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Simultaneous Adsorption of Chromium and Acidic Dye from Leather Tannery Model Wastewater Using a Novel Modified Nanoclay

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Abstract

Simultaneous removal of Cr^{3+} and acidic dye from model tannery wastewater was investigated using local nano clay modified by 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) surfactant. X-ray fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), carbon, hydrogen, nitrogen and sulfur analysis (CHNS), Brunauer-Emmet-Teller (BET) analysis and pH of zero point charge (pH_{ZPC}) analyses were carried out for characterization of the adsorbent, and adsorptive properties of the modified clay were investigated by batch experiments. The effects of essential parameters, such as adsorbent dosage, initial solution pH, initial solution concentration, contact time, and temperature, were studied. Maximum adsorption values (99.74% for Cr^{3+} and 83.26% for dye) were obtained in the following conditions: pH of 4, initial concentration of 100 mg/L, adsorbent dosage of 15000 mg/L, contact time of 30 min. The effect of contaminants' concentration was also investigated through response surface methodology (RSM), central composite face-centered (CCF) design and an empirical model was presented. The results of kinetic models' studies demonstrated that simultaneous adsorption of contaminants follows the pseudo-second-order model, and the adsorption data of single and binary solutions fitted nonlinearly to isotherm models showed that the adsorption of Cr (III) from binary and single solutions follow Langmuir and Dubinin-Radushkevitch (D-R) isotherms, respectively. Adsorption of dye from both single and binary solutions follows Redlich- Peterson (R-PT) isotherm. Maximum adsorption capacities were obtained to be 193.1390 $\frac{mg}{g}$ and 144.1782 $\frac{mg}{g}$ for Cr^{3+} and dye, respectively. Synergistic and antagonistic adsorptions were observed in binary solutions.

Keywords: Simultaneous Adsorption, Chromium, Dye, Modified clay, Response Surface Methodology, Leather Tannery.

1. Introduction

In real-life applications, wastewaters contain more than one contaminant, and the contaminants are usually of different chemical and physical properties (Tovar-Gómez *et al.*, 2015; Niu *et al.*, 2018). Heavy metals and dyes are two types of hazardous contaminants that can alter any ecosystem's properties and usually coexist in the effluent of many industries (Deng *et al.*, 2013; Fan *et al.*, 2014; Tovar-Gómez *et al.*, 2015; Aghdasinia and Asiabi, 2018). Chromium

(III) is an essential heavy metal for human metabolism, but when it enters the body in amounts more than the safe limit, it accumulates in live organs and can be oxidized to chromium (VI), which is a very hazardous heavy metal (Zaroual *et al.*, 2009; Gładysz-Płaska *et al.*, 2012; Seif, Marofi and Mahdavi, 2019). Dyes are widely used in various applications and industries, and it should be noted that about 10% of the dye used in a process is discharged into the hydrosphere, which is harmful to the environment due to being a visible public concern and a severe threat to human health and aquatic life (Samiey and Toosi, 2010; Yagub *et al.*, 2014; Ahmad *et al.*, 2015). The simultaneous presence of contaminants results in synergetic harm toward human health, animals and plants' lives (Liu *et al.*, 2016). So, investigating the highly efficient methods and techniques for removing contaminants from multi-component solutions is a priority (Deng *et al.*, 2013; Wang *et al.*, 2017). Adsorption is an advantageous and highly efficient method to remove contaminants from wastewaters (Gładysz-Płaska *et al.*, 2012; Fan *et al.*, 2014; Wang *et al.*, 2017; Keçeci, Usta and Uygur, 2020). If the adsorbent could simultaneously remove contaminants, it would reduce operation cost, complexity and equipment investment (Wang *et al.*, 2017). Clays are adsorbents with advantages, such as high cation exchange capacity (CEC), high chemical and mechanical stability, low cost, high abundance and easy manipulation and modification (Srinivasan, 2011; Oskui, Aghdasinia and Sorkhabi, 2019a). Clays are hydrophilic materials with negative surface charge and these properties limit their usage in the removal of various contaminants (Liu *et al.*, 2016). So, proper modifications are used to make them suitable adsorbents for different contaminants. Several methods have been used to modify the adsorptive properties of clays (Srinivasan, 2011; Behnamfard *et al.*, 2019). Modification of clays using organic surfactants prepares them to be used in the removal of organic and hydrophobic materials (Fan *et al.*, 2014; Liu *et al.*, 2016; Heinz *et al.*, 2017; Wang *et al.*, 2017). Several studies have been carried out on the adsorption of different heavy metals and dyes from single-contaminant aqueous solutions via different kinds of clays, but there are only a few studies on the simultaneous removal of heavy metals and dyes by clays (Fan *et al.*, 2014; Stawiński *et al.*, 2017). Furthermore, browsing through literature, one can find the following cases: Wang *et al.* (2017) modified montmorillonite via trimethyl tetradecyl ammonium chloride¹, hexadecyl trimethyl ammonium chloride², octadecyl trimethyl ammonium chloride³ quaternary ammoniums and cysteamine hydrochloride⁴ modifiers to investigate simultaneous adsorption of phenol and Zn²⁺ (Wang *et al.*, 2017). Liu *et al.* (2016) investigated the

¹ TTAC

² CTAC

³ STAC

⁴ CSH

modification of montmorillonite by amphoteric surfactant of octadecyl dimethyl betaine⁵ to study simultaneous adsorption of Cd^{2+} and bisphenol A⁶ (Liu *et al.*, 2016). Ma *et al.* (2016) modified montmorillonite by cationic and zwitterionic surfactants of hexadecyltrimethylammonium bromide and hexadecyldimethyl (3-sulphonatopropyl) ammonium, respectively, to simultaneously adsorb Cu (II) and phenol (Ma *et al.*, 2016). Fan *et al.* (2014) used dodecyl sulfobetaine modified montmorillonite to investigate the simultaneous adsorption of Cu^{2+} and methylene blue dye (Fan *et al.*, 2014). Gladysz-Plaska *et al.* (2012) modified natural polish red clay via hexadecyltrimethylammonium bromide⁷ to simultaneously adsorb Cr (VI) and phenol (Gładysz-Plaska *et al.*, 2012). Stawiński *et al.* (2017) investigated the simultaneous removal of cationic dyes and Cu^{2+} using vermiculite modified via acid, base and acid-base (Stawiński *et al.*, 2017). In this work, the simultaneous removal of chromium (III) and acid brown from leather tannery model wastewater was thoroughly investigated by a nanoclay modified with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) surfactant. The promising results show that this process might yield to a potential method to safely treat the high priority leather tannery wastewater.

2. Materials and methods

The local clay used in this study was obtained from Urmia, West Azerbaijan province, North West of Iran. To get a homogeneous size distribution, the clay was sieved and the particles with a smaller size than 845 μm were taken for the rest of the experiments. This clay is denoted as U- clay in this paper. The parameter of CEC for U-clay was obtained using the method suggested by Rhoades (Rhoades, 1983; Pansu and Gautheyrou, 2007). The chemical composition and properties of this clay are gathered in Table 1. Distilled water (1 $\mu Siemens/cm$) was used in all experiments. Solutions were prepared by dissolving Chromium (III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) salt (Samchun, Korea) and acid brown dye (Azar dye, a local Iranian dye company that provides the dyes consumed in the units of leather tannery in the region) in distilled water. Quaternary ammonium solution (3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC)) 60 wt. % in H_2O was purchased from Sigma-Aldrich.

⁵ BS-18

⁶ BPA

⁷ HDTMA

2.1. Adsorbent preparation

The modified clay was prepared by dissolving a given amount of the surfactant into distilled water and then adding 10 g of U-clay. The surfactant amount was equivalent to 5 CEC of the U-clay and mass ratio of clay/water was 1:20. The mixture was stirred under 100 rpm using a mechanical stirrer for 24 h at room temperature. The modified clay was collected and washed for several times with distilled water to remove the Cl^- ions. After that, the prepared adsorbent was dried in the oven for 16 h. The modified clay is denoted as CHPTAC-clay in this paper. The adsorbent was ground after drying and was used in the proceeding experiments (Ma *et al.*, 2016).

Table 1: Physical characteristics of the non- modified clay

Compound	%w/w	Element	ppm
CaO	43.23	As	0
SiO ₂	13.51	Ba	101
Al ₂ O ₃	3.03	Ce	0
Fe ₂ O ₃	1.85	Co	4
MgO	1.37	Cr	12
Na ₂ O	1.01	Cu	0
K ₂ O	0.66	Nb	1
TiO ₂	0.15	Ni	36
P ₂ O ₅	0.06	Pb	12
MnO	0.03	Rb	34
LOI ^a at 1100°C	35.1	Sr	454
CEC	322.4114 (mmol/kg clay)	V	30
		Y	11
		Zr	91
		Zn	41
		Mo	26

^a Loss of ignition

2.2. Adsorbent characterizations

2.2.1. X-ray fluorescence (XRF)

The U-clay chemical composition and elemental analysis were obtained via XRF analysis (Philips, PW1430, Netherland).

2.2.2. the pH of zero point charge (pH_{zpc}) measurement

Sodium chloride solutions with a concentration of 0.01 M were prepared. Their pHs were adjusted in the range of 3 to 11. 0.1 g of the adsorbent was added to 100 ml of each prepared solution. The mixtures were shaken in an incubator (Fanavaran Sahand Azar, 554D, Iran) for 48 h at the controlled temperature of 25 ± 0.1 °C. After 48 h, the pH of the mixtures was measured using a pH meter. The final pHs were depicted versus the initial pHs. pH_{zpc} was the intercept point of this curve with the diagonal line (Khormaei *et al.*, 2007).

2.2.3. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra for the non-modified and the modified clays were recorded using a Bruker, TENSOR 27 model (Germany) spectrometer. The spectra range and wavenumber accuracy measured by this spectrometer are 4000-400 cm^{-1} and 0.1 cm^{-1} , respectively. The readings are carried out at room temperature via *KBr* method. The tablets were prepared by the hydraulic press with a radius of 1 cm and a thickness of 1 mm.

2.2.4. X-ray diffraction (XRD)

XRD analysis was carried out by a Panalytical Xpert PRO X-Ray Diffractometer (Xpert Pro MPD model, Netherland). The conditions of measurement were as follows: anode material: Cu, 2θ range: $4.8500^\circ - 109.9500^\circ$, step size: 0.0500° , scan step time: 1.0000 s, divergence slit size: 1.0000° , receiving slit size: 0.1000 mm, measurement temperature: 25 °C. Phase analysis was performed by X'Pert HighScore Plus software. The samples were of random powder.

2.2.5. Scanning electron microscopy (SEM)

Morphologies of the non-modified and modified clays were observed using a scanning electron microscopy facilitated with energy-dispersive X-ray spectroscopy (EDX) detector (Philips XL30 ESEM, Netherland). The images were obtained under the operating conditions of 20 kV, vacuum pressure of less than 2×10^{-4} bar and the electron beam penetration of 1 μ . Using EDX, elements after Na were detectable.

2.2.6. CHNS analysis

Elemental analysis of C, H, N and S were performed in Elementar Vario EL III (Laos) analyzer. Using this analysis, the concentration of CHPTAC loaded on the organoclay was calculated using the following equation (Gładysz-Płaska *et al.*, 2012):

$$c_{CHPTAC} = \frac{c_m}{1 - c_m \cdot MW} \quad (1)$$

$$c_m = \frac{c_N}{n_N \cdot M_N \cdot 100} \quad (2)$$

In which c_m is the molar concentration of CHPTAC in the organoclay (mol/g) and MW is the molecular weight of the surfactant (g/mol). c_N is the nitrogen content in the sample in weight percent, n_N is the number of nitrogen atoms in the surfactant and M_N the molecular mass of N.

c_m was calculated from equation 2 and was inserted to the equation 1 and c_{CHPTAC} , the concentration of CHPTAC loaded on the clay, was calculated.

2.2.7. N_2 adsorption and desorption

N_2 adsorption and desorption were performed for non-modified and modified clays via Specific Surface Area and Porosity Analyzer PHS-1020 (PHSCHINA) using liquid nitrogen with the temperature of 77 K. Brunauer-Emmet-Teller (BET) equation and Barret-Joyner-Halenda (BJH), dBJH and MP-plot methods were applied to obtain the specific surface area and pore size distribution, respectively.

2.3. Adsorption processes

To study the adsorptive properties of CHPTAC- clay, all effective parameters were investigated using one factor at a time method in batch experiments. Five steps were included in the adsorption studies: (1) determination of the adsorbent's amount, (2) the pH effect studies, (3) the initial solution concentration effects, (4) studies on the contact time and (5) investigation of the temperature effect on the simultaneous adsorption of contaminants. The experiments were carried out using 100 ml of the solutions on magnetic stirrers. The range of each parameter was as follows: 2500 to 20000 mg/L for adsorbent dosage, 3 to 5 for the initial pH of solutions, 25 to 300 mg/L for the initial concentration of the contaminants, 1.5 to 240 min of contact time and temperatures of 15 to 45°C. All these experiments were carried out for binary solutions. After each experiment, the mixture was centrifuged at 4000 rpm for 15 minutes and the

concentrations of the Chromium and dye were measured by atomic absorption spectroscopy (AAS) (Analytikjena, novAA 400 P model, Germany) and ultraviolet-visible (UV-Vis) spectroscopy (Hanon, China), respectively. Adsorption efficiency and adsorption capacity were calculated using the following equations:

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_e}{C_0} * 100 \quad (3)$$

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (4)$$

Where, q_e is the equilibrium adsorption capacity of the adsorbent (mg/g), V is the volume of the solution (L), m is the mass of adsorbent (g), C_0 is the adsorbate's initial concentration (mg/L), C_e is the equilibrium concentration of adsorbate (mg/L) (Limousin *et al.*, 2007).

However, to study the synergistic and/or antagonistic effects in simultaneous adsorption in binary systems, adsorption of the contaminants from monocomponent solutions in the range of 25 to 300 mg/L were also investigated and the results were compared with the results of adsorption capacities from binary solutions via the parameter of $R_{q,i}$, which is defined as (Tovar-Gomez *et al.*, 2012):

$$R_{q,i} = \frac{q_{b,i}}{q_{s,i}} \quad (5)$$

Where $q_{b,i}$ and $q_{s,i}$ are the adsorption capacity of component i from the binary and single solutions (mg/g), respectively.

Kinetic models of pseudo-first-order (Eq.6) and pseudo-second-order (Eq.7) were linearly fitted to the obtained data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

$$h = k_2 q_e^2 \quad (8)$$

Where K_1 is the rate constant of the pseudo-first-order model ($1/min$), K_2 is the rate constant of the pseudo-second-order kinetic model ($g/mg \min$), q_t is the amount of adsorbed adsorbent (mg/g) at time t and h (Eq.8) gives the value of the initial velocity of the adsorption (Kim *et al.*, 2004; Ho, 2006; El-Ashtoukhy, Amin and Abdelwahab, 2008).

Adsorption modeling is a fundamental topic for engineering the wastewater treatment processes (for operation, design and optimization). Two parameter isotherm models of Langmuir (Eq.9) and Freundlich (Eq.10) and three-parameter isotherm models of Dubinin-Radushkevich (D-R) (Eq.11) and Redlich-Peterson (R-PT) (Eq.12) were non-linearly fitted to the adsorption data of the single and binary solutions via minimization of error functions of the sum of square errors (SSE), (Eq.13), the fractional HYBRID (Eq.14) and the nonlinear chi-square (Eq.15) using Add-in solver tool in Microsoft Excel. The equations of the isotherms and the error functions used are as follows (Allen *et al.*, 2003; Wong *et al.*, 2004; Foo and Hameed, 2010):

$$q_e = \frac{q_{mL} b C_e}{1 + b C_e} \quad (9)$$

$$q_e = K_F C_e^{1/n_F} \quad (10)$$

$$q_e = q_{SD} \exp(-K_{ad} \varepsilon^2) \quad (11)$$

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (12)$$

$$SSE = \sum_{i=1}^n (q_{e,cal} - q_{e,meas})_i^2 \quad (13)$$

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left(\frac{(q_{e,cal} - q_{e,meas})^2}{q_{e,meas}} \right)_i \quad (14)$$

$$\chi^2 = \sum_{i=1}^n \left(\frac{(q_{e,cal} - q_{e,meas})^2}{q_{e,meas}} \right)_i \quad (15)$$

Where q_{mL} is the Langmuir maximum adsorption capacity of the adsorbent (mg/g), b is the Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant ($mg^{1-n} L^n/g$), n_F is the Freundlich constant, q_{SD} is the D-R theoretical isotherm saturation capacity (mg/g), K_{ad} is the D-R isotherm constant related to the adsorption energy (mol^2/kJ^2) related to the mean adsorption energy(E) (Eq. 16), γ is the Polanyi potential, Eq.17, K_R is the R-PT isotherm constant (L/g), a_R is the R-PT isotherm constant (L/mg) and g is the R-PT isotherm exponent (Foo and Hameed, 2010; Parimal, Prasad and Bhaskar, 2010).

$$E = \frac{1}{\sqrt{2K_{ad}}} \quad (16)$$

$$\gamma = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (17)$$

R_L (separation factor) is a dimensionless constant and the main characteristic of the Langmuir isotherm:

$$R_L = \frac{1}{1 + bC_0} \quad (18)$$

Where b is the constant of the Langmuir isotherm (L/mg) and C_0 is the initial concentration of the contaminant (mg/L). $R_L > 1$, $R_L < 1$, $R_L = 1$ and $R_L = 0$ indicate unfavorable, favorable, linear and non-reversible adsorptions, respectively (Hameed, Mahmoud and Ahmad, 2008).

Thermodynamic parameters of variations of free Gibbs energy (ΔG°), variations of enthalpy (ΔH°) and variations of entropy (ΔS°) were also calculated using the equations below (Fil, Ozmetin and Korkmaz, 2012; Elmoubarki *et al.*, 2015):

$$\Delta G^\circ = -RT \ln(K_D) \quad (19)$$

$$K_D = \frac{q_e}{C_e} \quad (20)$$

$$\ln K_D = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (21)$$

Where K_D is the thermodynamic distribution coefficient (Eq.20).

2.4. Response surface methodology (RSM)

Differences in adsorbates' concentration in systems having more than one contaminant may result in variations in adsorption capacities. To study the effect of contaminants' concentration on the adsorption capacity of each contaminant, RSM, face-centered central composite design (CCD), by the Design Expert 10.0.7 software was used (Tovar-Gómez *et al.*, 2015). The initial concentration of the chromium and dye were considered as two independent variables (x_1 and x_2 are coded variables). In CCF design, each variable takes levels of $\pm\alpha$, ± 1 and 0, which are 250, 50 and 150, respectively. This method gives a quadratic equation that can predict the adsorption capacities. The equation is as follows:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^n \beta_{ij} X_i X_j \pm \varepsilon \quad (22)$$

Where Y is the predicted response or output (depended variable), n is the number of the patterns, i and j are the index numbers for pattern, $X_i, X_j, \dots, X_n$ are the input coded variables that affect the response Y , $X_i^2, X_j^2, \dots, X_n^2$ are the square effects, X_iX_j, X_iX_n and X_jX_n are the interaction effects, β_0 is the free or offset term called intercept term, β_i ($i = 1, 2, \dots, n$) is the linear (first-order) main effect, β_{ii} ($i = 1, 2, \dots, n$) is the squared (quadratic) effect, β_{ij} ($i = 1, 2, \dots, n; j = 1, 2, \dots, n$) is the interaction effect and ε is a random error or allows for discrepancies or uncertainties between the predicted and measured values (Oskui, Aghdasinia and Sorkhabi, 2019b).

3. Results and discussion

The “results and discussion” section contains nine sub-sections of adsorbent characterizations, adsorption processes, adsorption selectivity, kinetic, isotherm, thermodynamic and RSM studies, adsorption mechanism and comparison of the results with literature data.

3.1. Adsorbent characterizations

3.1.1. pH_{zpc}

The pH zero-point charge plays an important role in the adsorption process. pH_{zpc} values were obtained to be 9.75 and 8.6 for U-clay and CHPTAC-clay, respectively. In each adsorbent, for pH values higher than these, the adsorbents have a negative charge, and in pH values lower than these, the adsorbents have a positive charge (Wang *et al.*, 2017).

Figure 1 depicts the results of this analysis.

Fig. 1: Final pH versus initial pH of non-modified and modified clay

3.1.2. FTIR

Eventhough the $O-H$ stretching region is perhaps the most important diagnostic part of the spectrum, the positive identification of as many characteristic bands of individual minerals as possible in the whole $4000-400\text{ cm}^{-1}$ range is needed to recognize the mineral species. In the studies of clay minerals, the absorption bands, due to structural OH and Si-O groups, play an important role in the differentiation of clay minerals from each other. The $4000-3000\text{ cm}^{-1}$ range corresponds to $O-H$ stretching vibrations and $1300-400\text{ cm}^{-1}$ range in the spectra of the clay minerals show Si-O stretching and bending as well as $O-H$ bending absorptions.

Based on the thorough investigations carried out by researchers, the IR spectra of dioctahedral smectites show only a single band in the $O-H$ stretching region. A broad band near 3430 cm^{-1} , observed somewhat clearly in the spectra of all smectites, is due to H-O-H vibrations of the adsorbed water. The spectrum of the untreated sample shows

intensive bands at 1030 cm^{-1} attributed to the Si–O stretching vibrations, the 790 cm^{-1} band represents the Si – O stretching of quartz and silica and the 520 and 470 cm^{-1} bands are assigned to Si–O–Al (octahedral Al) and Si–O–Si bending vibrations, respectively.

Various arrangement within the layers (1:1 versus 2:1 and/or di- versus trioctahedral character) is reflected in the shape and positions of the bands. While the Si–O stretching vibrations of kaolinite and dickite give several well-resolved strong bands in the 1120–1000 cm^{-1} region, the main Si–O band of chrysotile is observed at a lower frequency of 960 cm^{-1} . Only one broad complex Si–O stretching band is present in the IR spectra of both di- and trioctahedral smectites. Montmorillonite and nontronite absorb at 1030 and 1019 cm^{-1} , respectively, while for hectorite and saponite the absorption is seen at 1012 and 1009 cm^{-1} , respectively.

The position of the O – H bending bands is strongly influenced by the occupancy of the octahedral sheet in both 1:1 or in 2:1 minerals. Thus, the dioctahedral minerals absorb in the 950–800 cm^{-1} region, while the OH absorption of the trioctahedral minerals is shifted to lower frequencies, the 700–600 cm^{-1} range.

Due to many applications of these modified minerals, organo-clays, researchers studied the interactions between the clay minerals and the organic molecules.

The C – H stretching bands of the alkylammonium cations occur in the 3020–2800 cm^{-1} region. The bands in 1580 – 1650 cm^{-1} represent the N – H bending. The spectrum of CHPTAC-clay shows a band near 3620 cm^{-1} owing to the stretching vibrations of the structural OH groups, and a broad band near 3440 cm^{-1} due to the O – H stretching vibrations of the present H_2O in the smectite.

The hydrophilic surface of clay minerals can be turned hydrophobic by replacing the naturally occurring inorganic cations with various alkyl- and/or aryl-organocations. An important consequence of this replacement is that the clay surface takes on hydrophobic character, which greatly enhances their affinity for organic pollutants (Madejová, 2003; Adikary and Wanasinghe, 2012; Tahir, Sultan and Qadir, 2013; Çakmak *et al.*, 2017; El Kassimi *et al.*, 2021; Namjoufar, Farzi and Karimi, 2021).

(a)

(b)

Fig. 2: The FT-IR spectra of (a) non- modified and (b) modified clay

3.1.3. XRD

Figure 3 depicts the XRD spectra of the non-modified and surfactant-modified clays. Based on the full report from the XRD analysis and the reported 2θ , the adsorbent has calcium carbonate $Ca(CO_3)$ (calcite) and silicon oxide SiO_2 (quartz). This finding is in full consistent with FTIR results. High value of Loss on ignition or LOI (35.1%), in XRF is also related to the presence of carbonate and silicate minerals (El Kassimi *et al.*, 2021).

The introduction of the surfactant into the clay resulted in the elimination of some peaks. The modification leads to a low increment of d- spacing in the modified clay (Ma *et al.*, 2016).

(a)

(b)

Fig. 3: XRD patterns of (a) non-modified and (b) modified clay

3.1.4. SEM

Figure 4 shows the SEM images of the non-modified and modified clays. SEM images are used as a proof of concept to observe the porous structure of the U-clay and CHPTAC-clay. The images show that the smoother surface of the U-clay has become more porous (Wang *et al.*, 2016). For a more detailed, thorough and quantitative result on the structures, BET test was also carried out for both modified and non-modified clays. And the results of this analysis confirms the increase in porosity. Using EDX analysis, elements present in the adsorbent after modification were also investigated and the results are demonstrated in Fig.4 (e).

(a)

(b)

(c)

(d)

Fig. 4: SEM images of (a) non-modified clay, 10μm, (b) non-modified clay, 1μm, (c) modified clay, 10μm, (d) modified clay, 1μm and (e) EDX analysis of the modified clay

3.1.5. CHNS analysis

Using CHNS analysis data and by applying Equations 1 and 2, C_{CHPTAC} was calculated to be 0.1703 mmol/g , 52.55 % of CEC.

3.1.6. N_2 adsorption and desorption

The data obtained by this analysis are shown in Table 2. The results show that the average pore diameter reduces, some mesopores become micropores, and the total pore volume after modification of the U-clay was significantly incremented. A significant increase was seen in the specific surface area value in the CHPTAC- clay, compared to the U-clay, which is consistent with the result of mesopores becoming micropores. This high increase in the specific surface area may be attributed to the cation exchange of the ions present in the structure with the long-chain alkylammonium cations. Also, mesopores volume was increased after the modification, but the mesopores' radii were constant.

Table 2: Porous properties of non-modified and modified clays

Samples	Non- modified clay	Modified clay
Specific surface area (m^2/g)	20.015	336.871
Total pore volume (cm^3/g)	0.032415	0.496
Average pore diameter (nm)	6.4782	0.7
Maximum radius of mesepores (nm)	1.21	1.26
Mesepores volume (cm^3/g)	0.028815	1.197

3.2. Adsorption processes

3.2.1. Effect of adsorbent dosage

To find the effect of adsorbent dosage, 0.25 g to 2 g of CHPTAC- clay was applied to solutions of 100 ml in pH of 4, containing 100 mg/L of each contaminant, and a contact time of 2 hr was given. The results are depicted in Figure 5 (a). As shown in this figure, the adsorbent values of 5000 to 15000 $\frac{mg}{L}$ lead to the maximum removal of Cr (III) and dye, respectively. For each contaminant, when the adsorbent value was lower than this, a lower removal was obtained, showing that there were not enough adsorbent and adsorption sites available for contaminants. For Cr (III), the adsorbent values up to 15000 $\frac{mg}{L}$ resulted in a constant removal value of 99%, and then the removal efficiency was decreased. For the dye, up to 15000 $\frac{mg}{L}$, an increase in removal efficiency was seen, and afterward, the efficiency decreased. Agglomeration of the adsorbent was the reason for this decrease in the removal efficiency (Hafshejani *et al.*, 2015). The adsorbent value of 15000 $\frac{mg}{L}$ was the value chosen to be applied in the upcoming experiments.

(a)

(b)

Fig. 5: Effect of (a) adsorbent dosage, (b) initial solution pH, (c) initial concentration of Cr (III) and dye, (d) contact time and (e) temperature on Cr (III) and dye removal

3.2.2. Effect of initial pH of the solution

To see the effect of the initial pH of solution on the simultaneous adsorption of contaminants, 15000 $\frac{mg}{L}$ of CHPTAC-clay was added to solutions containing 100 mg/L of each contaminant with the pHs of 3, 4 and 5, and a contact time of 2 hr was given. The results are depicted in Figure 5 (b). As it can be seen in this figure, the initial pH of the solutions had no significant impact on the removal of dye, but for Cr (III), the removal was slightly higher in pH=4. In pHs of 3 and 4, Cr (III) is in the forms Cr^{3+} and $CrOH^{2+}$ and this cationic species may be adsorbed by the pores of the adsorbent and/or by the hydroxide groups on the adsorbent surface. In the pH of 5, $Cr(OH)_2^+$ and $Cr(OH)_3^0$ species are also present in the solution and $Cr(OH)_3^0$ results in precipitation (Richard and Bourg, 1991). In this pH for Cr (III), precipitation will occur instead of adsorption. It should be noted that pHs lower and higher than this range were not investigated in this study since the studied solution is a leather tannery model wastewater, and this is the pH range present in this industry's wastewater.

3.2.3. Effect of initial concentration of the solution

To investigate the effect of the solutions' initial concentration, 15000 $\frac{mg}{L}$ of the CHPTAC-clay was applied to solutions in pH of 4 and containing 25 to 300 mg/L of each contaminant, and a contact time of 2 hr was given. The results are depicted in Figure 5 (c). Based on this figure, Cr (III) removal efficiencies were higher than 99% in all the investigated concentrations. For the dye, the initial concentration shows no significant effect on the adsorption capacity, and there was only a slight increase in the removal value in the initial concentration of 100 mg/L . These results show that the adsorbent has enough active sites for the adsorption of contaminants in this wide range of initial concentrations. The reason for no more adsorption of the dye in all these initial concentrations can be attributed to reaching an equilibrium that limits the adsorption capacity to be no more than this.

3.2.4. Effect of contact time

To study the effect of contact time, 15000 $\frac{mg}{L}$ of the CHPTAC-clay was applied to solutions in pH of 4 and containing 100 mg/L of each contaminant, and the contact times of 1.5 to 240 min were given. The results are depicted in Figure 5 (d). As it can be seen in this figure, adsorption of Cr (III) and dye were completed in the first 3 and 10 to 30 minutes, respectively. The reason for this rapid removal of contaminants is the vacancy of adsorption sites in the adsorbent in the first minutes. After this time, an equilibrium is reached.

3.2.5. Effect of temperature

To study the effect of temperature, 15000 $\frac{mg}{L}$ of the CHPTAC-clay was applied to solutions in pH of 4 and containing 100 mg/L of each contaminant, and a contact time of 120 min was given. The tests were carried out in water baths with controlled temperatures of 15 to 45 °C. The results are depicted in Figure 5 (e). As it can be seen in this figure, the temperature has no effect on Cr (III) adsorption but a significant effect on dye adsorption. An increase in temperature leads to a decrease in dye adsorption and it is consistent with typical adsorption cases.

Based on the results of these investigated five steps, the CHPTAC-clay gives promising results in the adsorption of both Cr (III) and dye. The removal efficiency of Cr (III) using U-clay was adequate, but adsorption of the dye using the raw clay was so negligible, and this alteration leads to high values of dye removal.

3.3. The ratio of binary adsorption capacities and adsorption selectivity

Comparing the adsorption capacity values obtained for each contaminant in single and binary solutions, it was accepted that both antagonistic and synergistic adsorption was observed in the simultaneous removal of contaminants. This result is seen in Figure 6 (a) and Figure 6 (b) that show the adsorption capacities of contaminants in single and binary solutions. Investigating the $R_{q,i}$ s for the dye, in the concentration of 25 mg/L , $R_{q,i}=1.0167$ that can be assumed to be equal to 1. There are two possible explanations for this: (1) Cr (III) is adsorbed on the active sites and provides a positively charged surface, preparing the surface to adsorb negatively charged dye via electrostatic attraction forces, the positive surface created by the adsorption of Cr (III) acts more effective in the adsorption of dye than the vacant active sites of the adsorbent, which may be due to spontaneity of Cr (III) adsorption and non-spontaneity of dye adsorption, (2) in this low concentration there are enough active sites for both contaminants and they show no synergistic or antagonistic effects in adsorption. When the concentrations of contaminants increase up to 100 mg/L , the $R_{q,i}$ s are less than 1 indicating that Cr (III) occupies the active sites and limits dye adsorption. In concentrations of 150 and 200 mg/L , $R_{q,i}$ s are more than 1, indicating that Cr (III) occupies the active sites and provides more positive charged groups, thus creating more adsorption sites for the dye due to electrostatic attraction forces. In concentration of 300 mg/L , the $R_{q,i}$ is less than 1, in this concentration, the condition explained for the concentrations of 150 and 200 mg/L is still established and the positively charged surface helps, and much higher dye adsorption occurs, and this is due to a much higher $q_{s,i}$ that $R_{q,i}$ becomes less than 1 (Deng *et al.*, 2013).

For Cr (III) adsorption in all the investigated concentrations, $R_{q,i,s}$ are less than 1, indicating that Cr (III) competes with the dye for adsorption sites and if there were no dye contaminations in the solution, the adsorption capacities of Cr (III) would be much higher, meaning a need for much less adsorbent to remove the Cr (III) from these solutions. This has been proven thoroughly in our previous work, which studied the removal of Cr (III) from single solutions using this raw clay.

Fig. 6: Comparison of (a) adsorption efficiencies and (b) adsorption capacities of each contaminant vs. initial concentration of solutions in both single and binary solutions

3.4. Kinetic studies

Based on the results, the data obtained for the simultaneous adsorption of Cr (III) and dye were fitted to the pseudo-second-order model with $R^2 = 1$ and $R^2 = 0.9999$ for Cr (III) and dye, respectively. Using Eq.8, initial adsorption velocities are obtained to be 40.725 mg/g min for Cr (III) and 28.2633 mg/g min for dye.

3.5. Isotherm studies

Based on the calculations (SM, Tables 1, 2, 3 and 4), it was found that the adsorption of Cr (III) from a single and a binary solution follows D-R and Langmuir isotherms, respectively, and the adsorption of dye from both single and binary solutions follows R-PT isotherm. For adsorption of Cr (III), HYBRID and Chi, and for the adsorption of dye, HYBRID error functions had the minimum error and gave the best fit to the experimental data, respectively. As said above, Cr (III) adsorption from binary solutions follows Langmuir isotherm. Based on the parameters of this isotherm, it was concluded that the maximum monolayer adsorption capacity of Langmuir for Cr (III) in binary solutions is 193.1390 mg/g . Since q_e s obtained for the adsorption of Cr (III) from binary systems in the range investigated are all lower than q_{mL} , it is understood that monolayer adsorption processes have been carried out in which the adsorbent surface has not been filled completely (SM, Table 5) (Taty-Costodes *et al.*, 2003). The values of R_L parameter shows that the adsorption carried out is a favorable process (SM, Table 6). Based on Eq.16, adsorption energy of Cr (III) from single solutions is obtained to be 0.6983 KJ/mol , which shows that this adsorption process is physical (Sari, Tuzen and Soylak, 2007). In the adsorption of Cr (III) from both single and binary solutions, the parameter of g in R-PT isotherm was obtained to be 0, so it can be said that this isotherm follows Henry's law, and in the single solution of dye, $a_R C_e^g \gg 1$, so it can be noted that Freundlich isotherm is applied to the system (Vijayaraghavan *et al.*, 2006; Liu and Liu, 2008).

3.6. Thermodynamic studies

For Cr (III) adsorption from binary solutions, thermodynamic parameters were calculated to be -17.4893 and -0.0272 KJ/mol for ΔH° and ΔS° , respectively, and for dye ΔH° and ΔS° are 31.3305 and -0.1109 KJ/mol , respectively. In temperatures of 15, 25, 35 and 45 °C, -9.5877 , -9.4683 , -9.2060 and -8.7551 KJ/mol were the values of ΔG° for Cr (III) adsorption process and 0.7592 , 1.3309 , 3.1918 and 3.8396 KJ/mol were the values obtained for ΔG° of the dye adsorption process. Based on the results, it was found that the adsorption process is spontaneous for Cr (III) removal

but non-spontaneous for dye removal. Cr (III) adsorption is exothermic, while adsorption of dye was obtained to be endothermic. Entropy is also decreasing when both contaminants are adsorbed on the adsorbent.

3.7. RSM results

By applying the multivariate regression model on the CCF design and Table 3, quadratic equations for predicting the adsorption capacities of each contaminant are obtained:

$$Ln(Y_1) = 2.89 + 0.74x_1 + 0.016x_2 + 0.28x_1x_2 - 0.77x_1^2 + 0.29x_2^2 \quad (23)$$

$$Ln(Y_2) = 1.93 - 0.16x_1 + 0.78x_2 + 0.024x_1x_2 - 0.066x_1^2 - 0.38x_2^2 \quad (24)$$

Where Y_1 and Y_2 are the predicted values of the adsorption capacities for the Cr (III) and dye (mg/g). The negative and positive coefficients of the model are representatives of antagonistic and synergistic effects in the adsorption, respectively (Yetilmezsoy, Demirel and Vanderbei, 2009). Table 3 shows the observed and predicted values of the adsorption capacities and the error percentages.

Table 3: Observed, predicted and error values of CCF design

Run. No	Coded variable		Adsorption capacity of $Cr^{3+}(mg/g)$		Adsorption capacity of dye (mg/g)		Error of $Cr^{3+}(\%)$	Error of dye (%)
	x_1	x_2	Observed	Predicted	Observed	Predicted		
1	-1	-1	7.3731	6.9171	2.7390	2.4303	6.1843	11.2718
2	1	1	35.7525	31.3746	7.8209	8.3980	12.2449	-7.3796
3	-1	0	3.3151	3.9749	6.4963	7.5685	-199029	-16.5054
4	0	-1	19.7633	23.6651	1.8351	2.1598	-19.7425	-17.6920
5	-1	1	4.5024	4.0796	11.2488	11.0232	9.3904	2.0058
6	1	-1	19.3252	17.3571	1.7333	1.6820	10.1843	2.9581
7	0	1	19.2367	24.4346	10.9080	10.2779	-27.0207	5.7761
8	1	0	13.7726	17.4615	5.7562	5.4959	-26.7845	4.5223
9	0	0	19.6039	17.9933	7.0286	6.8895	8.2157	1.9789
10	0	0	19.6033	17.9933	7.0087	6.8895	8.2128	1.7006
11	0	0	19.6036	17.9933	7.0186	6.8895	8.2143	1.8392
12	0	0	19.6039	17.9933	7.0097	6.8895	8.2157	1.7146
13	0	0	19.6039	17.9933	7.0180	6.8895	8.2157	1.8309

Analysis of variance (ANOVA) results, shown in Tables 4 and 5 for Cr (III) and dye, were used to evaluate the significance of the quadratic equations fitted to the experimental data. The significance of each coefficient is determined via probability values (P-value) shown in Tables 4 and 5. Low P-values confirm that the parameter in the model is significant. In the simultaneous adsorption of the Cr (III) and dye, first and second-order factors of Cr (III) concentration and interactive effects of Cr (III) and dye concentrations are significant. In dye adsorption, the first-order factor of Cr (III) concentration and dye's first and second-order factors are substantial. P-values of the given quadratic models also show the significance of models. High values of the regression coefficients and the adjusted regression coefficients of the models ($R^2 = 0.9534, 0.9825$ for Cr (III) and dye, respectively, $R_a^2 = 0.9201, 0.9701$ for Cr (III) and dye, respectively) also show the significance of the models. The graphs depicted based on the results of models obtained show that in the graphs of the predicted values vs. the actual values and in normal probability

plots, the points are close to the diagonal line, meaning that the variations of the experimental and predicted values are minor and the models are highly significant (SM, Figures 1 and 2).

Table 4: ANOVA for adsorption of Cr (III)

Factors (coded)	Statistics ^a				
	SS ^b	df ^c	MSS ^d	F-value ^e	P-value Prob > F
Model	5.27	5	1.05	28.64	0.0002
x_1	3.31	1	3.31	89.98	<0.0001 ^f
x_2	1.5×10^{-3}	1	1.5×10^{-3}	0.041	0.8457
$x_1 x_2$	0.31	1	0.31	8.34	0.0234 ^f
x_1^2	1.65	1	1.65	44.81	0.0003 ^f
x_2^2	0.23	1	0.23	6.16	0.0421 ^f
Residual	0.26	7	0.037		
Pure Error	$SS_E = 7.5 \times 10^{-10}$	4	$MSS_E = 1.9 \times 10^{-10}$		
Total	5.53	12			

^a E is the subscript indicating the error.

^b Sum of squares.

^c Degree of freedom.

^d Mean of squares ($MSS = SS/df$, $MSS_E = SS_E/df_E$).

^e F-value = MSS/MSS_E

^f P-values < 0.05 were considered to be significant.

Table 5: ANOVA for adsorption of dye

Factors (coded)	Statistics				
	SS	df	MSS	F-value	P-value Prob > F
Model	4.73	5	0.87	78.75	<0.0001
x_1	0.15	1	0.15	13.31	0.0082
x_2	3.68	1	3.68	331.73	<0.0001
x_1x_2	0.0002	1	0.0002	0.20	0.6688
x_1^2	0.012	1	0.012	1.09	0.3317
x_2^2	0.40	1	0.40	35.64	0.0006
Residual	0.078	7	0.011		
Pure Error	$SS_E = 5.3 \times 10^{-6}$	4	$MSS_E = 1.3 \times 10^{-6}$		
Total	4.45	12			

To study the effects of independent variables and their interactive effects, three-dimensional response surfaces and contour plots (Figures 7) were obtained based on Eq.23 and Eq.24. Based on this figure, it was concluded that an increase in the concentration of each contaminant leads to a rise in its adsorption, while an increase in the concentration of each contaminant has no significant effect on the adsorption of other contaminants.

Fig. 7: 3D response surface diagrams and contour plots (a) Adsorption capacity of dye (mg/L) and (b) Adsorption capacity of Cr (III) (mg/L)

3.8. Study of the adsorption mechanism

It is well known that clay minerals have a negative surface charge (Liu *et al.*, 2016; Oskui, Aghdasinia and Sorkhabi, 2019a). In a previous paper carried out by the authors that thoroughly investigated the Cr^{3+} on the U-clay, adsorption was studied in an acidic pH range. The results showed that a lower pH, H^+ concentration increases and the Cr^{3+} adsorption decreases due to competitive adsorption between H^+ and Cr^{3+} cations on the surface hydroxyl groups. So, it was concluded that high adsorption of Cr^{3+} is due to the electrostatic attraction between Cr (III) cations and negatively charged clay framework (Gładysz-Płaska *et al.*, 2012). The same mechanism is believed to be responsible for the adsorption of Cr^{3+} on CHPTAC-clay. Adsorption of Cr^{3+} on clay can also be contributed to ion exchange (Liu *et al.*, 2016; Wang *et al.*, 2017).

In this work, at first, acidic dye adsorption tests were carried out by the U-clay, and it showed almost zero efficiencies. This is believed to be due to similar ions in acidic dye and clay surfaces. So, the organic modifier was intercalated into the interlayers of U-clay via Van der Waals forces, and the modified clay showed a significant increase in dye adsorption (Gładysz-Płaska *et al.*, 2012). Thus, it was understood that the surfactant was successfully introduced into the clay. Based on the previous studies in the literature using different surfactants, the surface properties of U-clay

could have changed from hydrophilic to hydrophobic when this organic molecules were intercalated into the interlayer space of U-clay and high adsorption of dye occurred through hydrophobic interaction between dye and alkyl ammonium chains (Wang *et al.*, 2017).

3.9. Comparison of the results with literature data

For further comparison with other studies, the adsorption data obtained from literature in different papers carried out on the simultaneous adsorption of a heavy metal and a dye or an organic contaminant via surfactant modified clays are gathered in a table 6.

Complete investigation of Cr (III) adsorption via non-modified U-clay was previously carried out by the authors (Oskui, Aghdasinia and Sorkhabi, 2019a, 2019b). To prevent the repetition and making this paper lengthy, that data are not brought in this paper again. Various tests were also carried out on the adsorption of dye by non-modified U-clay, but the non-modified U-clay showed very low adsorption capacity for the acid brown dye. That is the reason why, authors investigated the U-clay modification using CHPTAC surfactant.

It should be noted that, obviously, the real wastewater of the leather tannery industry is a multi-component sample. Still, we have to do step by step experimental studies for a better understanding of the process and the mechanism. And that is the reason why model wastewater containing only Cr (III) and dye was used in this step of the study. Carrying out the experiments using real samples, columnar studies, doing other modifications to this clay and clay granulation to approach the pilot scales are the next steps of authors' studies in hand.

Table 6: Comparison of the results with literature dat

	(Gładysz-Płaska <i>et al.</i> , 2012)	(Fan <i>et al.</i> , 2014)	(Wang <i>et al.</i> , 2017)	(Liu <i>et al.</i> , 2016)	(Ma <i>et al.</i> , 2016)	
Contaminants	Cr (VI) and phenol	Cu^{2+} and methylene blue	Zn^{2+} and phenol	Cd^{2+} and BPA	Cu (II) and phenol	Cr (III) and acid brown
Adsorbent	Natural red clay	Montmorillonite	Montmorillonite	Montmorillonite	Montmorillonite	U-clay
The modifier used	HDTMA	SB12	CSH, TTAC, CTAC, STAC	BS-18	Cationic HDTMA (C16) and zwitterionic Z16 surfactants	CHPTAC
Adsorbent dosage	$\frac{0.4\text{ g}}{100\text{ ml}}$	$\frac{0.05\text{ g}}{50\text{ ml}}$	$\frac{0.4\text{ g}}{40\text{ ml}}$	$\frac{0.05\text{ g}}{25\text{ ml}}$	$\frac{0.1\text{ g}}{20\text{ ml}}$	$\frac{1.5\text{ g}}{100\text{ ml}}$
Solution initial pH	5.5	5	11	4	5	4
Solution initial concentration	$0.2\frac{\text{mmol}}{\text{dm}^3}$ for Cr (VI) $0.6\frac{\text{mmol}}{\text{dm}^3}$ for phenol	$Cu^{2+}=15\frac{\text{mg}}{\text{L}}$ and MB=0 to $330\frac{\text{mg}}{\text{L}}$ MB= $250\frac{\text{mg}}{\text{L}}$ and $Cu^{2+}=0$ to $32\frac{\text{mg}}{\text{L}}$	$40\frac{\text{mg}}{\text{L}}$	$Cd^{2+}=40\frac{\text{mg}}{\text{L}}$ BPA= $10\frac{\text{mg}}{\text{L}}$	$60\frac{\text{mg}}{\text{L}}$ for Cu (II) $150\frac{\text{mg}}{\text{L}}$ for phenol	$100\frac{\text{mg}}{\text{L}}$
Contact time (min)	360	Not reported	10	1440	30	30
Temperature (°C)	Room temperature	Not reported	Higher temperatures	30	25	15
Isotherm model	Langmuir-Freundlich for Cr (VI) Dual site Langmuir-Freundlich for phenol	Not reported	Freundlich	Freundlich for Cd^{2+} Langmuir for BPA	Langmuir for Cu (II) Linear equation for phenol	Langmuir for Cr (III) Redlich-Peterson for dye
Kinetic model	First order	Not reported	Not reported	Pseudo-second order	Pseudo-second order	Pseudo-second order
Maximum adsorption capacity	$0.086\frac{\text{mmol}}{\text{g}}$ for Cr (VI) $0.012\frac{\text{mmol}}{\text{g}}$ for phenol	$9.5\frac{\text{mg}}{\text{g}}$ for Cu^{2+} $150.2\frac{\text{mg}}{\text{g}}$ for MB	Not reported	$42.11\frac{\text{mg}}{\text{g}}$ for Cd^{2+} $80.77\frac{\text{mg}}{\text{g}}$ for BPA	$14.12\frac{\text{mg}}{\text{g}}$ via Z16-Mt for Cu (II) $3.75\frac{\text{mg}}{\text{g}}$ via C16-Mt for Cu (II)	$193.1390\frac{\text{mg}}{\text{g}}$ for Cr (III) $144.1782\frac{\text{mg}}{\text{g}}$ for dye
Removal efficiency	90% for Cr (VI) 8% for phenol	Not reported	100% ($3.99\frac{\text{mg}}{\text{g}}$) for Zn^{2+} 65.5% ($2.62\frac{\text{mg}}{\text{g}}$) for phenol	Not reported	Not reported	99.74% for Cr(III) 83.26% for dye

4. Conclusions

Local nano clay modified via CHPTAC surfactant was used to simultaneously remove Cr (III) and acidic dye from model tannery wastewaters. The results showed that simultaneous adsorption of contaminants from a solution with pH of 4, containing 100 mg/L of each contaminant, using $15000 \frac{mg}{L}$ of the modified adsorbent, in contact time of 3 min for Cr (III) and 30 min for dye, reached its maximum value $q_e = 6.63151 \text{ mg/g}$, (Cr) and $q_e = 5.61194 \text{ mg/g}$ (dye). Synergistic and antagonistic adsorptions were observed in the binary solutions. The results of kinetic models' studies demonstrated that simultaneous adsorption of contaminants follows the pseudo-second-order model. The results of isotherms' studies showed that the adsorption of Cr (III) from a binary solution and a single solution follows Langmuir and D-R isotherm. The adsorption of dye from both single and binary solutions follows the R- PT isotherm. Based on the thermodynamic results, the adsorption process of Cr (III) is spontaneous, and the adsorption process of dye is non-spontaneous. Cr (III) adsorption is exothermic, while adsorption of dye is endothermic. Entropy also decreases when both contaminants are adsorbed on the adsorbent. It was understood from the results of the RSM that an increase in the concentration of Cr (III) and dye leads to an increase in the adsorption capacities of Cr (III) and dye, respectively. In contrast, this increase in the concentration of Cr (III) and the dye had a negligible effect on the adsorption of the other contaminant.

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