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 surfactant. X-ray fluorescence, Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, carbon, hydrogen, nitrogen and sulfur analysis, Brunauer–Emmet–Teller 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 15,000 mg/L, contact time of 30 min. The effect of contaminants’ concentration was also investigated through response surface methodology, central composite face-centered 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 isotherms, respectively. Adsorption of dye from both single and binary solutions follows Redlich–Peterson isotherm. Maximum adsorption capacities were obtained to be 193.1390 $\text{mg g}^{-1}$ and 144.1782 $\text{mg g}^{-1}$ 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

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; Gladysz-Płaska et al. 2012; Seif et al. 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.

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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 et al. 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 et al. 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 chloride, hexadecyl trimethyl ammonium chloride, octadecyl trimethyl ammonium chloride quaternary ammoniums and cysteamine hydrochloride modifiers to investigate simultaneous adsorption of phenol and Zn\(^{2+}\) (Wang et al. 2017). Liu et al. (2016) investigated the modification of montmorillonite by amphoteric surfactant of octadecyl dimethyl betaine to study simultaneous adsorption of Cd\(^{2+}\) and bisphenol A (Liu et al. 2016). Ma et al. (2016) modified montmorillonite by cationic and zwitterionic surfactants of hexadecyltrimethylammonium bromide and hexadecylidimethyl (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). Gładysz-Płaska et al. (2012) modified natural polish red clay via hexadecyltrimethylammonium bromide to simultaneously adsorb Cr (VI) and phenol (Gładysz-Płaska 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.

### 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

| 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   |
| Ti\(_2\)O | 0.15 | Ni      | 36  |
| P\(_2\)O\(_5\) | 0.06 | Pb      | 12  |
| MnO      | 0.03 | Rb      | 34  |
| LOI\(^a\) | 35.1 | Sr      | 454 |
|          |      | V       | 30  |
|          |      | Y       | 11  |
| CEC      | 322.4114 (mmol/kg clay) | Zr | 91 |
|          |      | Zn      | 41  |
|          |      | Mo      | 26  |

\(^a\)Loss of ignition
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 μ Siemens/cm) was used in all experiments. Solutions were prepared by dissolving Chromium (III) chloride hexahydrate (CrCl₃·6H₂O) 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 CHPTAC 60 wt% in H₂O was purchased from Sigma-Aldrich.

**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).

**Adsorbent characterizations**

**X-ray fluorescence (XRF)**

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

**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).

**Fourier-transform infrared (FT-IR) spectroscopy**

FT-IR spectra for the non-modified and the modified clays were recorded using a Brucker, 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.

**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° – 109.9500°, 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.

**Scanning electron microscopy (SEM)**

Morphologies of the non-modified and modified clays were observed using a SEM 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.

**CHNS analysis**

Elemental analyses 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):

\[
C_{\text{CHPTAC}} = \frac{c_m}{1 - c_m MW} \tag{1}
\]

\[
c_m = \frac{c_N}{n_N M_N 100} \tag{2}
\]

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 Eq. 2 and was inserted to the Eq. 1 and \(C_{\text{CHPTAC}}\), the concentration of CHPTAC loaded on the clay, was calculated.

**N₂ adsorption and desorption**

\(N₂\) 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.

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 20,000 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 min 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:

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

\[ q_e = \frac{V}{m}(C_0 - C_e) \]  \( \text{(4)} \)

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, adsorptions of the contaminants from mono-component 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):

\[ R_{q,i} = \frac{q_{b,i}}{q_{s,i}} \]  \( \text{(5)} \)

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.

\[ \ln(q_e - q_t) = \ln q_e - k_1t \]  \( \text{(6)} \)

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \]  \( \text{(7)} \)

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 et al. 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):

\[ q_e = \frac{q_{ma}bC_e}{1 + bC_e} \]  \( \text{(9)} \)

\[ q_e = K_F C_e^{1/n_f} \]  \( \text{(10)} \)

\[ q_e = q_{SD} \exp(-K_{SE}C_e^2) \]  \( \text{(11)} \)

\[ q_e = \frac{K_R C_e}{1 + a_R C_e} \]  \( \text{(12)} \)

\[ \text{SSE} = \sum_{i=1}^{n}(q_{e,cal} - q_{e,meas})^2 \]  \( \text{(13)} \)

\[ \text{HYBRID} = \frac{100}{n - p} \sum_{i=1}^{n}(q_{e,cal} - q_{e,meas})^2 \]  \( \text{(14)} \)

\[ \chi^2 = \sum_{i=1}^{n}(\frac{(q_{e,cal} - q_{e,meas})}{q_{e,meas}})^2 \]  \( \text{(15)} \)
where \( q_{\text{ad}} \) 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\(^{-1}\)L\(^n\)/g), \( n_F \) is the Freundlich constant, \( q_d \) is the D–R theoretical isotherm saturation capacity (mg/g), \( K_{ad} \) is the D–R isotherm constant related to the adsorption energy (\( \text{mol}^2/\text{kJ}^2 \)) related to the mean adsorption energy \( (E) \) (Eq. 16), \( \gamma \) 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 et al. 2010).

\[
E = \frac{1}{\sqrt{2K_{ad}}} \tag{16}
\]

\[
\gamma = RT\ln(1 + \frac{1}{C_r}) \tag{17}
\]

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

\[
R_L = \frac{1}{1 + bC_0} \tag{18}
\]

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 et al. 2008).

Thermodynamic parameters of variations of free Gibbs energy (\( \Delta G^0 \)), variations of enthalpy (\( \Delta H^0 \)) and variations of entropy (\( \Delta S^0 \)) were also calculated using the equations below (Fil et al., 2012; Elmoubarki et al. 2015):

\[
\Delta G^0 = -RT\ln(K_D) \tag{19}
\]

\[
K_D = \frac{q_d}{C_r} \tag{20}
\]

\[
\ln K_D = \frac{-\Delta G^0}{RT} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{21}
\]

where \( K_D \) is the thermodynamic distribution coefficient (Eq. 20).

**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 concentrations 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 ±\( \alpha \), ±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:

\[
Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} X_i X_j \pm \epsilon \tag{22}
\]

where \( Y \) is the predicted response or output (dependent variable), \( n \) is the number of the patterns, \( i \) and \( j \) are the index numbers for pattern, \( X_1, X_2, \ldots, X_n \) are the input coded variables that affect the response, \( X_1^2, X_2^2, \ldots, X_n^2 \) are the square effects, \( X_1X_2, X_1X_3, \ldots, X_1X_n \) are the interaction effects, \( \beta_0 \) is the free or offset term called intercept term, \( \beta_i (i = 1, 2, \ldots, n) \) is the linear (first-order) main effect, \( \beta_{ii} (i = 1, 2, \ldots, n) \) is the squared (quadratic) effect, \( \beta_{ij} (i = 1, 2, \ldots, n; j = 1, 2, \ldots, n) \) is the interaction effect and \( \epsilon \) is a random error or allows for discrepancies or uncertainties between the predicted and measured values (Oskui, Aghdasinia and Sorkhabi 2019b).

**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.

**Adsorbent characterizations**

**\( \text{pH}_{\text{zpc}} \)**

The pH zero-point charge plays an important role in the adsorption process. \( \text{pH}_{\text{zpc}} \) 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. Table 2 also gives a comparison of \( \text{pH}_{\text{zpc}} \) values for other clays reported in the literature.

**FTIR**

Identification of the clay minerals can be carried out using this method since it gives a great deal of information on the structure of layers. In the studies of clay minerals, the absorption bands, due to structural O – H and Si – O groups, play important role in the differentiation of clay minerals from each other. The 4000–3000 cm\(^{-1}\) range corresponds to O – H stretching vibrations and 1300–400 cm\(^{-1}\) range in
the spectra of the clay minerals show Si – O stretching and bending as well as O – H bending absorptions.

Absorption bands in the IR spectra of U-clay are: 873.20 cm\(^{-1}\), 1030.12 cm\(^{-1}\), 1438.17 cm\(^{-1}\) and 3435.24 cm\(^{-1}\). The bands for CHPTAC-clay are: 872.13 cm\(^{-1}\), 1030.30 cm\(^{-1}\), 1425.73 cm\(^{-1}\), 1459.96 cm\(^{-1}\), 1513.87 cm\(^{-1}\), 1645.30 cm\(^{-1}\), 3441.88 cm\(^{-1}\), 3614.51 cm\(^{-1}\) and 3743.30 cm\(^{-1}\).

Based on the studies carried out by other researchers on the IR spectra of different clays, it is obtained that, the IR spectra of dioctahedral smectites show only a single band in the O – H stretching region (4000–3000 cm\(^{-1}\) range). 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 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 O – H absorption of the trioctahedral minerals is shifted to lower frequencies, the 700–600 cm\(^{-1}\) range. 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. Only one broad complex Si – O stretching band is present in the IR spectra of both di- and trioctahedral smectites. Different types of smectites absorb at different wavelengths in the Si – O range (1300–400 cm\(^{-1}\)) and montmorillonite absorb at 1030 cm\(^{-1}\).

So it is concluded from the IR spectra studies that our local clay is a dioctahedral smectite and it contains montmorillonite. 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. This also confirms the result obtained from XRD analysis.

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\(_2\)O in the smectite. 1438.17 – 1425.73 cm\(^{-1}\) bands seen in the spectra of both U-clay and CHPTAC-clay are representatives of C = O bonds (Pavia et al. 2014).

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 et al. 2013; Çakmak et al. 2017; El Kassimi et al. 2021; Namjoufar et al. 2021) (Fig. 2).

![Fig. 1 Final pH versus initial pH of non-modified and modified clay](image-url)

**Table 2** Comparison of pH\(_{\text{zpc}}\) values

| Clay name and origin | pH\(_{\text{zpc}}\) | p\(H_{\text{zpc}}\) values | References |
|----------------------|------------------|---------------------------|------------|
| Turkish clay         |                  | 6                         | (Çakmak et al. 2017) |
| Kaolinite clay from northeastern Zimbabwe | 5.49 | (Chaukura et al. 2020) |
| Natural Safiot Clay (NSC) | 7.2 | (El Kassimi et al. 2021) |
| Montmorillonite from Roussel (Maghnia, Algeria), activated thermally | 5.11 | (Feddal et al. 2019) |
| AS-300               |                  | 11.6                      | (Çakmak et al. 2017) |
| AC-300               |                  |                           | (El Kassimi et al. 2021) |
| U-Clay               |                  | 9.75                      | (El Kassimi et al. 2021) |
| CHPTAC-Clay          |                  | 8.6                       | (El Kassimi et al. 2021) |
Fig. 2  The FT-IR spectra of a non-modified and b modified clay
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 $2\theta$, the adsorbent has calcium carbonate $\text{Ca} (\text{CO}_3)$ (calcite) and silicon oxide $\text{SiO}_2$ (quartz). A comparison on the d-spacing values of U-clay with characteristic peaks of montmorillonite (13.6 Å, 4.47 Å, 3.13 Å, 2.56 Å) and quartz (3.342 Å, 4.257 Å, 2.457 Å) showed that U-clay contains these two minerals (Adikary and Wanasinghe, 2012). 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).

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 CHP-TAC-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. 4e.
CHNS analysis

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

$N_2$ adsorption and desorption

The data obtained by this analysis are shown in Table 3. 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.

![Fig. 4 SEM images of a non-modified clay, 10 μm, b non-modified clay, 1 μm, c modified clay, 10 μm, d modified clay, 1 μm and e EDX analysis of the modified clay](image-url)
Adsorption processes

Effect of adsorbent dosage

To find the effect of adsorbent dosage, 0.25 g to 2 g of CHP-TAC 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 h was given. The results are depicted in Fig. 5a. As shown in this figure, the adsorbent values of 5000 to 15,000 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 15,000 mg/L resulted in a constant removal value of 99%, and then the removal efficiency was decreased. For the dye, up to 15,000 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 15,000 \( \text{mg L}^{-1} \) was the value chosen to be applied in the upcoming experiments.

**Effect of initial pH of the solution**

To see the effect of the initial pH of solution on the simultaneous adsorption of contaminants, 15,000 \( \text{mg L}^{-1} \) 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 h was given. The results are depicted in Fig. 5b. 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 \( \text{Cr}^{3+} \) and \( \text{CrOH}^{2+} \) 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, \( \text{Cr(OH)}^{2+} \) and \( \text{Cr(OH)}^{3+} \) species are also present in the solution and \( \text{Cr(OH)}^{3+} \) 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.

**Effect of initial concentration of the solution**

To investigate the effect of the solutions’ initial concentration, 15,000 \( \text{mg L}^{-1} \) 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 h was given. The results are depicted in Fig. 5c. 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 which limits the adsorption capacity to be no more than this.

**Effect of contact time**

To study the effect of contact time, 15,000 \( \text{mg L}^{-1} \) 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 Fig. 5d. As it can be seen in this figure, adsorption of Cr (III) and dye were completed in the first 3 and 10 to 30 min, 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.

**Effect of temperature**

To study the effect of temperature, 15,000 \( \text{mg L}^{-1} \) 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 Fig. 5e. 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.

**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 Fig. 6a and b that shows the adsorption capacities of contaminants in single and binary solutions. Investigating the \( R_{qj} \) s for the dye, in the concentration of 25 mg/L, \( R_{qj}=1.0167 \) 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 \( R_{qj} \) 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, \( R_{qj} \) 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.

**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.

**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 $q_e$ 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 show 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 (Sarı et al. 2007). In the adsorption of Cr (III) from both single and binary solutions, the parameter of $g$ in R–PT isotherm was
Table 4 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 | 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 | -199.029 | -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 | 17.6920 |
| 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 |

Table 5 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\(^d\)    |
| \(x_1^2\)       | 1.65    | 1       | 1.65     | 44.81       | 0.0003\(^d\)    |
| \(x_2^2\)       | 0.23    | 1       | 0.23     | 6.16        | 0.0421\(^d\)    |
| 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\(_E\)

Table 6 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 |
| \(x_1 x_2\)     | 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 |          |            |          |
obtained to be 0, so it can be said that this isotherm follows Henry’s law, and in the single solution of dye, \( a_R C^g e \gg 1 \), so it can be noted that Freundlich isotherm is applied to the system (Vijayaraghavan et al. 2006; Liu and Liu 2008).

**Thermodynamic studies**

For Cr (III) adsorption from binary solutions, thermodynamic parameters were calculated to be \(-17.4893\) and \(-0.0272\) kJ/mol for \( \Delta H^\circ \) and \( \Delta S^\circ \), respectively, and for dye \( \Delta H^\circ \) and \( \Delta S^\circ \) 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 \( \Delta G^\circ \) for Cr (III) adsorption process and \(0.7592, 1.3309, 3.1918\) and \(3.8396\) kJ/mol were the values obtained for \( \Delta G^\circ \) 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.

**RSM results**

By applying the multivariate regression model on the CCF design and Table 4, quadratic equations for predicting the adsorption capacities of each contaminant are obtained:

\[
\ln(Y_1) = 2.89 + 0.74x_1 + 0.016x_2 + 0.28x_1x_2 - 0.77x_1^2 + 0.29x_2^2 \\
(23)
\]

\[
\ln(Y_2) = 1.93 - 0.16x_1 + 0.78x_2 + 0.024x_1x_2 - 0.066x_1^2 - 0.38x_2^2 \\
(24)
\]

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 et al. 2009). Table 4 shows the observed and predicted values of the adsorption capacities and the error percentages.

Analysis of variance (ANOVA) results, shown in Tables 5 and 6 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 5 and 6. 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, \( R^2_a = 0.9201, 0.9701 \) 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, Figs. 1 and 2).

\( P \)-values < 0.05 were considered to be significant.
Table 7  Comparison of the results with literature data

| Contaminants | Adsorbent | The modifier used | Adsorbent dosage | Solution initial pH | Solution initial concentration | Contact time (min) | Temperature (°C) | Isotherm model | Kinetic model | Maximum adsorption capacity | Removal efficiency |
|--------------|-----------|------------------|-----------------|-------------------|-------------------------------|-------------------|-----------------|--------------|---------------|-----------------------------|------------------|
| Cr (VI) and phenol | Cu$^{2+}$ and methylene blue | Montmorillonite | 0.05g | 5.5 | Cu$^{2+}=15 \frac{mg}{L}$ and MB = 0 to 330 $\frac{mg}{L}$ | 360 | Room temperature | Langmuir–Freundlich for Cr (VI) | First order | 0.086 $\frac{mmol}{g}$ for Cr (VI) | 90% for Cr (VI) |
| | Zn$^{2+}$ and phenol | Montmorillonite | 0.05g | 6 | Cu$^{2+}=40 \frac{mg}{L}$ | 1440 | Not reported | Freundlich | Not reported | 42.11 $\frac{mg}{g}$ for Cd$^{2+}$ | Not reported |
| | Cd$^{2+}$ and BPA | Montmorillonite | 0.05g | 4 | BPA = 10 $\frac{mg}{L}$ | 30 | Not reported | Freundlich for Cd$^{2+}$ | Not reported | 80.77 $\frac{mg}{g}$ for BPA | 65.5% (2.62 $\frac{mg}{g}$) for phenol |
| | Cu (II) and phenol | Montmorillonite | 0.1g | 5 | Zn$^{2+}=0$ to 32 $\frac{mg}{L}$ | 25 | Not reported | Freundlich for Cu (II) | Pseudo-second order | 14.12 $\frac{mg}{g}$ via Z16-Mt for Cu (II) | Not reported |
| | Cr (III) and acid brown | Cationic HDTMA (C16) and zwitterionic Z16 surfactants | 1.5g | 4 | Cu$^{2+}=150 \frac{mg}{L}$ for phenol | 15 | Not reported | Langmuir for Cr (III) | Pseudo-second order | 193.1390 $\frac{mg}{g}$ for Cr (III) | 99.74% for Cr(III) |
| | BPA | BS-18 | 0.2 $\frac{mmol}{dm^{3}}$ for Cr (VI) | | | | | Hybrid | | | |
| | | | 0.6 $\frac{mmol}{dm^{3}}$ for phenol | | | | | | | | |

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.

**Study of the adsorption mechanism**

It is well known that clay minerals have a negative surface charge (Liu et al. 2016; Oskui et al. 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-Plaska 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-Plaska 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).
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 7.

Since leather tannery wastewater is a serious environmental concern in our region, the authors are carrying out a number of hierarchy studies on treatment of leather tannery wastewater. This paper is a continuation our previous works. Complete investigation of Cr (III) adsorption via non-modified U-clay was previously carried out by the authors. The effect of initial pH and concentration, adsorbent dosage, contact time and temperature were examined and the maximum adsorption capacity $(294.12 \text{ mg/g})$ was obtained in the following condition: pH of 4, initial concentration of $140 \text{ mg/L}$, adsorbent dosage of $750 \text{ mg/L}$, contact time of 30 min and temperature of $20^\circ \text{C}$ (Oskui et al. 2019a, b).

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.

Conclusion

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 15,000 mg/g 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 (II) 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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Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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