#### **ORIGINAL ARTICLE**



# Preparation of cationic surfactant-modified kaolin for enhanced adsorption of hexavalent chromium from aqueous solution

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Received: 11 November 2019 / Accepted: 12 December 2019 / Published online: 24 December 2019 © The Author(s) 2019

#### Abstract

In the current work, we have reported a cationic surfactant-modified Ethiopian kaolin for improved adsorption of Cr(VI) from aqueous solution. The raw kaolin was modified by treating with CTAB to enhance the adsorption properties. The crystal structure and vibrational analysis of CTAB–kaolin were investigated by Fourier transform infrared spectroscopy (FTIR) and powder X-ray diffraction (p-XRD) techniques. The successful modification of kaolin by CTAB through intercalation and coating was investigated by XRD and FTIR. p-XRD confirms the raw kaolin obtained from *Belesa*, *Tigo* kebele is kaolinite mineral. The study has also focused on the application of kaolin–CTAB for adsorption of hexavalent chromium. The percent removal of Cr(VI) was investigated at different parameters such as pH, contact time, concentration of Cr(VI) and adsorbent dosage. CTAB–kaolin shows 99% removal of Cr(VI) at the adsorption equilibrium (time = 180 min, 100 mg CTAB–kaolin, 10 ppm/100 ml). The Langmuir and Freundlich isotherm models were used to investigate the adsorption process of chromium onto kaolin–CTAB composites. The equilibrium data obeyed Langmuir model than Freundlich, which shows that the adsorption process proceeds through monolayer adsorption and maximum adsorption capacity was found to be  $Q_0 = 22.72$  mg/g. The *pseudo*-second-order kinetics model is found to be well fitted than *Pseudo*-first-order kinetics, which implies that the adsorption mechanism more favors electrostatic interaction between chromium and kaolin–CTAB composites. In conclusion, CTAB–kaolin was found to be a promising adsorbent for the efficient removal of Cr(VI) from the aqueous solution.

Keywords  $CTAB \cdot Kaolin \cdot Cr(VI) \cdot Adsorption$ 

## Introduction

During the last decades, water pollution was one of the major concerns for the sustainability of life on earth. Toxic effluents discharged without being treated from various industries have taken huge responsibility for the pollution of water bodies. Among the toxic pollutants, chromium is the subject of many types of research and has taken huge attention in the last few years (Yusuff 2019; Pakade et al. 2019). Chromium can be found in stable Cr(VI) or Cr(III) oxidation states. More importantly, Cr(VI) is considered the most toxic

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s13201-019-1121-7) contains supplementary material, which is available to authorized users.

Neway Belachew neway.du@gmail.com form of Cr, which usually exists in association with oxygen as chromate  $(CrO_4^{2-})$  or dichromate  $(Cr_2O_7^{2-})$  oxyanions (Sharma and Bhattacharyya 2005). Cr(III) is less toxic and less mobile and is mainly found bound to the organic matter in the aquatic environments and soil (Raji and Anirudhan 1998). The Agency for Toxic Substances and Disease Registry classifies Cr(VI) as the top 16th hazardous substance due to its severe toxicity (ATSDR 1999). The maximum value of chromium intended for human consumption is estimated as 0.1 mg L<sup>-1</sup> (World Health Organization 1993; Duranoğlu et al. 2012). Therefore, the removal of Cr(VI) from water bodies is of prime importance.

Numerous technologies have been applied for the removal of Cr(VI) from aqueous solutions such as adsorption (Gupta et al. 2013), reduction (Bhati et al. 2019), ion exchange (Rengaraj et al. 2001) and membrane processes (Zolfaghari and Kargar 2019). The adsorption process is one of the most frequently encountered techniques for the removal of Cr(VI). Adsorption on activated carbon has been widely used for the removal of a broad range of water pollutants, especially



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for low-to-moderate-concentration pollutants (Pérez-Candela et al. 1995; Demirbas et al. 2004; Khezami and Capart 2005). However, because of the high cost of activated carbon, it is desirable to search for a low-cost and efficient adsorbent for the removal of Cr(VI) (Belachew and Bekele 2019; Saleem et al. 2019).

In this regard, because of having high cation exchange capacity, swelling capacity, high specific surface area and strong adsorption capacity, clay minerals play an important role in the environment by acting as a natural adsorbent of pollutants (Bhattacharyya and Gupta 2006). Among clay types, kaolin shows the potential for removal of water contaminants (Deng et al. 2014). Kaolinite is the most important mineral component in kaolin, which has received considerable attention as an adsorbent because of its high adsorption capacity, large specific surface area and good physical and chemical stability (Saada et al. 2003). However, the adsorption capacity of raw kaolin is still insufficient for the removal of water pollutants below the recommended level. Hence, modification of kaolinite through intercalation of inorganic and organic compounds has brought additional adsorption efficiency (Duarte-Silva et al. 2014; Zenasni et al. 2014; Diab et al. 2015; Shaban et al. 2018).

In this study, we have reported cetyl trimethyl ammonium bromide (CTAB)-modified kaolinite (CTAB–kaolinite) for efficient adsorption of Cr(VI) aqueous solution. The adsorption efficiency of CTAB–kaolinite has been investigated at different adsorption parameters such as pH, adsorbent type, adsorbent dose and Cr(VI) dose. The adsorption kinetics and adsorption isotherm analyses of Cr(VI) adsorption were also investigated.

## Experimental

#### Materials

Natural raw kaolin was obtained from the South Region, Hadiya Zone, Belesa district, Ethiopia. Hydrochloric acid (HCl 36%), sodium chloride (NaCl 60%), sodium hydroxide (NaOH 97%) potassium dichromate ( $K_2Cr_2O_7$ ) and cetyl trimethyl ammonium bromide (CTAB) used for CTAB–kaolin preparation were purchased from Sigma-Aldrich. Analytical-grade  $K_2Cr_2O_7$  was purchased from Merck Chemicals. Distilled water was used throughout the whole experiment.

#### Preparation of CTAB-kaolin

The raw kaolin sample was washed three times with distilled water to remove surface contaminants and then dried in a ceramic crucible at 105 °C for 5 h. The dried kaolin sample was crushed to fine particles. The  $< 2 \mu m$  fraction of powdered kaolin was collected for further use. For the



preparation of CTAB–kaolin, 5 gm of powdered kaolin was added to 250 ml of 5 mmol, 10 mmol, 15 mmol and 20 mmol CTAB solutions. The solution was shaken for 5 h at 70 °C, and then, the CTAB-modified kaolin solution was aged overnight to settle down the CTAB–kaolin. The precipitate was washed at least three times with distilled water until all bromide removed from the solution. The presence of bromide ions is indicated by the formation of the white precipitate by adding AgNO<sub>3</sub>. The CTAB–kaolin was finally filtered and dried at 105 °C for 2 h and gently ground using a mortar and pestle to fine powder particles.

## Characterizations

The UV–visible absorption spectra were recorded using a Shimadzu 2450—SHIMADZU spectrometer. The FTIR spectra of powder samples were recorded in the range of 400–4000 cm<sup>-1</sup> using a SHIMADZU-IR PRESTIGE-2 spectrometer by mixing the samples thoroughly with KBr and pressing them into thin transparent pellets range. X-ray diffraction (XRD) patterns were recorded by PANalytical X'Pert Pro diffractometer at 0.02 deg/s scan rate using Cu-k $\alpha$ l radiation (1.5406 Å, 45 kV, 40 mA). The morphologies of the samples were characterized using scanning electron microscopy (SEM, JEOL-JSM6610 LV).

#### Batch adsorption study of chromium(VI)

All experiments were carried out in batch adsorption mode. In particular, 50 mg of CTAB–kaolin was mixed with 100 ml of Cr(VI) in 250-ml Erlenmeyer glass flask. The bottles were then stirred at a different predetermined time intervals. Then, 3 ml of the solution was withdrawn and centrifuged (2500 rpm). The pH was adjusted by 0.1 M HCl and 0.1 M NaOH. The sample was taken and filtered by the Whatman membrane filter paper of pore size 0.45  $\mu$ m using a syringe. Finally, the absorbance of the residual Cr(VI) concentration in the solution was determined using UV–Vis spectrophotometer. The adsorption process was optimized at different pH, contact times, Cr(VI) concentrations and adsorbent doses at room temperature. The removal (%) and adsorption capacity (mg/g) of CTAB–kaolin were calculated using Eqs. 1 and 2 respectively:

Removal (%) = 
$$(A_0 - A_t)/A_0 * 100$$
 (1)

$$q_{\rm t} = \left(C_{\rm o} - C_{\rm e}\right) V/m \tag{2}$$

where  $A_0$  represents initial absorbance and  $A_t$  is absorbance of Cr(VI) at a time t. Co denotes the initial Cr(VI) concentration (ppm),  $C_e$  is the equilibrium Cr(VI) concentration (mg/L) in solution after adsorption, V is the volume (L) of the aqueous solution and m is the mass (g) of CTAB–kaolin.



Fig. 1 Schematic diagram of the preparation of CTAB-kaolin



Fig. 2 FTIR spectra of a CTAB and b kaolin–CTAB

The point of zero charge of CTAB-kaolin was determined by solid addition method as it is shown in SI.1.

## **Results and discussions**

## Modified kaolin

The modification was carried out by coating and intercalation into the interlayer spacing of the kaolin using CTAB as shown in Fig. 1. Hence, the surface of kaolin became positively charged. The positive surface charge of CTAB–kaolin is reasonable for the electrostatic interaction between the negative charge species of hexavalent chromium ( $Cr_2O_7^-$  and  $CrO_4^-$ ). The intercalation of CTAB has also created an additional interlayer surface area for adsorption of Cr(VI).

## Characterization

## **FTIR analysis**

Figure 2 shows the FTIR spectra of CTAB and CTAB-kaolin. CTAB and kaolin–CTAB show a band  $3444 \text{ cm}^{-1}$ , which is due to O–H stretching vibrations of adsorbed water. The most intense absorption bands at 2913 and 2844 cm<sup>-1</sup> in the spectrum of CTAB are associated with the antisymmetric and symmetric C–H stretching vibration modes of the methylene groups (Padalkar et al. 2009). The FTIR spectrum



**Fig. 3** Powder X-ray diffractogram of **a** reference kaolinite and **b** raw kaolin sample obtained from *Hadya*, Ethiopia



Fig. 4 Powder XRD diffractogram of a pure kaolin and b CTAB-kaolin

of CTAB-kaolin (Fig. 2a) shows the characteristic absorption bands of kaolinite at 3700, 3670, 3650 and 3620 cm<sup>-1</sup> due to the inner OH attached to Al or O (Padalkar et al. 2009; Tironi et al. 2012). When the band at 3670 cm<sup>-1</sup> disappears, the kaolinite structure is disordered and more easily dehydrated (Padalkar et al. 2009). The stretching peak at 908 cm<sup>-1</sup> is ascribed to Si–O or Si–O–Al (Nakamoto 1986).

## XRD and SEM analysis

The kaolin structure before and after modification by CTAB was further investigated by powder XRD. Figure 3 shows the XRD pattern of raw Ethiopian kaolin. The raw kaolin was indexed to the diffraction pattern of crystalline-layered kaolinite, which is matched with COD card number 00-900-9230 (Bish 1989). The peaks at  $12.3^{\circ}$ , 20,  $32^{\circ}$ ,  $21.22^{\circ}$ ,  $23.1^{\circ}$ ,  $24.86^{\circ}$ ,  $35.96^{\circ}$ ,  $38.48^{\circ}$  and  $55.2^{\circ}$  can be indexed to the plane due to kaolinite (001), (110), (111), (002), (131), (202) and (133), respectively. As shown in Fig. 4, the characteristic (001) diffraction peak of kaolinite shifts from  $12.2776^{\circ}$  to



12.3735° after treatment by CTAB, which ascribes the intercalation of CTAB to kaolin layer. The d-spacing of kaolinite at (001) shows expansion from 7.14531 to 7.14763 Å, which is shown to be further strengthening the intercalation of CTAB. The surface morphology of CTAB–kaolin was investigated using SEM. CTAB–kaolin shows porous surface morphology (Figure S1), which is suitable for adsorption purpose.

## **Adsorption study**

#### Point of zero charge (pH<sub>PZC</sub>) and effect of pH

The pH<sub>PZC</sub> is the pH at which the adsorbent has a neutral charge on the surface. The pH<sub>PZC</sub> of the adsorbent was determined by using the solid addition method (Balistrieri and Murray 1981; Zubrik et al. 2017). The pH<sub>PZC</sub> for the CTAB–kaolin was found to be 6.2 (Fig. 5). Hence, when the pH of solution is less than pH<sub>PZC</sub>, the CTAB–kaolin surface becomes positive and attracts anions (such as  $CrO_4^{2-}$ ) from the aqueous solution, and when it is greater than pH<sub>PZC</sub>, the surface becomes negative and attracts cations from the solution.

Figure 6 shows the Cr(VI) removal (%) efficiency of CTAB-kaolin as a function of pH. The maximum removal (%) of hexavalent chromium is higher at low pH 2. As the pH increases, the surface of kaolin becomes more negatively charged, which reasonably increases the repulsion between  $CrO_4^{2-}$  [Cr(VI)] and kaolin–CTAB. Hence, the removal efficiency decreases with an increase in pH.

#### Effect of adsorbent type and contact time

The effect of CTAB on the adsorption efficiency of kaolin was examined (Figure S2). CTAB-kaolin showed superior adsorption efficiency than pure kaolin, which is due to the enhanced electrostatic interaction of  $Cr_2O_7^{-}/CrO_4^{-}$  with an adsorbed cationic surfactant, CTAB.



Fig. 5 Point of zero charge analysis of CTAB-kaolin

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**Fig. 6** Effect of pH on the adsorption removal efficiency of CTAB– kaolin (*inset: the plausible electrostatic adsorption mechanism between CTAB–kaolin and*  $CrO_4^-$ )

Figure 7 shows the effect of time on adsorption. The adsorption process was completed within 180 min where total surface coverage of CTAB–kaolin was completed and no further adsorption was observed. Hence, the adsorption within 180 min contact time could be considered as adsorption equilibrium. The adsorption removal of chromium is increased upon the increasing contact time and 95% removal efficiency (50 mg CTAB–kaolin and 5 ppm Cr(VI) solution). The fast adsorption rate of Cr(VI) was observed in the first 90 min.

#### Effect of initial concentration

The effect of initial concentration of Cr(VI) is shown in Fig. 7. Initial concentration was varied from 5 to 20 ppm. Results show that the removal (%) decreases as the initial concentration of hexavalent chromium increased. This implies the adsorption of Cr(VI) onto kaolin–CTAB is strongly dependent on initial metal ion concentration. At low initial hexavalent chromium concentrations, the available



Fig. 7 Effect of initial concentration on Cr(VI) on the adsorption efficiency of CTAB-kaolin (50 mg)

adsorption sites were easily occupied by hexavalent chromium resulting in higher removal efficiencies. However, as the initial concentration of hexavalent chromium increased, most of the available adsorption sites became occupied, leading to a decrease in the removal efficiency. The minimum and maximum removal efficiencies were found to be 69% and 95.08% for 20 ppm and 5 ppm solution, respectively.

#### Adsorbent dose

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of a metal ion in the solution. The adsorption removal (%) of Cr(VI) at different doses of CTAB–kaolin is depicted in Fig. 8. The removal of Cr(VI) increases with an increase in CTAB–kaolin dose. The results showed that 99% removal efficiency was achieved using 100 mg CTAB–kaolin for 10 ppm Cr(VI) in a 100 ml solution.

#### Adsorption isotherm

100

80

60

40

20

0

0 30 60 90

Removal (%)

The adsorption isotherms are used to estimate the maximum adsorption efficiency  $(q_0)$  of CTAB-kaolin at the adsorption equilibrium time. The adsorption isotherm curves of Cr(VI) on CTAB-kaolin are depicted in Figs. 9 and 10. The adsorption of Cr(VI) onto the surface of CTAB-kaolin was validated using Langmuir (Langmuir 1916) and Freundlich (Freundlich 1907) models. The linear line form of Langmuir and Freundlich equations is shown in Eqs. 3 and 4, respectively:

$$C_{\rm e}/q_{\rm e} = 1/Q_{\rm o} \cdot b_{\rm L} + C_{\rm e}/Q_{\rm o}$$
 (3)

where  $q_e (mg/g)$  is the equilibrium amount of Cr(VI) adsorption,  $Q_o (mg/g)$  refers to the maximum adsorption capacity and  $b_L (L/mg)$  is the Langmuir equilibrium constant related to the enthalpy of the process.

25 mg

50 mg

75 mg

100 mg

120 150 180



Contact Time (min)



Fig. 9 Langmuir adsorption isotherm curve of Cr(VI) adsorption on CTAB-kaolin

$$\log q_{\rm e} = \log K_{\rm f} + (1/n) * \log C_{\rm e} \tag{4}$$

 $K_{\rm F}$  (mg/g) is Freundlich constant representing the adsorption capacity at a unit equilibrium concentration that is defined as the adsorption or distribution coefficient, and 1/n is related to the adsorption intensity. The value of 'n' greater than 1.0 indicates that Cr(VI) shows favorable adsorption on CTAB–kaolin.

The correlation coefficient ( $R^2$ ) of the Langmuir adsorption isotherms curve is 0.999 (Table 1), which showed that the adsorption process is well fitted to the Langmuir model than the Freundlich model ( $R^2 = 0.943$ ). Therefore, the sorption of Cr(VI) onto the activated CTAB-kaolin took place predominantly through monolayer adsorption. The maximum monolayer adsorption capacity was theoretically calculated to be 22.72 mg/g. As shown in Table 1, the value of  $R_L$  was between zero and one; as the result indicates, the adsorption process is favorable.



Fig. 10 Freundlich adsorption curve of Cr(VI) adsorption on CTAB-kaolin



Isotherm models	Parameters					
	$\overline{Q_{ m o}}$ (mg/g	$q_{ m e\ (exp)}$	$q_{ m e\ (cal)}$	$b_{\rm L}$	$R^2$	
Langmuir isotherm	22.72	19.82	19.859	36.77	0.9999	
Freundlich isotherm	Ν	1/n	$k_{\rm f} ({\rm mg}^{1-1/n}{\rm L}^{1/n}{\rm g}^{-1})$	$q_{\rm e\ (cal)}$	$R^2$	
	6.6	0.151	23.3	16.78	0.943	

 Table 1
 Langmuir and Freundlich adsorption isotherm parameters



 $\ensuremath{\mbox{Fig.11}}$  Pseudo-first-order kinetic curve of  $\ensuremath{\mbox{Cr}}(\ensuremath{\mbox{VI}})$  adsorption onto CTAB–kaolin

#### **Adsorption kinetics**

The adsorption kinetics of Cr(VI) onto CTAB–kaolin was investigated using Lagergren *pseudo*-first-order equation (Eq. 5) and *pseudo*-second-order equation (Eq. 6) models. The Lagergren *pseudo*-first-order equation is used to express fast adsorption of adsorbate from solution and the process dominantly controlled by diffusion (Lagergren and Vetenskapsakademiens 1898).

$$\log\left(q_{\rm e} - q_{\rm t}\right) = \log q_{\rm e} - \left(K_1 / 2.303\right) * t \tag{5}$$

where  $k_1$  is the pseudo-first-order rate constants of and  $q_e$  denotes the equilibrium amount of Cr(VI) adsorption. The *pseudo*-second-order kinetic model is based on chemisorption as the rate-determining step, and it implies that adsorption occurs through the electrostatic interaction between adsorbate and adsorbent (Ho 1995).

$$t/q_{\rm t} = 1/K_2 q_{\rm e}^2 + (1/q_{\rm e}) * t \tag{6}$$

where  $k_2$  is pseudo-second-order kinetic models.

The adsorption kinetics evaluated by the two models is presented in Fig. 11 (*pseudo*-first) and Fig. 12 (*pseudo*second). The results showed that the adsorption of Cr(VI) onto CTAB-kaolin is well fitted to the *pseudo*-secondorder model ( $R^2 > 0.99$ ) than the *pseudo*-first-order model ( $R^2 < 0.9$ ) and the rate-limiting step could be controlled





Fig. 12 Pseudo-second-order kinetic curve of  $\mbox{Cr}(\mbox{VI})$  adsorption onto CTAB-kaolin

 Table 2
 Pseudo-first- and second-order kinetic parameters

Parameters	Initial conce	ium	
	10 ppm	15 ppm	20 ppm
Pseudo-first-order ki	netics		
$q_{\rm e}, \exp{({\rm mg}/{\rm g})}$	9.9786	14.99	19.82
$q_{\rm e}$ , cal(mg/g)	20.23	50.11	46.02
$k_1 ({\rm min}^{-1})$	0.014	0.047	0.0034
$R^2$	0.794	0.797	0.895
Pseudo-second-order	r kinetics		
$k_1 ({\rm min}^{-1})$	0.002	0.0581	00018
$q_{\rm e}$ , cal (mg/g)	9.998	15.04	19.859
$R^2$	0.992	0.997	0.989

by the electrostatic interaction between CTAB–kaolin and Cr(VI). As shown in Table 2, the maximum adsorption efficiency of CTAB–kaolin from pseudo-second-order kinetics ( $q_{cal}$ =19.859) was found to be in good agreement with experimental ( $q_{exp}$ =19.82).

## Conclusion

In conclusion, we have successfully prepared and characterized CTAB-intercalated kaolin for improved adsorption of chromium(VI). FTIR and XRD analyses affirm the kaolin modification through intercalation and surface coating using CTAB. The adsorption removal Cr(VI) using CTAB–kaolin was found to be strongly dependent on pH, initial Cr(VI) concentration and adsorbent dose. The acidic pH is suitable for uptake of Cr(VI) by CTAB–kaolin. The monolayer adsorption process is suggested based on the best fitted Langmuir model. 99% removal (100 mg, 10 ppm/100 ml) and 22.72 mg/g maximum adsorption efficiency were achieved by CTAB–kaolin. The kinetic study reveals that the *pseudo*-second-order expresses well the adsorption process than *pseudo*-first-order model, which attributes to the chemisorption is the rate-determining step. Hence, it is inferred that CTAB–kaolin was found to promising for efficient removal Cr(VI) from the aqueous solution, especially at low concentrations of Cr(VI).

**Acknowledgements** The authors are kindly acknowledging the Debre Berhan University (Chemistry Department) and Ministry of Education of Ethiopia for supporting the work.

**Funding** The chemical and characterization cost of the research work was covered by Debre Berhan University and Ministry of Education of Ethiopia under the regular fund for graduated students.

#### **Compliance with ethical standards**

**Conflict of interest** The authors declare that there is no conflict of interest.

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