CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2020,
Vol. 14, No. 3, pp. 362–371

Chemical Technology

CHROMIUM(VI) REMOVAL USING ACTIVATED *THUJA OCCIDENTALIS* LEAVES CARBON POWDER – ADSORPTION ISOTHERMS AND KINETIC STUDIES

Vaddi Dhilleswara Rao[1, ✉], Mushini Venkata Subba Rao[1], M.P.S.Murali Krishna[2]

https://doi.org/10.23939/chcht14.03.362

Abstract. This study investigates the capability of *Thuja occidentalis* leaves carbon powder (TOLC) as a viable adsorbent for the expulsion of chromium(VI) from aqueous solutions. By batch mode, the removal percentage of Cr(VI) is observed to be pH perceptive and furthermore relies upon the time of equilibration, amount of the TOLC adsorbent and Cr(VI) concentration. TOLC adsorbent before and after adsorption of Cr(VI) was characterized with FTIR, SEM and EDX. Adsorption isotherm results divulge that the Langmuir model was a better fit. The kinetic studies divulge that the pseudo-second-order model was the best fit. TOLC adsorbent can be easily regenerated and utilised for several adsorption/desorption cycles.

Keywords: *Thuja occidentalis* leaves, Cr(VI) adsorption, adsorption isotherm, kinetics.

1. Introduction

Eco-harmfulness to living beings has turned into a prime worry in the last couple of decades. Due to increasing urbanisation and additionally industrialisation [1], a large number of contaminants, mainly heavy metals, are generated. The heavy metals, *viz*., Cr, Cd, Ni, As, Cu, Pb, *etc*. draw widespread attention due to persistent character, toxicity and carcinogenic nature even in lesser amounts [2]. The most important sources of heavy metals are electroplating industries, mining industries, metal plating industries, tannery effluents, *etc*. The introduction of industrial effluents having these heavy metals into natural water resources is a reason of severe ecological problems [3], since the discharged industrial effluents also contaminate the groundwater [4]. One of such dangerous heavy metal is chromium, arising due to the use of toxic chromium salts in leather, metal cleaning, tannery and metallurgical industries, paints, wood preservatives and ceramics [5]. The chromium metal exits in the hexavalent and trivalent forms in water. Cr(VI) is considered more perilous mainly due to its carcinogenic nature [6] and is 100 times more toxic than Cr(III) ion due to its high aqueous solubility and easy accumulation and absorption in stomach, kidneys and liver [7]. Exposure of Cr(VI) in humans has been connected with a variety of respiratory diseases, respiratory tract disorders, allergies and lung carcinoma [8, 9]. Depending on the solution pH, chromium exits in solution in anionic forms as CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_4O_{13}^{2-}$ and neutral form as H_2CrO_4 [10]. The maximum allowable concentration of chromium in drinking water, as per the recommendations of WHO (World Health Organisation) and US-EPA (United States-Environmental Protection Agency), is 0.05 and 0.1 mg/l, respectively [11, 12]. Hence, increasing ecological awareness attached with strict regulation standards has triggered different industries to confront themselves looking for suitable wastewater treatment methods [13].

Several technologies (precipitation, electrochemical treatment, filtration membrane, ion exchange method) have been adopted for the expulsion of chromium metal ion from waste water [4, 14]. However, these technologies have some drawbacks, such as low selectivity, expensiveness, incomplete metal removal, high energy requirements, *etc*. The adsorption strategy using an adsorbent is a reasonably new process and is developing as a favoured option since it gives easy operation, high-quality treated effluent, high efficiency, low cost. The used adsorbent can be regenerated several times and regenerated material is used for the conversion of heavy metal contaminated water to heavy metal free water in order to obtain environmental regulations [15]. The main advantage of adsorption process is that there is no sludge generation [16]. Specifically, activated carbon is a splendid adsorbent with good chemical properties, as well as large surface area, high porous nature, great number of active sites for adsorption, and strong adsorption capacity [17, 18]. On the other hand, commercially available activated carbons are highly expensive and hence recently activated carbon derived from agricultural wastes (due to existence of

---

[1] G M R Institute of Technology, affiliated to JNTUK, Rajam, A.P, India
[2] Department of Chemistry, Andhra Polytechnic, Kakinada 533003, A.P, India
✉ *dhilleswararao.v@gmrit.edu.in*

functional groups containing oxygen, *e.g.*, carboxyl, carbonyl, hydroxyl and phenolic groups) is used for the expulsion of Cr(VI) such as Mangifera indica seed shell [19], wheat straw and Eupatorium adenophorum [20], Prosopis juliflora bark [21], rice straw [22], Longan seed [23], African biomass residues [24], sugarcane baggage [25], *etc*. The adsorption mechanisms are associated with surface complexation, chemisorptions, diffusion through micropores, electrostatic interactions and ion-exchange [26]. Thus, the potential use of *Thuja occidentalis* leaves carbon (TOLC) as an abundant, economical, renewable and useful material for the expulsion of Cr(VI) metal ions is altogether examined in this paper. If the carbon prepared from *Thuja occidentalis* leaves is confirmed to be successful in the expulsion of Cr(VI), it would give the industries a plentiful source of the inexpensive carbon-based adsorbent for the effective treatment method and remediation of Cr(VI) rich water. However, there is no published literature available on the use of TOLC for the expulsion of Cr(VI). The fundamental parameters considered are varying pH, varying Cr(VI) initial concentration, time of contact period and TOLC dosage utilizing characteristic adsorbent by adsorption system with batch adsorption mode. Langmuir and Freundlich's models are considered to explain the equilibrium character of Cr(VI) adsorption onto the adsorbent material. The adsorption and rate-limiting step of the transport mechanism is also studied using kinetic models.

2. Experimental

2.1. Plant Description

Thuja occidentalis is also called as northern white-cedar or eastern arborvitae, and it is broadly utilized as an ornamental tree, especially, for screens and supports. The leaf and its leaf oil have been utilized for the treatments of respiratory tract diseases, bacterial skin contaminations and hair arrangements and so forth. The leaves of *Thuja occidentalis* [27] are collected from the local region of Srikakulam district, Andhra Pradesh, India as a forerunner for preparing activated carbon.

2.2. Preparation of *Thuja Occidentalis* Leaves Carbon Adsorbent

Thuja occidentalis leaves were washed with triple distilled water thoroughly to take away grime and dust particles on it. The washed leaves were put in sunlight for 4–5 days. The dried leaves were grinded to a fine powder. The fine powder was taken in a conical flask and concentrated sulphuric acid was added to the fine powder slowly under constant stirring with the ratio of 1:1.8 (w/w). The resultant product was heated at 433±5 K on a hot plate for 5 h [28-30]. After heating, the obtained material was washed with distilled water for few times until free from sulphuric acid. The material was dried out in the oven at 378±5 K. Finally, the material (TOLC) was grinded to the required size of <75 μm and the material was stored in a plastic container for future use.

2.3. Materials and Methods

1000 mg/l of standard Cr(VI) solution was prepared using potassium dichromate. The necessary operational concentrations of Cr(VI) can be made from 1000 mg/l solution by accurate dilution. 0.01N H_2SO_4 and 0.01N NaOH were used for pH adjustments. All chemicals were of analytical reagent (AR) grade. The surface area and porous volume of the TOLC were determined by quantachrome instrument (surface area analyzer Nova 3200), using nitrogen as adsorbate at 77 K. The FTIR spectrum was measured within 4000–400 cm^{-1} using a single beam, Perkin Elmer BX FTIR; anhydrous potassium bromide was used as a pellet material. Scanning electron microscopic images were taken using Philips XL 30 microscope equipped with an energy dispersive X-ray analyzer to study the surface morphology of the CATLC and elemental composition analysis. The amount of Cr(VI) present in the solution was measured using UV-Vis double beam spectrophotometer (Systronics, AU 2701). Systronics digital pH/mv meter, model 335 was used for the measurement of pH. The TOLC characteristics were: surface area 798.4 m^2/g; pore volume 0.572 cm^3/g; particle size <75 μm and pH_{ZPC} 6.54.

2.4. Batch Adsorption Studies

The batch mode study was executed by taking predetermined concentrations (80–150 mg/l) of 50 ml of Cr(VI) solution with predetermined amounts (2.0–20 g per litre of Cr(VI) solution) of TOLC at predetermined pH values (2.5–9.0) in 250 ml conical flasks and agitated using an orbital shaker (stirring rate 180 rpm) for 10–80 min. After agitation with successful time intervals, the solid residuals were separated using Whatman filter paper-41 with vacuum filtration pump, and the filtrate containing Cr(VI) was analyzed using UV-Visible double beam spectrophotometer (Systronics, Model AU 2701) to know the optimum condition of the time interval. The same procedure was carried out, when one parameter was varied and remaining parameters were kept fixed under knowing optimum conditions of pH, TOLC dosage and Cr(VI) concentration. The entire process was conducted at room temperature. The percentage expulsion of Cr(VI), R, and quantity of Cr(VI) uptake, Q_e, can be determined by Eqs. (1) and (2).

$$R = \frac{C_i - C_f}{C_0} \cdot 100\% \quad (1)$$

$$Q_e = \frac{C_i - C_f}{m} \cdot V \quad (2)$$

where C_i and C_f are initial and final concentration of Cr(VI), respectively, mg/l; m is the quantity of TOLC, g; V is the volume of Cr(VI) solution, l.

3. Results and Discussion

3.1 Adsorption Studies for the Expulsion of Cr(VI)

3.1.1. Influence of TOLC dosage

It is important to fix the dosage of TOLC to plan the optimum treatment systems for fast response of the examination. To achieve this, a series of batch mode experiments were performed with the TOLC dose of 2.0 to 20.0 g per litre of the working solution (100 mg/l Cr(VI) solution) at the predetermined pH 3.00 and the period of 70 min. It is noticed that the Cr(VI) expulsion efficiency increases by increasing the TOLC dosage from 2.0 to 16.0 g. A maximum percentage expulsion of 95.7 % (Fig. 1a) is obtained at 16.0 g of TOLC per litre of Cr(VI) solution. When the adsorbent dosage increases, there is an enhancement of the active binding sites number [31] available on the surface of TOLC adsorbent, and hence the expulsion of Cr(VI) increases. But an additional increment in the amount of TOLC dosage does not have any considerable increment in the expulsion of Cr(VI) ion due to the existence of an equilibrium between adsorbate and TOLC adsorbent. However, the Cr(VI) uptake (Q_e) on the adsorbent surface decreases from 18.95 to 4.785 mg/g of Cr(VI) on the adsorbent surface when the adsorbent dosage increases from 2 to 20 g/l of Cr(VI) solution, as shown in Fig. 1a, since the number of Cr(VI) ions are fixed to adsorb on the surface. Based on this observation, the adsorbent dosage of 16 g/L of Cr(VI) solution was taken as fixed for further studies.

3.1.2. Influence of initial pH

Adsorption is mainly controlled by pH which influences the speciation of metals through redox reactions, hydrolysis and complexation during metal recuperation. There is a favourable pH range for the maximum adsorption of each metal on an adsorbent surface [32]. The pH reliance of Cr(VI) adsorption mainly is associated with the ionic state and type of different functional groups on the TOLC as well as Cr(VI) speciation in aqueous solution. The pH value needed to confer zero point charge was determined for TOLC [33]. A graph drawn between final pH *versus* initial pH gives a curve, from where the pH_{zpc} for TOLC was identified as the point, at which the change of pH is zero. The experimental results show that pH_{zpc} (zero point charge) of TOLC is obtained as 6.54. This indicates that TOLC adsorbent surface is positively charged below 6.54 and negatively charged above 6.54 [34, 35]. The experiments are performed by altering the pH from 2.5 to 9.0 per 50 ml of the working solution (100 mg/l of Cr(VI) solution) at the predetermined dosage of 16 g per litre of Cr(VI) solution and the period of 70 min. Chromium shows various kinds of pH-dependent equilibriums in aqueous solution. As the solution pH changes, there is a shift in the equilibriums. $Cr_2O_7^{2-}$ and $HCrO_4^{-}$ species are in equilibrium at pH of 2.0–6.0, $Cr_4O_{13}^{2-}$and $Cr_3O_{10}^{2-}$ are present at lower pH values. At lower pH values a strong electrostatic attraction exits between positively charged adsorbent surfaces and chromate anions. Lower adsorption of chromium that takes place at pH $\geq$ 6 might be owing to competition between two anions (OH^{-} and CrO_4^{2-}) on the adsorbent surface [36]. In this investigation, the adsorption rate was enhanced from 93.1 to 95.7 % by increasing pH from 2.5 to 3.0. As the pH value is increased, the adsorption competence quickly reduced. The percentage expulsion of Cr(VI) is greater than 80 % when pH ranges from 3.0 to 4.0, however, the highest percentage of removal is obtained at pH of 3.0. Overall, as pH is varying from 3.0 to 9.0, the Cr(VI) expulsion decreases from 95.7 to 42.7 %. The possible explanation for higher adsorption in an acidic medium is that the Cr(VI) is oxidized to Cr(III) state[37]. A maximum percentage expulsion of 95.7 % (Fig. 1b) is obtained at pH of 3.0 and is considered for further studies. The Cr(VI) uptake Q_e on the TOLC surface decreases from 5.981 to 2.668 mg/g of Cr(V) on the adsorbent surface as the pH increases from 3.0 to 9.0.

3.1.3. Influence of initial Cr(VI) concentration

Cr(VI) solutions with different concentrations of 80–150 mg/l at optimum pH of 3.0 were equilibrated utilizing optimum dosage of 16 g per lire of Cr(VI) solution. Fig. 1c demonstrates that the Cr(VI) uptake on the TOLC adsorbent surface enhanced from 4.918 to 6.55 mg/g and expulsion efficiency reduced from 98.3 to 69.8 % when the concentration was varied from 80 to 150 mg/l. The increasing Cr(VI) uptake on TOLC surface by increasing initial concentration is due to more Cr(VI) ions being accessible in the solution, and hence more adsorption takes place because of the improvement in contact [38].The expulsion of Cr(VI) is decreased by increasing the initial concentration of Cr(VI), which is mostly due to the active sites being saturated and exchange sites getting almost filled. This trend represents that very small number of sites are involved in the adsorption by increasing Cr(VI) concentration.

3.1.4. Influence of contact time

Cr(VI) solutions of concentration 100 mg/l with various time intervals from 10 to 80 min at optimum pH value of 3.0 were equilibrated utilizing the optimum dosage of 16.0 g. The impact of the contact period between the TOLC adsorbent with Cr(VI) solution on the adsorption capability of TOLC and Cr(VI) uptake on the TOLC surface is represented in Fig. 1d. There is a sharp increment in the adsorption with the increase in the contact period of up to about 70 min and then it tends to settle at a consistent value, since initially more number of active sites were present on the TOLC adsorbent surface. Thus, adsorption takes place more rapidly, whereas desorption takes place at a lower rate. Therefore, the net impact is a greater increment in the degree of adsorption. When the active sites get filled, the rates of adsorption, as well as desorption, have a tendency to be equivalent and degree of adsorption decreases and inevitably turns out to be about consistent at equilibrium [39].

3.2. Adsorption Isotherm Studies

The adsorption isotherms usually specify how the masses of required ions are dispersed among the solid and liquid phases at equilibrium condition. Also, it corresponds to the relation between the extent of Cr(VI) adsorbed per unit mass of the TOLC under equilibrium condition at a constant temperature. Here, Langmuir [40] and Freundlich [41] isotherm models are considered to identify the adsorption capacity for Cr(VI) removal using TOLC.

The Langmuir isotherm is represented by Eq. (3):

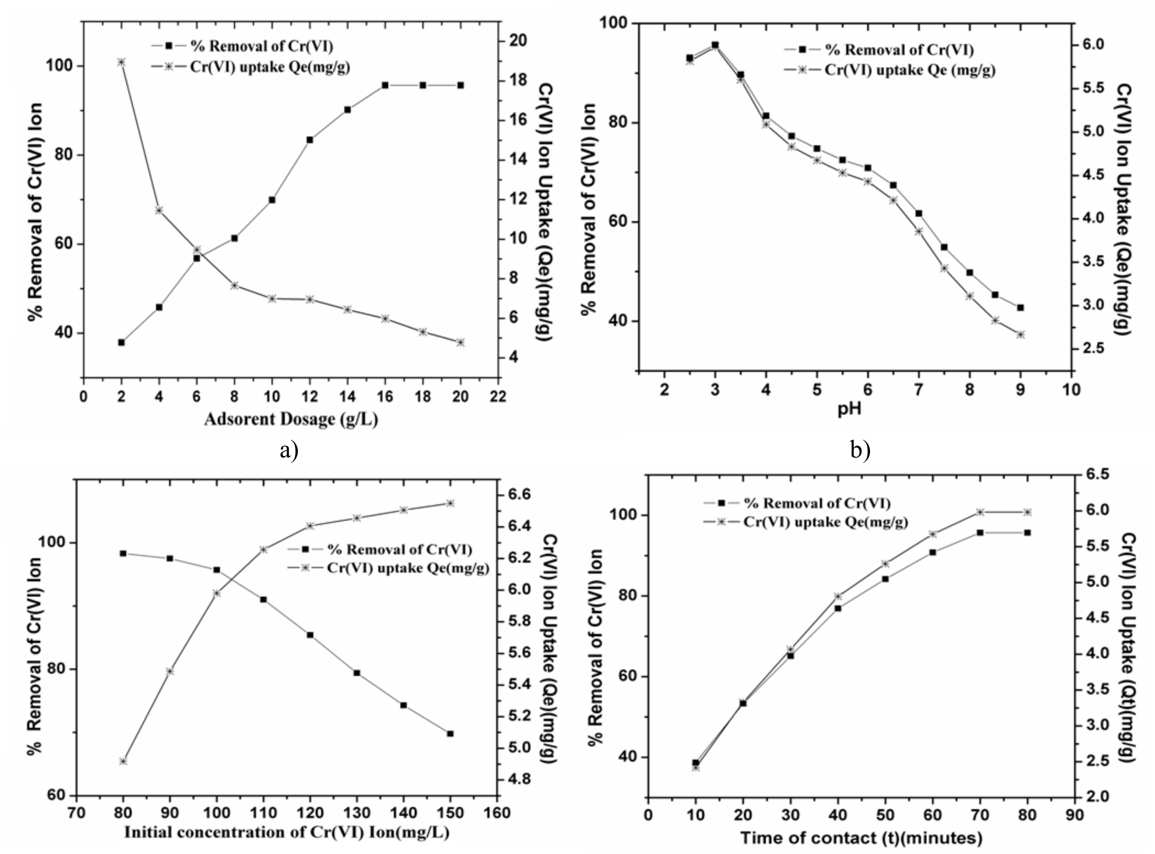
$$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m} \qquad (3)$$

where Q_e is the mass of Cr(VI) uptake, mg/g; Q_m is the maximum adsorption capability of TOLC, mg/g; C_e is the equilibrium concentration, mg/l; b is a constant indicating the energy of adsorption.

The Freundlich isotherm is represented by Eq. (4):

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \qquad (4)$$

where Q_e is the mass of Cr(VI) uptake, mg/g; C_e is the equilibrium concentration, mg/l; K_f is associated with adsorption capability and $1/n_f$ is the quantity of adsorption intensity.



a) b)

c) d)

Fig. 1. Impact of various parameters on percentage expulsion of Cr(VI) and Cr(VI) ions uptake (mg/gm) using TOLC: TOLC dosage (a); solution pH (b), initial concentration of Cr(VI) (c) and time of contact (d)

The Langmuir and Freundlich adsorption isotherm constants are measured from the graphs of $1/Q_e$ *vs.* $1/C_e$ and $\ln C_e$ *vs.* $\ln Q_e$ (Fig. 2). The obtained values are represented in Table 1. The obtained correlation coefficient value R^2 for Langmuir is 0.999 and for Freundlich – 0.8776. It represents that Langmuir isotherm is a better fit than Freundlich model and also represents that Cr(VI) uptake takes place on the homogenous surface of adsorbent by unilayered adsorption [42].

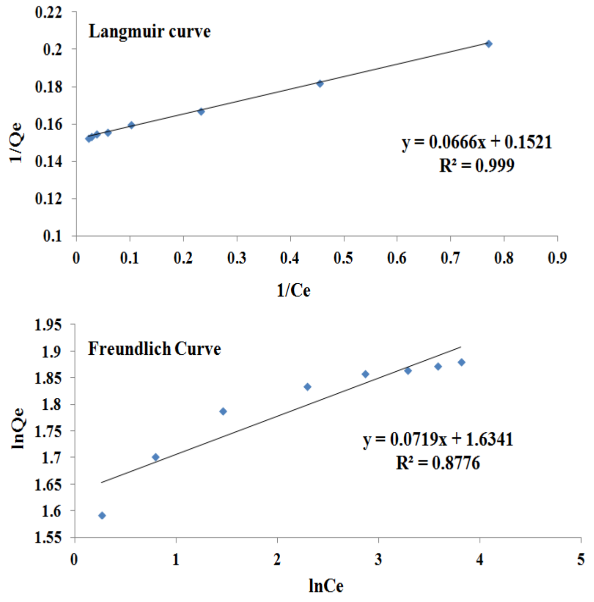


Fig. 2. Langmuir and Freundlich trendline curves using TOLC (particle size < 75 μm)

The important characteristic of Langmuir may also be indicated regarding dimensionless equilibrium separation factor R_L and is measured by Eq. (5).

$$R_L = \frac{1}{1+bC_i} \tag{5}$$

where C_i is the initial Cr(VI) concentration, mg/l and b can be determined by Langmuir plot.

The R_L value represents the adsorption process either favorable $(0 < R_L < 1)$, unfavourable $(R_L > 1)$ or irreversible $(R_L = 0)$ [43]. The obtained R_L value is 0.0419, which shows that adsorption process is favourable using TOLC for the Cr(VI) removal.

3.3. Kinetic Studies

Adsorption kinetics examination gives a comprehension of adsorption rate and controlling mechanism of the procedure. With a specific end goal to clarify the adsorption energy of Cr(VI) by TOLC adsorbent, four kinetic adsorption isotherm models, for example, pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich [44] were studied.

The lineralized type of the four models and calculated kinetic parameters are represented in Table 2. The respective kinetic adsorption graphs are shown in Fig. 3. It is observed that the regression constant proximity to the value of R^2 = 0.9927 represents that the pseudo-second-order isotherm is a better fit. Hence, the chemisorptions are the rate-limiting step for the adsorption of Cr(VI) [45].

Table 1

Values of adsorption isotherm constants

Adsorption isotherm models	Linear form	Graph	R^2	Parameters	Obtained value
Langmuir Model	$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m}$	$1/C_e$ *vs.* $1/Q_e$	0.999	b	0.2283
				R_L	0.0419
Freundlich Model	$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e$	$\ln C_e$ *vs.* $\ln Q_e$	0.8776	K_f	5.124
				$1/n_f$	0.0719

Table 2

Values of kinetic adsorption constants

Kinetic model	Linear expression	Graph	R^2	Constants	Q_e
Pseudo-first order kinetic	$\ln(Q_e - Q_t) = \ln Q_e - K_1 t$	$\ln(Q_e - Q_t)$ *vs.* t	0.9626	$K_1 = -0.047$	6.841
Pseudo-second order kinetic	$t/Q_t = 1/k_2 Q_e^2 + 1/Q_e t$	t/Q_t *vs.* t	0.9927	$K_2 = 0.0046$	8.07
Intra particle diffusion	$Q_t = K_i t^{0.5}$	Q_t *vs.* $t^{0.5}$	0.970	$K_i = 0.722$	–
Elovich	$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	Q_t *vs.* $\ln t$	0.9869	$\alpha = 0.621$ $\beta = 0.539$	–

Notes: Q_e and Q_t are the Cr(VI) uptake at equilibrium and time t (min), respectively, mg/g; k_1 is the pseudo-first-order rate constant, min^{-1}; k_2 is the pseudo-second-order rate constant, g·(mg/min)$^{-1}$; k_i is the intraparticle diffusion rate constant, mg·(g·min$^{0.5}$)$^{-1}$. Initial adsorption rate is represented as α, mg·(g·min) and β is the surface coverage, g/mg, as well as activation energy for chemisorptions.

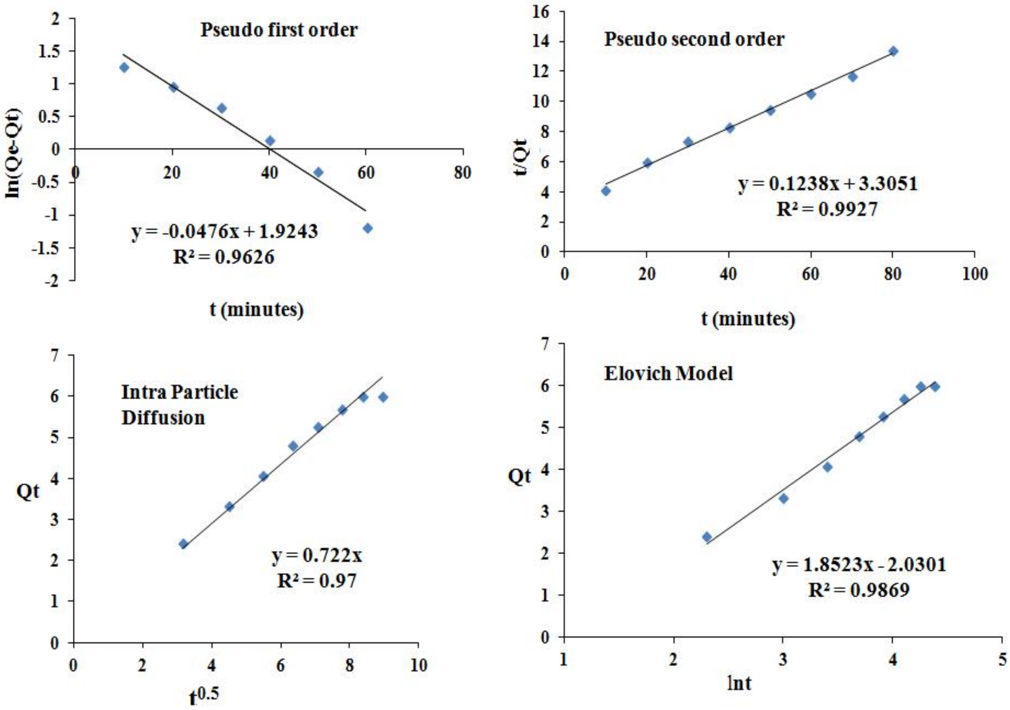


Fig. 3. Kinetic adsorption isotherm graphs: the pseudo-first order model, the pseudo-second-order model, the intra-particle diffusion model, and the Elovich model

3.4. Characterization Studies of TOLC

3.4.1. FTIR study

FTIR spectra are recorded for examining the presence of various functional groups in the TOLC adsorbent. FTIR spectra of TOLC material before Cr(VI) and after Cr(VI) adsorption are shown in Fig. 4 and the corresponding FTIR data are presented in Table 3. The spectra of TOLC before adsorption shows a vibrational peak at 3374 cm^{-1} correspond to –OH stretching value in hydroxyl groups. It is shifted to 3389 cm^{-1} after Cr(VI) was adsorbed. The peak at 3071 cm^{-1} before adsorption represents the hydroxyl stretching band in the carboxylic group and is shifted to 2995 cm^{-1} after Cr(VI) adsorption. The stretching vibration peak at 1707 cm^{-1} indicates the C=O group in carboxylic acid and is shifted to 1712 cm^{-1}. The carboxylic groups are typically apparent to partake in the heavy metal adsorption [46]. These groups most probably act as proton donors and undergo deprotonation. The peak at 2879 cm^{-1} corresponds to the presence of –CH– or –CH$_2$– on the TOLC surface and is shifted to 2924 cm^{-1}. The peak at 1596 cm^{-1} corresponds to the stretching vibration band of C=C in aromatic groups. The peaks at 1171 and 1030 cm^{-1} represent the existence of –C–O in alcoholic, carboxylic or phenolic functionalities on the TOLC surface and are shifted to 1237 and 1044 cm^{-1} respectively. The peak at 625 cm^{-1} indicates the C–S stretching band on the TOLC surface and is shifted to 630 cm^{-1}. There is also a shift in the vibrational bands occurring mainly due to adsorption of Cr(VI) by TOLC adsorbent since the existence of polar functional groups on the TOLC surface probably provides significant ion exchange to the TOLC adsorbent [47]. The EDX spectra reveal the presence of chromium on the adsorbent surface after adsorption treatment. Also, no band vanishing is seen during the procedure of adsorption showing that TOLC is a magnificent inexhaustible adsorbent for treatment of wastewater.

3.4.2. SEM study

The SEM images (Fig. 5) illustrates morphology of the TOLC adsorbent before (a, b) and after (c, d) Cr(VI) adsorption on TOLC at different magnifications. The TOLC raw powder surface before Cr(VI) adsorption has particles with the small size of 74–214 nm, and also some larger particles are observed with non-regular shape. The micro- and macroporous nature of certain regions in the particles are observed, which provides sufficient active sites for adsorption [48]. The surface of the TOLC powder after Cr(VI) adsorption have particles with the sizes ranging from 74 to 214 nm and more. Partial porous regions in the TOLC are observed, perhaps due to the decreased porosity and being simultaneously covered by the adsorbed Cr(VI) ions on the surface. This is apparent for the Cr(VI) adsorption on the TOLC surface.

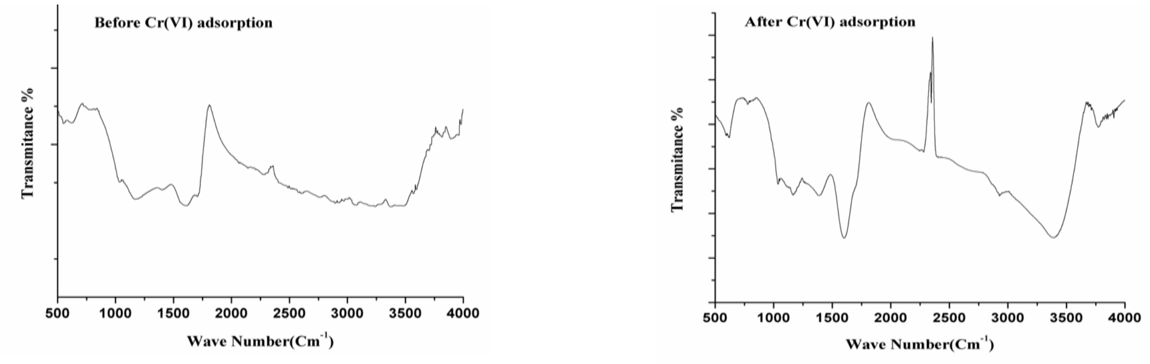


Fig. 4. FTIR spectra of TOLC before and after Cr(VI) adsorption

Table 3

FTIR data of TOLC before and after Cr(VI) adsorption

TOLC (before Cr(VI) adsorption)	TOLC (after Cr(VI) adsorption	Bond stretching values
3566	3682	Phenolic – OH stretching band
3374	3389	Hydroxyl – OH stretching band
3071	2995	Carboxylic acid – OH stretching band
2879	2924	–CH– , –CH$_2$ antisymmetric stretching vibration
2354	2277	C=O stretching in CO$_2$
1707	1712	C=O stretching in carboxylic acid
1596	1600	C=C in aromatic
1414	1388	–C–H bending vibration
1171, 1030	1237,1044	C–O stretching in hydroxyl, acids or phenolic
777	782	Aromatic –C–H bending vibration
625	630	C–S stretching band

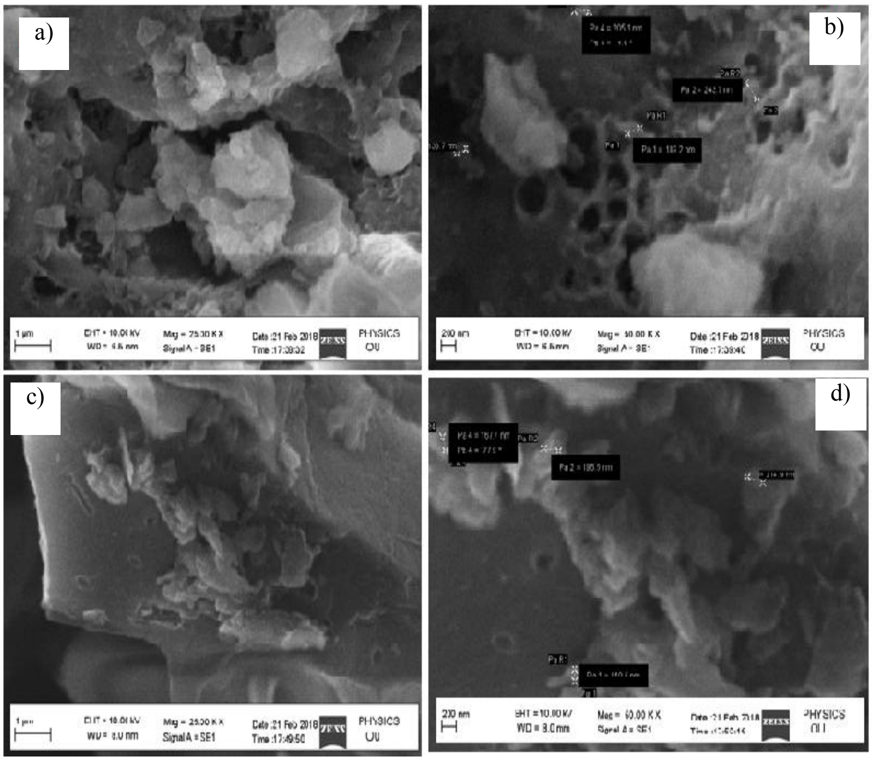


Fig. 5. SEM image of TOLC before(a, b) and after (c, d) Cr(VI) adsorption

3.4.3. EDX study

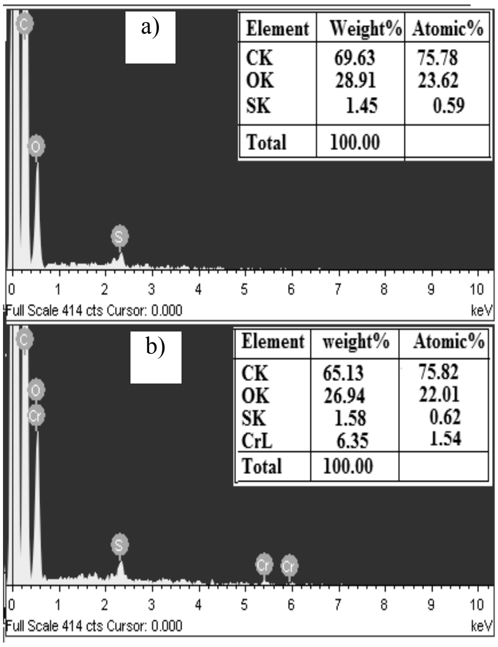
The EDX spectra and elemental composition of an adsorbent give the information about the composition changes of the elements on the TOLC surface before and after Cr(VI) adsorption. EDX spectra portray the presence of elements like carbon, oxygen and sulphur of raw powder TOLC before adsorption and presence of elements like carbon, oxygen, sulphur, and chromium of TOLC after adsorption. The Cr(VI) adsorption is affirmed by the EDX investigation, which is demonstrated by the appearance of the peak of Cr(VI) in the EDX of TOLC after Cr(VI) adsorption. The peak of Cr(VI) was not seen on the surface of TOLC before Cr(VI) adsorption as shown in Fig. 6. Also, it can be observed that TOLC has higher carbon and oxygen content and these are major components in TOLC adsorbent. Hence, hydroxyl and carboxyl groups are possible functional groups for the Cr(VI) adsorption. The presence of these groups was proved by the FTIR spectral data [49] earlier. Based on the above discussion, TOLC can permit the development of sufficient sites and required functional groups for complexation and chelation with Cr(VI) ions.

3.5. Possible Mechanism for the Expulsion of Cr(VI) Using TOLC Adsorbent

The polar functional groups, for example, carboxylic acid, hydroxyl groups and aromatic hydroxy groups there on the surface of the TOLC adsorbent can participate in chemical bonding, and these are accountable for the ion exchange capacity of the TOLC; additionally, there is an electrostatic attraction between the positively charged adsorbent with negatively charged chromate ion. So, the TOLC/Cr(VI) reaction might be indicated in two possible ways as represented in Fig. 7.

3.6. Regeneration

Recovering and reusability of the adsorbent would diminish handling costs and is imperative for industrial applications. The reusability of TOLC is tried by performing consecutive adsorption and desorption cycles with a regenerating agent of 0.01N H_2SO_4. The recovered TOLC adsorbent is utilized for the expulsion of Cr(VI) with the same 100 mg/l of Cr(VI) concentration. Desorption of Cr(VI) studies were carried out with 1 g/l of Cr(VI) adsorbed utilizing 100 ml of 0.01N H_2SO_4 solution. The % expulsion of Cr(VI) using regenerated TOLC is 86.2 % for the first cycle, 81.4 % for the second cycle and 78.1 % for the third cycle. After the 3rd–4th cycles, the measures of adsorption and desorption had superb execution, demonstrating that TOLC could be a monetarily plausible technique for the expulsion of Cr(VI).



Element	Weight%	Atomic%
CK	69.63	75.78
OK	28.91	23.62
SK	1.45	0.59
Total	100.00	

Element	weight%	Atomic%
CK	65.13	75.82
OK	26.94	22.01
SK	1.58	0.62
CrL	6.35	1.54
Total	100.00	

Fig. 6. EDX spectra along with elemental composition of TOLC before (a) and after (b) Cr(VI) adsorption

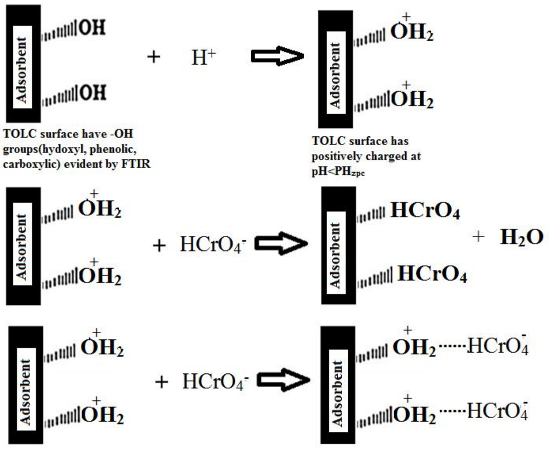


Fig. 7. Possible mechanism for the expulsion ofCr(VI) using TOLC adsorbent

3.7. Comparative Studies of TOLC and Other Available Adsorbents

A relative report has been considered for adsorption capacity of various adsorbent materials and the present adsorbent TOLC. The immediate connection of TOLC with various adsorbents is not simple because of various working conditions. An exertion is made (Table 4) for examination with some detailed adsorbents, and in perspective of the acquired results, the adsorption capability of TOLC for Cr(VI) is surprisingly more significant than other available low-cost adsorbents.

Table 4

Comparison of TOLC with other existing adsorbents for the expulsion of Cr(VI)

Adsorbent	pH of the solution	Maximum adsorption capability, mg/g	References
Coconut tree sawdust activated carbon	3.0	3.46	[50]
Bael fruit shell activated carbon	2.0	17.27	[51]
Maize corn cob	2.0	0.28	[52]
Sugarcane bagasse	2.0	1.76	[53]
Cactus	2.0	7.08	[54]
Swietenia mahagoni fruit shell	3.0	2.3	[55]
TOLC	3.0	5.981	present work

4. Conclusions

TOLC turned out to be an extremely capable and exceedingly effective adsorbent of Cr(VI) adsorption in aqueous solutions. Cr(VI) adsorption is impacted by different parameters, for example, the initial dosage of TOLC, initial solution pH, Cr(VI) concentration, and period of TOLC contact. The maximum expulsion of Cr(VI) has taken place at pH of 3.0. The working $pH < pH_{zpc}$ of TOLC indicates that the surface of adsorbent is positively charged at pH of 3.0. FTIR and SEM studies confirmed the presence of various polar groups on the TOLC surface and porous nature. EDX gives evidence of the existence of chromium peak after adsorption of chromium using TOLC. The Langmuir and Freundlich isotherm models were utilised to clarify the adsorbate expulsion. The equilibrium adsorption of Cr(VI) over the whole concentration range was best depicted by the Langmuir isotherm, as shown by the high value of R^2 equal to 0.999. The kinetic study indicates that the pseudo-second order (R^2 = 0.9927) is the best fit and chemisorption is the rate-limiting step for the Cr(VI) adsorption on to the TOLC adsorbent. Finally, Cr(VI) can be desorbed by 0.01N H_2SO_4 solution and ultimately regenerated and recovered for several cycles. Hence, using TOLC for the expulsion of Cr(VI) is viewed as a supportable, financially affordable and effortlessly executed wastewater treatment innovation, as it does not require expensive pre-treatments.

References

[1] Djebbar M., Djafri F.: Chem. Chem. Technol., 2018, **12**, 272. https://doi.org/10.23939/chcht12.02.272

[2] Mehdipour S., Vatanpour V., Kariminia H.: Desalination, 2015, **362**, 84. https://doi.org/10.1016/j.desal.2015.01.030

[3] Skiba E., Kobyłecka J., Wolf W.: Environ. Pollut., 2017, **220B,** 882. https://doi.org/10.1016/j.envpol.2016.10.072

[4] Wu L., Liao L., Lv G. *et al.*: J. Hazard. Mater., 2013, **254**, 277. https://doi.org/10.1016/j.jhazmat.2013.03.009

[5] Lv X., Xu J., Jiang G. *et al.*: J. Colloid Interface Sci., 2012, **369**, 460. https://doi.org/10.1016/j.jcis.2011.11.049

[6] Cheng Q., Wang C., Doudrick K., Chan C.: Appl. Catal. B, 2015, **176-177**, 740. https://doi.org/10.1016/j.apcatb.2015.04.047

[7] Sharma D., Forster C.: Bioresour. Technol., 1995, **52,** 261. https://doi.org/10.1016/0960-8524(95)00035-D

[8] Focardi S., Pepi M., Focardi S.: Microbial Reduction of Hexavalent Chromium as a Mechanism of Detoxification and Possible Bioremediation Applications. [in:] R. Chamy (Ed.), Biodegradation – Life of Science. InTechOpen 2013. https://doi.org/10.5772/56365

[9] Miretzky P., Cirelli A.: J. Hazard. Mater., 2010, **180**, 1. https://doi.org/10.1016/j.jhazmat.2010.04.060

[10] Hsu N-H., Wang S-L., Liao Y-H. *et al.*: J. Hazard. Mater., 2009, **171**, 1066. https://doi.org/10.1016/j.jhazmat.2009.06.112

[11] Sereshti H., Farahani M., Baghdadi M.: Talanta, 2016, **146**, 662. https://doi.org/10.1016/j.talanta.2015.06.051.

[12] Crisostomo C., Lima F., Dias R. *et al.*: Water Air Soil Pollut., 2016, **227**, 51. https://doi.org/10.1007/s11270-016-2747-9

[13] Teh C., Budiman P., Shak K., Wu T.: Ind. Eng. Chem. Res., 2016, **55**, 4363. https://doi.org/10.1021/acs.iecr.5b04703

[14] Kazeminezhad I., Mosivand S.: J. Magn. Magn. Mater., 2017, **422**, 84. https://doi.org/10.1016/j.jmmm.2016.08.049

[15] Ronda A., Della Zassa M., Martín-Lara M. *et al.*: J. Hazard. Mater., 2016, **308**, 285. https://doi.org/10.1016/j.jhazmat.2016.01.045

[16] Choi K., Lee S., Ock J. *et al.*: Nature, 2018, **8**, 1438. https://doi.org/10.1038/s41598-018-20017-9

[17] Guo Z., Zhang J., Liu H., Kang Y.: Powder Technol., 2017, **318**, 459. https://doi.org/10.1016/j.powtec.2017.06.024

[18] Huang M., Wang Z., Liu S.: J. Environ. Chem. Eng., 2016, **4**, 1555. https://doi.org/10.1016/j.jece.2016.02.019

[19] Shashikant M., Trupti Nagendra P.: J. Inst. Eng. India Ser. A, 2015, **96**, 237. https://doi.org/10.1007/s40030-015-0124-0

[20] Song D., Pan K., Tariq A. *et al.*: PLoS One, 2016, **11(12)**, **e0167037.** https://doi.org/10.1371/journal.pone.0167037.

[21] Kumar M., Tamilarasan R.: Arabian J. Chem., 2013, **10**, S1567. https://doi.org/10.1016/j.arabjc.2013.05.025

[22] Hsu N-H., Wang S-L., Liao Y-H. *et al.*: J. Hazard. Mater., 2009, **171**, 1066. https://doi.org/10.1016/j.jhazmat.2009.06.112

[23] Yang J., Yu M., Chen W.: J. Ind. Eng. Chem., 2015, **21**, 414. https://doi.org/10.1016/j.jiec.2014.02.054

[24] Gueye M., Richardson Y., Kafack F., Blin J.: J. Environ. Chem. Eng., 2014, **2**, 273. https://doi.org/10.1016/j.jece.2013.12.014

[25] Cronje K., Chetty K., Carsky M. *et al.*: Desalination, 2011, **275**, 276. https://doi.org/10.1016/j.desal.2011.03.019

[26] Oliveira R., Hammer P., Guibal E. *et al.*: Chem. Eng. J., 2014, **239**, 381. https://doi.org/10.1016/j.cej.2013.11.042

[27] The Gymnosperm Database 2018. https://www.conifers.org/cu/Thuja_occidentalis.php

[28] Singanan M., Peters E.: J. Environ. Chem. Eng., 2013, **1**, 884. https://doi.org/10.1016/j.jece.2013.07.030

[29] Singanan M.: Science Asia, 2011, **37**, 115. https://doi.org/10.2306/scienceasia1513-1874.2011.37.115

[30] Mengistie A., Siva Rao T., Prasada Rao A.: Global J. Sci. Frontier Res. Chem., 2012, **12**, 5.

[31] Esposito A., Pagnanelli F., Lodi A. *et al*.: Hydrometallurgy, 2001, **60**, 129. https://doi.org/10.1016/S0304-386X(00)00195-X

[32] Liu C., Liang X., Liu J. *et al*.: J. Colloid Interface Sci., 2017, **488**, 294. https://doi.org/10.1016/j.jcis.2016.11.013

[33] Srivastava V., Mall I., Mishra I.: J. Hazard. Mater., 2006, **B134**, 257. https://doi.org/10.1016/j.jhazmat.2005.11.052

[34] Hsua N-H., Wanga S-L., Liaoa Y-H. *et al*.: J. Hazard. Mater., 2009, **171**, 1066. https://doi.org/10.1016/j.jhazmat.2009.06.112

[35] Rangabhashiyam S., Selvaraju N.: J. Mol. Liq., 2017, **207**, 39. https://doi.org/10.1016/j.molliq.2015.03.018

[36] Huang C-P., Wu M-H.: Water Res., 1977, **11**, 673. https://doi.org/10.1016/0043-1354(77)90106-3

[37] Hamadi N., Chen X., Farid M., Lu M.: Chem. Eng. J., 2001, **84**, 95. https://doi.org/10.1016/S1385-8947(01)00194-2

[38] GuptaV., Ali I., SalehT. *et al*.: Environ. Sci. Pollut. Res., 2013, **20**, 1261. https://doi.org/10.1007/s11356-012-0950-9

[39] Rai M., Shahi G., Meena V. *et al*.: Res. Efficient Technol., 2016, **2**, S63. https://doi.org/10.1016/j.reffit.2016.11.011

[40] Langmuir I.: J. Am. Chem. Soc., 1918, **40**, 1361. https://doi.org/10.1021/ja02242a004

[41] Frendlich H.: J. Phys. Chem., 1906, **57**, 385.

[42] Sujitha R., Ravindhranath K.: J. Fluorine Chem., 2017, **193**, 58. https://doi.org/10.1016/j.jfluchem.2016.11.013

[43] Masoud M., El-Saraf W., Abdel-Halim A. *et al*.: Arabian J. Chem., 2016, **9**, S1590. https://doi.org/10.1016/j.arabjc.2012.04.028

[44] Kilic M., Apaydin-Varol E., Pütün A.: J. Hazard. Mater., 2011, **189**, 397. https://doi.org/10.1016/j.jhazmat.2011.02.051

[45] Dundar M., Nuhoglu C., Nuhoglu Y.: J. Hazard. Mater., 2008, **151**, 86. https://doi.org/10.1016/j.jhazmat.2007.05.055

[46] Huang H., Tang L., Wu C.: Environ. Sci. Technol., 2003, **37**, 4463. https://doi.org/10.1021/es034193c

[47] Abdel Ghani N., Hegazy A., El-Chaghaby G.: Int. J. Environ. Sci. Technol., 2009, **6**, 243. https://doi.org/10.1007/BF03327628

[48] Chen Y., An D., Sun S. *et al*.: Materials, 2018, **11**, 269. https://doi.org/10.3390/ma11020269

[49] Abdolali A., Ngo H., Guo W. *et al*.: Bioresour. Technol., 2015, 193, 477. https://doi.org/10.1016/j.biortech.2015.06.123

[50] Selvi K., Pattabi S., Kaadirvelu K.K.: Bioresour. Technol., 2001, **80**, 87. https://doi.org/10.1016/S0960-8524(01)00068-2

[51] Anandkumar J., Mandal B.: J. Hazard. Mater., 2009, **168**, 633. https://doi.org/10.1016/j.jhazmat.2009.02.136

[52] Garg U., Kaur M., Garg V., Sud D.: J. Hazard. Mater., 2007, **140**, 60. https://doi.org/10.1016/j.jhazmat.2006.06.056

[53] Aloma I., Rodriguez I., Calero M., Blazquez G.: Desalin. Water Treat., 2014, **52**, 5912. https://doi.org/10.1080/19443994.2013.812521

[54] Dakiky M., Khamis M., Manassra A., Mereb M.: Adv. Environ. Res., 2002, **6**, 533. https://doi.org/10.1016/S1093-0191(01)00079-X

[55] Rangabhashiyam S., Anu N., Selvaraju N.: Res. J. Chem. Environ, 2014, **18**, 30.

Received: September 09, 2018 / Revised: November 05, 2018 / Accepted: April 08, 2019

ВИДАЛЕННЯ ХРОМУ(VI) З ВИКОРИСТАННЯМ КАРБОНОВОГО ПОРОШКУ З ЛИСТЯ THUJA OCCIDENTALIS – ІЗОТЕРМИ АДСОРБЦІЇ ТА КІНЕТИЧНІ ДОСЛІДЖЕННЯ

Анотація*. Досліджено адсорбційну здатність карбонового порошку з листя туї західної (Thuja щccidentalis) для витіснення хрому(VI) з водних розчинів. Встановлено, що кількість видаленого Cr(VI) залежить від pH, часу встановлення рівноваги, кількості адсорбенту і концентрації Cr(VI). За допомогою методів Фур'є-спектроскопії, скануючої електронної мікроскопії та енергодисперсійної рентгенівської спектроскопії визначено характеристики адсорбенту до і після адсорбції Cr(VI). Одержаним ізотермам адсорбції найбільше відповідає модель Ленгмюра. Згідно кінетичних досліджень, найкращою є модель псевдо-другого порядку. Показана можливість легкої регенерації адсорбенту та його використання для кількох циклів адсорбції/десорбції.*

Ключові слова*: листя Thuja occidentalis, адсорбція Cr(VI), ізотерми адсорбції, кінетика.*