Bentonite-Based Functional Material for Chromium Species Adsorption

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Abstract

A functional material (Bt-MCCs) for the simultaneous adsorption of trivalent and hexavalent chromium has been synthesized by modification of natural bentonite with cetyltrimethylamoniumromide and chitosan. This functional material was characterized by Fourier Transform Infra-Red, SEM and X-Ray Diffraction spectroscopy, while the evaluation of adsorption performance against Cr species was evaluated by batch method. The results obtained show that the adsorption of Cr species was influenced by pH, contact time, and initial concentration of Cr species. Langmuir and Freundlich models were used to evaluate the adsorption isotherm, and the adsorption kinetics was studied with pseudo-first and pseudo-second order kinetics models. The experimental data showed that the adsorption of chromium species followed well the Langmuir and Freundlich isotherms model, with adsorption capacity of 16.89 and 15.38 (mg/g) for Cr(III) and Cr(VI) respectively. The adsorption kinetics of chromium species by Bt-MCCs is best illustrated by the pseudo-second order kinetics model with the rate constants 0.0232 and 0.0024 (g.mg^{-1}.min^{-1}) for Cr(III) and Cr(VI). Bentonite modification with cetyltrimethylamoniumbromide and chitosan provides adsorption capacity for Cr species much better than unmodified bentonite and capable for adsorbing both Cr species simultaneously from aqueous solutions.

Keywords: Adsorption, Cr species, functional materials**,** modified-bentonite

1. Introduction

The presences of heavy metal ions in the environment, one of the pollutants that are harmful to health, are generally derived from a variety of industrial wastes. Chromium and its compounds is one of heavy metal that is widely used on tanning industry, preservation of wood, electroplating, and others (Wen, Y.,et al. 2011, Atia, A.A., 2008).The role of toxicity and other effects are very dependent on the form of the species where these elements are present in the system, so the presence of toxic metals in the environment is not sufficient to be expressed only in terms of the total concentration of the element. Chromium can change from one chemical form to another in water and soil, depending on the conditions present. Cr(III) and Cr (VI) exhibit very different properties, Cr(III) is an essential dietary mineral at low doses. On the other hand, Cr(VI) compounds are carcinogenic. Cr(VI) is generally considered to be 1,000 times more toxic than Cr (III) should therefore be determined on the basis of the chemical species (Kota, J & Stasica, 2000; Madavi, V. et al, 2013).Various methods have been used to reduce the content of Cr species such as solvent extraction (Wandoyo, V.W., et al, 2006, Ihesinachi, K.A., et al., 2011), ion exchange (Narin, et al., 2002; Neagu, V., & Mikhalovsky, S., 2010), adsorption and others (Huang, R.,et al 20012; Pandey, S., et al., 2011; Yuan Peng et al, 2010, Sadaoui, Z et al., 2009; Copello, G.J., et al.2008 ; SpinelliV.A., et al 2004).

Adsorption has been proven as an effective method to remove heavy metal pollutants from wastewater when compared with other processes, because it is easy to operate, can be done with a batch method or a column, can be regenerated and reused, and high availability of a wide range of materials that can be used as adsorbent (Wen, Y, et al., 2011, Battacharyya, K.G., & Gupta, S. 2008; Kumar, 2013 Mohan, D., et al. 2006). Bentonite which has high content of montmorillonite, a layered structure, porous, mechanically and chemically stable, large surface area and high cation exchange capability can be used as an adsorbent. Bentonite has been proved to be efficient in removing many toxic metal ions such as lead, cobalt, nickel, copper, zinc, cadmium, chromium and silver from an aqueous solution (Chen Y.G., 2012; Karapinar, N. &Donat, R., 2009; Stefan, M. et al, 2008; Chakir, A.B., et al 2002). However, its ability to absorb anionic species such as Cr(VI) and organic molecules is very low and the active site of bentonite is not uniform, so a solution is needed to improve its adsorption performance.

The adsorption capacity of bentonite can be increased through its modification into organoclay as a functional material for heavy metal adsorption (Bhattacharya, S.S. and Mandot A., 2014; Sadeghalvad, B., et al., 2013; Abdel Khalek, M.A., et al., 2012; Wan Ngah, W.S., et al., 2011; Paiva, L.B, 2008;Bergaya and Lagaly, 2001). Bentonite-based functional material developed in this study is chemically modified bentonite using cationic surfactants N-Cetyl-N,N,N-trimethylammoniumbromide (CTAB) and chitosan. The use of CTAB as modifier may change the surface charge of bentonite (Brum, M.C., et al, 2010), while chitosan has an active group $-NH_2$ and OH which have the capability to adsorb cationic or anionic species depend the condition of the solution (Guibal, 2004). Therefore, the use of two types of modifiers will produce a new functional material capable of adsorbing Cr(III) and Cr(VI) simultaneously from the solution without the need for reduction or oxidation of the chromium species. The synthesis and characterization of functional materials such as these have not been systematically reported. Bentonite (Na-Bt) and Bt-MCCs were characterized using FTIR, SEM-EDX and XRD to evaluate the success of the modification process, while characterization of adsorption properties and factors affecting Cr species adsorption were studied by batch method.

2. Materials and Methods

2.1 Materials

The bentonite used in this study was obtained from the Cipatatarea of West Java-Indonesia with a chemical composition as shown in Table 1, chitosan DD 81% (Biotech-Surindo) and distilled water were used throughout all the experiments. The chemicals are analytical grade and used without further purification, such as $K_2Cr_2O_7$ (Merck),$Cr(NO_3)_3.9H_2O$ (Merck), NaCl (Merck), HNO_3 (Merck), Cetyltrimethyl ammonium bromide (CTAB, Merck), NaOH (Merck), and CH_3COOH (Merck).

2.2 Instrumentation

X-ray Fluorescence (XRF) and X-ray diffraction (XRD), were used to determine the mineralogy of the sample and its elemental analysis, Fourier Tranform Infra-red (FTIR) Spectrocopy was used to identify the presence of functional groups in the bentonite and modified bentonite (Bt-MC and Bt-MCCs). The surface morphology of adsorbent was observed using a scanning electron microscope (SEM). The concentration of Cr species solution was determined by using the Atomic Absorption Spectrometry (AAS).

2.3 Methods

2.3.1 Preparation of the adsorbent Bt-MC (Modification of bentonite with CTAB)

A total of 5 grams of Na-bentonite (Na-Bt) with particle size of +200/-100 mesh was dispersed into 250 mL CTAB solution with a concentration of 0.01 M and stirred for 24 hours at room temperature. Bt-MC formed filtered and washed with distilled water until free Br^- ions then dried at 60 ^OC for 24 hours, and finally crushed and sieved to obtain a certain particle size.

2.3.2 Preparation of Bt-MCCs (Modification of Bt-MC with Chitosan)

Preparation of Bt-MCCs was prepared by the following procedure: 5 grams Bt-MC was added to 250 mL of distilled water to obtain a 2% Bt-MC suspension and then chitosan solution was prepared by dissolving 5 g chitosan in 250 mL acetic acid solution (1% v/v). Then chitosan solution was slowly added to Bt-MC suspension.

The mixture was stirred for 24 hour at room temperature and finally the formed functional materials was washed with distilled water until the pH of filtrate reached neutral, and then dried at 60 ^{O}C in an oven for 24 hours, and finally crushed and sieved to obtain a particle size of +200/-100 mesh. The material functional was named as Bt-MCCs.

2.3.3Adsorption studies

The Cr species [Cr(III)–Cr(VI)] adsorption experiments were carried out by using the batch method. All the adsorption experiments were conducted in a 100 mL glass reactor using a magnetic stirrer for mixing at room temperature. The influence of the parameters such as pH (2 - 6), contact time (30–360 min), dosage of adsorbent (0.05–0.5g) and initial concentration (20 – 250 mgL^{-1}) of Cr species adsorption was investigated and finally, the optimized conditions were determined for maximizing Cr species adsorption.

Adsorbent Performance

The adsorption capacity (qe, mg/g), of an adsorbent against adsorbate are determined using the equation:

$$q_e = \frac{(Ci - Ce)V}{m} \quad (1)$$

and the adsorption efficiency (% Ads) can be calculated using the equation:

$$\%Ads = \frac{(Ci - Ce)}{Ci} x100 \quad (2)$$

where, V is the volume of the solution (L), C_i and C_e are the initial concentration and final concentration (mg/L, after adsorption) of Cr species in the solution, respectively, and m is the mass of the adsorbent Bt-MCCs (g).

Table-1 Chemical Composition of Bentonite (XRF analysis)

Bentonite	**Composition (%)**									
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**K_2O**	**Na_2O**	**CaO**	**MgO**	**TiO_2**	**MnO**	**P_2O_5**
Natural Bentonite	60,01	16,40	2,04	0,26	0,24	0,84	4,72	0,36	0,02	0,39
Na-Bt	61,36	17,23	2,04	0,07	2,32	0,11	4,08	0,32	0,02	0,01

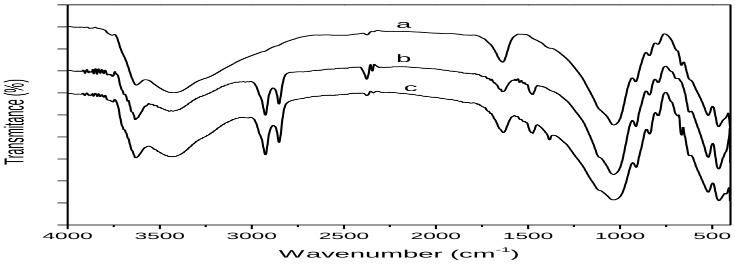
3. *Results and Discussion*

The modification of bentoniteusing CTAB and chitosan aims to obtain a functional material which has better adsorption properties and can be used as an adsorbent for Cr species.

3.1. Characterization of Bt-MCCs

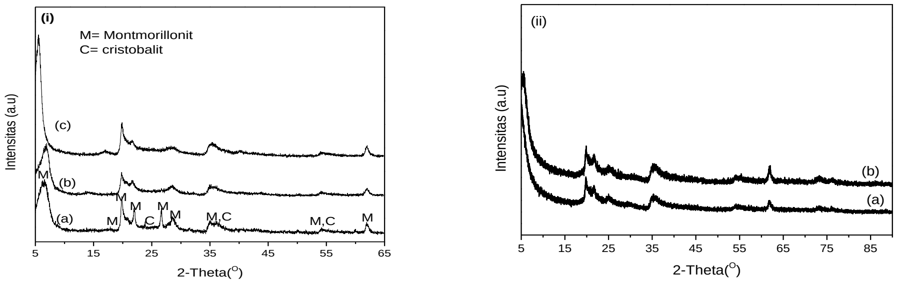
To evaluate the success of modification process, bentonite (Na-Bt) and modified bentonite (Bt-MCCs) need to be characterized. Na-Bt and Bt-MCCs were characterized using FTIR, XRD and SEM.IR spectrum of bentonite (Na-Bt), surfactant-modified bentonite (Bt-MC) and CTAB-chitosan modified bentonite are shown in Fig. 1. The Bt-MCCs IR spectrum shows the combination of the characteristic absorption bands of the bentonite, CTAB, and chitosan groups, and in general there is a shift in wave numbers and changes in the intensity of several peaks, such as 3429 cm^{-1} which is the -OH and -NH vibrational bands of chitosan. In addition, the Bt-MC and Bt-MCCs IR spectrum shows a new absorption band at 2927 cm^{-1} (asymmetric stretching -CH_2), 2854 cm^{-1} (symmetrical -CH_2 stretching) and two absorption bands at 1471, 1373 cm^{-1} (CH bending region) of methylene or $(CH_3)_3N^+R$ and 1519 cm^{-1}attributed to deformation vibration of the protonated amine group (-NH_3^+) of the chitosan. The absorption band intensity at 1637 cm^{-1} increases, which indicates the -NH group bending vibration of chitosan overlap with -OH bending vibration of H_2O of the Bt. The broad absorption band at 1030 cm^{-1} compared to Na-Bt indicates that glucopyranose overlaps with Si-O-Si vibration in Na-Bt.

Fig.1 FTIR spectrum of adsorbent: (a) Na-Bt, (b) Bt-MC and (c) Bt-MCCs



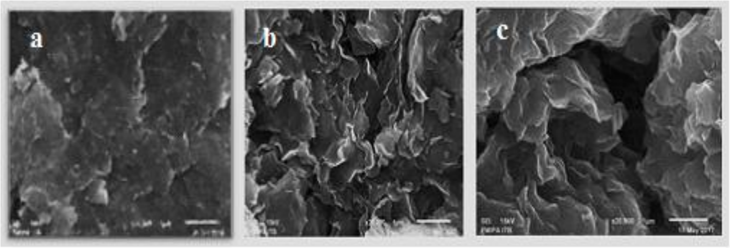
X-ray diffraction (XRD) has been used to determine the presence of montmorillonite minerals in bentonite, and modified-bentonite. Fig. 2 indicates that the natural bentonite obtained from Cipatat has the same relative diffraction pattern when compared to commercial bentonite from Sigma Aldrich. The main mineral component of Montmorillonite has a characteristic of high intensity at 2θ between 5°-9° with basal spacing (d_{001}) 12.87-16.26 Å, while the saturation of bentonite with NaCl (Na-Bt formation), Bt-MC and Bt-MCCs shows a shift of peak and basal distance depending on the type of modifier used. However, there is no structural change in Montmorillonite which is characterized with a 2θ peak which still shows the typical peak of montmorillonite. It also indicates that the modification process is possibly occur through an intercalation process. If the modifying agent unable to penetrate the interlayer space, the value of d_{001} will not change (increase) (Kozak and Domka, 2004).

Fig. 2 XRD pattern of the (i): Bt-Sigma (a) Na- Bt (b) and Bt-Cipatat (c)(ii): Bt-MCCs (a) and Bt-MC (b)



The surface morphology of NaBt and Bt-MCCs with 20,000 x magnification is shown in Fig. 3. This figure shows the difference between the surface morphology of NaBt, Bt-MC and Bt-MCCs. Na-Bt has a smooth surface that is less porous than modified bentonite (Bt-MC and Bt-MCCs). The SEM results show a tendency to form lumps and agglomeration of modified clay particles from bentonite.

Fig. 3 Surface morphology of adsorbent: (a) Na-Bentonite(b) Bt-MC and (c) Bt-MCCs



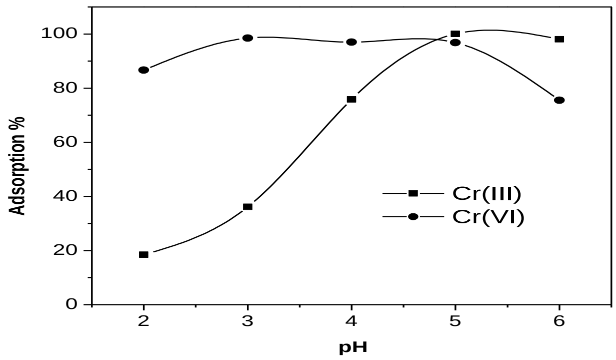
3.2 Adsorption Studies (Batch Method)

The study of adsorption parameters was performed to determine the optimum condition of Cr species retention. The effects of various parameters such as the effect of pH, the influence of contact time, dose of adsorbent and initial concentration of Cr species were investigated.

3.2.1Effect of pH

pH is an important factor in the adsorption process, in addition to its role in controlling the surface properties of the adsorbent, this parameter also affects the chemical form of Cr species, thus affecting the interaction between adsorbent and adsorbate. Studying the effect of solution pH in the range of 2-6 as shown in Fig. 4 shows that the quantity of Cr species adsorbed is highly dependent on pH. At low pH, the amount of Cr (VI) adsorbed is much higher than Cr(III). This is because Bt-MCCs functional groups such as $-NH_2$ is protonated to $-NH_3^+$ so the adsorbent surface is positively charged and will reduce the interaction between Bt-MCCs functional groups and Cr species in cationic form. The same phenomenon was reported by other researchers (Pandey, S. et al 2011; Zulfikar, M.A, et al 2014). The optimum pH for Cr(III) and Cr(VI) adsorption are respectively at pH 5 and 3. Another important conclusion is the Bt-MCCs adsorbents can be used for the selective separation of Cr species and allowing to simultaneously adsorb Cr species from aqueous solutions.

Fig. 4 Effect of pH on Cr species adsorption onto Bt-MCCs

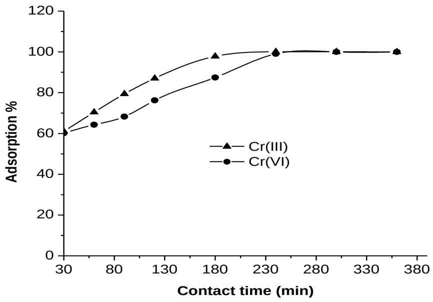


Analysis condition: adsorbent dosage: 0.2 g; contact time: 240 min; initial concentration:Cr(III) 50 and Cr(VI) 25 mg/L;volume of the solution 25 mL.

3.2.2 Effect of Contact Time

To determine the optimum contact time, a certain amount of adsorbent was contacted with Cr species solution at optimum pH. The influence of contact time on per cent of adsorption can be seen in Fig. 5. This figure shows that the amount of Cr adsorbed from minutes 30 to 120 increases sharply, and after 240 min adsorption tends to be constant, it is because the adsorbent has saturated.

Fig. 5 Effect of Contact time on Cr species adsorption onto Bt-MCCs

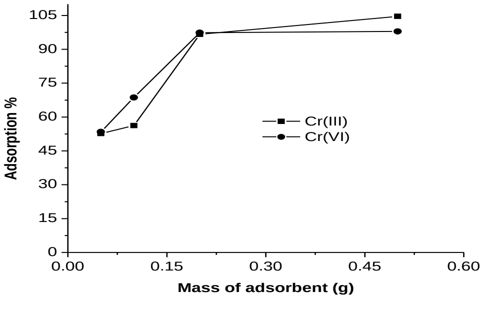


Analysis condition:adsorbent dosage: 0.2 g; pH of the solution: Cr(III) pH-5, Cr(VI) pH-3; initial concentration 50 mg/L; volume of the solution 25 mL.

3.2.3. Effect of amount of adsorbent

To optimize the adsorbent dose on Cr species adsorption, the adsorption process was carried out using different doses of adsorbents. The percentage of adsorption of Cr species by Bt-MCCs is presented in Fig. 6. It can be observed that the percentage of adsorption increases with increasing adsorbent doses, due to the increase in the number of active sites on the adsorbent.

Fig.6 Effect of dosage adsorbent on the adsorption of Cr species



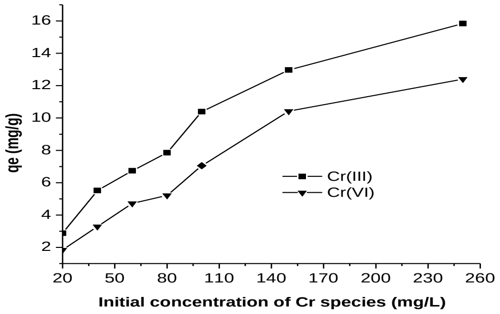
Analysis condition: contact time: 240 min; initial concentration: Cr(III) 50 and 25 mg/L Cr(VI); pH of the solution: Cr(III) pH- 5, Cr(VI) pH-3; volume of the solution 25 mL.

A significant increase in the adsorption percentage is observed where the adsorption capacity increases from a dose of 0.05 to 0.2 g of adsorbent and additional adsorbents do not cause significant changes in percentage of adsorption. Therefore, the optimum dosage for adsorption of Cr species is 0.2 g.

3.2.4. Effect of initial concentration of Cr species

The effect of initial concentration of Cr species on the amount of Cr adsorbed is shown in Fig. 7. Increasing the initial concentration of Cr causes an increase in the amount of adsorbed ions (qe), this is due to an increase in the number of ions that can interact with the adsorbent active site. The maximum adsorption capacity (q_{max}) based on the isotherm Langmuir models is 16.86 mg/g for Cr(III) and 15.39 mg/g for Cr (VI).

Fig.7 Effect of initial concentration on the adsorption of Cr species



Analysis condition: adsorbent dosage: 0.2 g;contact time: 240 min; pH of the solution: Cr(III) pH-5,Cr(VI) pH-3; volume of the solution 25 mL.

3.3 Adsorption isotherms

The adsorption isotherm was studied for the initial concentration ranging from 20 – 250 mg/L at optimum condition. Langmuir and Freundlich isotherm models were used to analyze the experimental results.

The linear form of Langmuir isotherm is expressed as:

$$\frac{Ce}{qe} = \frac{1}{KL.qm} + \frac{Ce}{qm} \tag{3}$$

where C_e is concentration of Cr species in aqueous solution at equilibrium (mg/L), q_e is the Cr species adsorption capacity for adsorbent at equilibrium(mg/g), qm is the maximum adsorption capacity (mg/g) and K_L is Langmuir constants related to energy of adsorption (L/mg). The Freundlich adsorption isotherm model is empirical equation applicable for description of the adsorption process, which based on the assumption that the adsorbent has a heterogeneous surface composed of different adsorptive site. The linear form of Freundlich isotherm can be expressed as:

$$\ln qe = \ln Kf + {}^{1}/_{n} \ln Ce \tag{4}$$

where Ce is concentration of Cr in aqueous solution at equilibrium (mg/L), qe is the Cr species adsorption capacity for adsorbent at equilibrium(mg/g), K_f and n are constants related to adsorption capacity of adsorbent and adsorption intensity, respectively.

Fig.8 Linier plot of adsorption isotherm of Cr(III) on Bt-MCCs

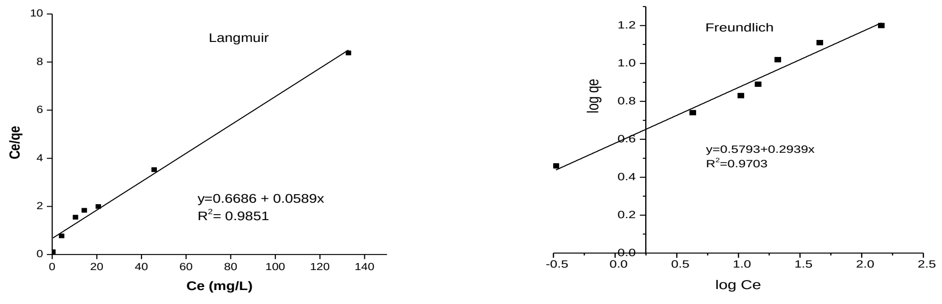


Fig.9 Linier plot of adsorption isotherm of Cr(VI) on Bt-MCCs

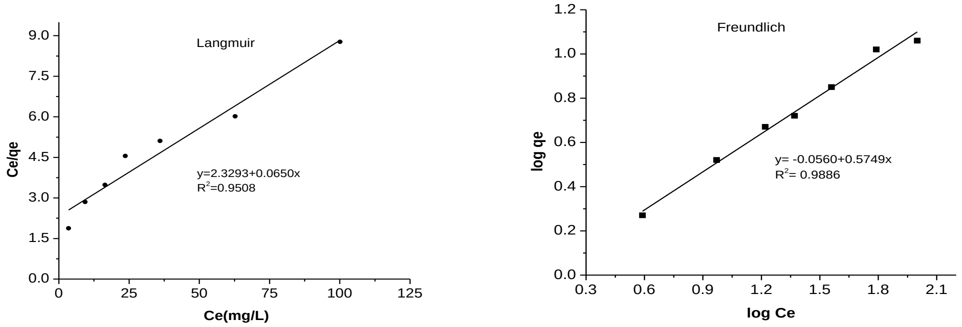
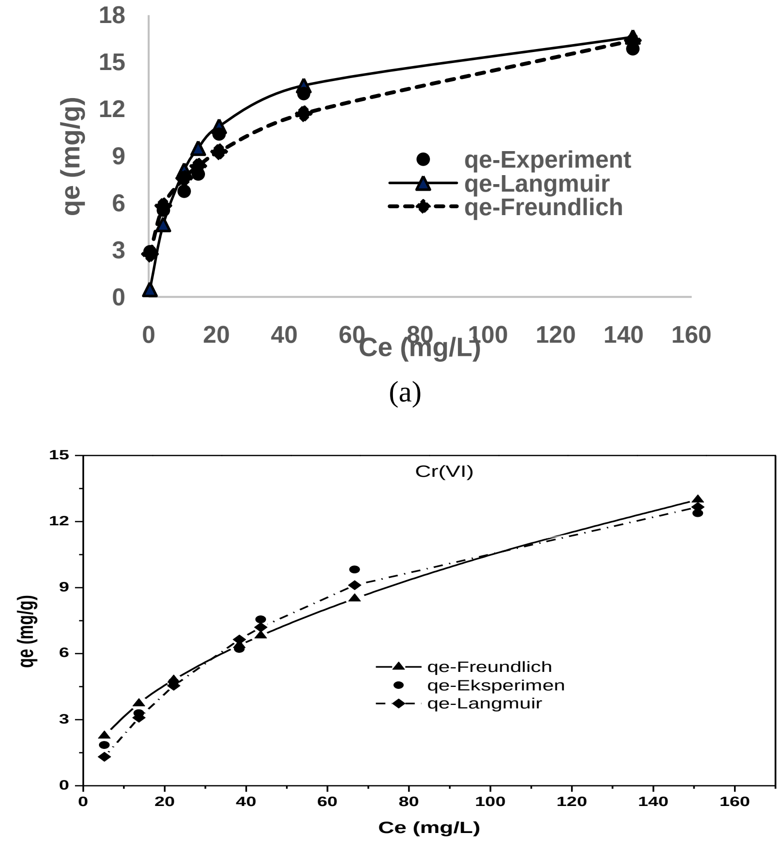


Fig. 10 Isotherm Curve for the adsorption of Cr species by Bt-MCCs: (a)Cr(III) and (b) Cr(VI)



(a)

(b)

Analysis condition: contact time : 240 min, Volumeof the solution 25 mL, pH of the solution: Cr(III) pH-5 and Cr(VI) pH-3, dosage Bt-MCCs 0.2 g.

As shown in Table 2, the experimental data for Cr(III) follows the Langmuir isotherm models whereas Cr(VI) fits the Freundlich model. The R_L value between 0-1 and n values between 1-10 shows a good interaction between the adsorbent with the adsorbate (Kumar, A.S.K., et al., 2012).

Table -2 Adsorption isotherm parameters of Bt-MCCs toward Cr species

Species	$qe_{Exp.}$ (mg/g)	Langmuir			Freundlich		
		q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)(L/mg)$^{1/n}$	R^2
Cr(III)	15.84	16,98	0.0881	0,9851	3.4025	3.7958	0.9703
Cr(VI)	12.38	15.38	0.0279	0.9508	1.7394	0.8789	0.9886

Table-3 R_L values based on Langmuir adsorption

R_L	**Initial Concentration (C_o), mg/L**						
	20	40	60	80	100	150	250
Cr(III)	0.3618	0.2209	0.1589	0.1241	0.1018	0.0703	0.0434
Cr(VI)	0.6859	0.5219	0.4212	0.3531	0.0703	0.2255	0.1487

3.4 Adsorption kinetics

Adsorption kinetics is used to study the mechanism of adsorption and this study used modelkinetics pseudo-first, and a pseudo-second order. The pseudo-first-order rate expression was evaluated with the following equation as:

$$\ln(qe - qt) = \ln qe - kt \tag{5}$$

Where qe and qt, are amount of Cr species, (mg/g) adsorbed on adsorbent at equilibrium and at time t, respectively and k is the rate constant (min^{-1}).

The pseudo-second order rate equation assumes that the adsorption capacity is proportional to the number of active sites on the surface. The pseudo-second order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \tag{6}$$

whereq_e and q_t are the amounts of Cr (mg/g) adsorbed on adsorbent at equilibrium, and at time t, respectively and k is the rate constant ($g.mg^{-1}min^{-1}$). Adsorption kinetics parameters are summarized in Table 4, under experimental conditions: amount of the adsorbent 0.2 g, the initial concentration of 50 mg/L, the volume of 25 mL, pH 3 to Cr(VI) and pH 5 to Cr (III). From these data it can be seen that the adsorption of Cr(III) and Cr(VI) in the adsorbent Bt-MCCs followed model pseudo-second order.

Fig. 11 Pseudo-second-order model plots for Cr species

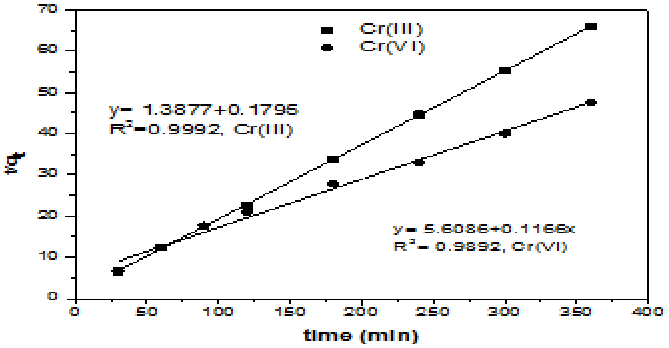


Table - 4 Adsorption Kinetic Parameters of Bt-MCCs toward Cr Species

Pseudo-first Order			**Pseudo-second Order**			**qe $_{Exp}$ ($mg.g^{-1}$)**	**Cr Species**
q_e(mg/g)	**K_{-1}(min^{-1})**	**R^2**	**q_e($mg.g^{-1}$)**	**K_{-2}($g\ mg^{-1}.min^{-1}$)**	**R^2**		
7.61	0.0181	0.9653	5.57	0.0232	0.9992	5.47	Cr(III)
6.14	0.0106	0.8917	8.58	0.0024	0.9892	7.60	Cr(VI)

4. Conclusions

A functional material for the adsorption of Cr species has been successfully synthesized and characterized by modification of bentonite with CTAB and chitosan (Bt-MCCs). This functional material is able to improve the performance of bentonite to adsorp Cr species both selectively and simultaneously. Adsorption capacity is affected by pH, contact time, dosage of adsorbent and initial concentration of Cr species. The adsorption capacity for Cr(III) was 16.89 mg/g at pH 5 and 15.38 mg/g at pH 3 for Cr(VI). The adsorption isotherm of the functional material developed follows both Langmuir and Freundlich models while its adsorption kinetics follows the pseudo-second-order model with rate constants of 0.0232 and 0.0024 $g.mg^{-1}min^{-1}$ for Cr(III) and Cr(VI) respectively.

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