimum number of the hidden layer.