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ORIGINAL

Performance of MWCNTs and a low-cost adsorbent for Chromium(VI) ion removal

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Abstract In the present study, adsorption of Cr(VI) ions from aqueous solutions was investigated and compared under various conditions using two different nano-structured adsorbents, i.e., carbon nanotubes (CNTs) and low-cost activated carbons (AC). Walnut shell, an agricultural solid waste, was used as a raw material for the preparation of ACs. Multi-walled CNTs (MWCNTs) with average diameter of 20 nm and length of about 2 mm were also used for comparison purposes. Adsorption studies were carried out by varying the parameters such as: treatment time, metal ion concentration, adsorbent amount and pH. The adsorption capacities of AC and MWCNT for Cr(VI) ions were measured as 35 and 24 mg g^{-1}, respectively. The efficiency was observed fairly high at pH = 2–3 for AC and pH = 5–6 for MWCNTs. The adsorption was significantly enhanced by increasing the adsorbent dose up to 0.4 and 0.3 g for AC and MWCNTs, respectively. It was also determined that Cr(VI) adsorption behavior follows both Langmuir and Freundlich isotherms. The content of functional groups, which was obtained by applying the Boehm's method, revealed that phenolic groups are mostly present on the surface of MWCNTs, while basic groups are predominant on the walnut shell AC structures.

Keywords Chromium · Nano-structured adsorbents · MWCNT · Langmuir · Freundlich

Introduction

Heavy metals are often present in the aquatic streams through different industrial wastewaters. Due to their toxicological importance in the ecosystem, agriculture and human health, pollution by heavy metals has received wide spread attention [1, 2]. Chromium, one of the extremely toxic heavy metals affecting the environment, is present in the waste water as a result of its industrial application such as tanning, metallurgy, plating and metal finishing. Once chromium is introduced into the environment, it exists in two stable oxidation states, i.e., Cr(III) and Cr(VI) [3]. The trivalent form is relatively innocuous, but the hexavalent chromium is very toxic, highly mobile in soil and aquatic system, and also is a strong oxidant capable of being adsorbed by the skin [4]. Therefore, the tolerance limit of Cr(VI) for discharge into the inland surface water is set to 0.05 mg L^{-1} [5].

Various methods were employed by researchers for the removal of heavy metals from aqueous solutions such as: chemical precipitation [6], reverse osmosis [7], ion exchange [8], coagulation [9], and adsorption [10–12]. Biosorption method is also a property of certain types of inactive, dead, microbind biomass to bind and concentrate heavy metals from very dilute aqueous solutions such as green algae, bagass fly ash and some other adsorbents [13–25].

Most commonly, the recommended adsorbents for Cr(VI) ion removal are alumina, silica and activated carbons. Several researches have been also performed some studies on the development of low-cost activated carbons

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from cheaper and readily available materials for the removal of heavy metals from waters [26–29]. Walnut shell is one of the agricultural waste products, which is mainly used as a fuel. On the other hand, carbon nanotubes (CNTs) are increasingly attracting interest in the field of metal adsorption [30–34]. Their small sizes, large surface areas, high mechanical strength and remarkable electrical conductivities have indicated their tremendous potential for several engineering applications.

Although there are many studies on the removal of chromium using ACs and to some extend by CNTs, but there is no comparison between the adsorption activities of these two different types of carbon-based materials. In the present study, the adsorptions of Cr(VI) ions from aqueous solutions are investigated and compared under various conditions using two different types of adsorbents; an ordinary low-cost sorbent, i.e., walnut shell-activated carbon and multi-walled carbon nanotubes.

Materials and methods

Materials

Potassium dichromate was obtained from Merck Company in analytical grade. Stock solutions were prepared by dissolving potassium dichromate in de-ionized water. Activated carbon (AC) was prepared by physical activation using carbon dioxide as an activating agent according to the method described elsewhere [35]. Briefly, walnut shell (WS) was washed with distilled water to remove all soluble impurities. Sample was then dried in an electrical oven for 24 h at 110 °C. Dried sample was carbonized in nitrogen atmosphere and then activated for 12 h at 800 °C by CO_2. The activated carbon was ground and sieved to obtain particle sizes in the range of 1–2 mm. The iodine number and BET surface area (measured by Quantachrome, ASAP-2010) of AC products were measured as 830 mg g^{-1} and 900 m^2 g^{-1}, respectively.

The MWCNTs with an average diameter of 20 nm, length of about 2 mm, and purity >95 % were supplied by Iran research institute of petroleum industry (RIPI). The nanotubes had been produced by the CVD method using methane gas.

Boehm's test

The Boehm's test was performed to measure main functional groups on the adsorbents surfaces. The procedure can be described as follows: 0.5 g sorbent was placed in a series of flasks, each containing 50 mL of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide and hydrochloric acid, respectively. Flasks were sealed and shaken for 24 h, after which the solutions were filtered. Then 10 mL of each solution was titrated with 0.05 N sodium hydroxide and/or hydrochloric acid, depending on the original solution used. The amount of acidic groups on the sorbent was calculated under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups and $NaHCO_3$ only neutralizes carboxylic group. The number of surface basic sites was calculated from the amount of HCl reacted with the sorbent. The reaction between reagents and acidic oxygenated functional groups on the surface is based on the difference in acid/base strength. The strength of acidic and basic groups is in the order of: Carboxylic > Lactonic > Phenolic [36].

Batch adsorption

Adsorption of Cr(VI) ion from solutions was studied by the batch technique. The general method used is described as follows: the specified doses of adsorbent were mixed with 50 mL of 100 ppm Cr(VI) solution in the 250 mL conical flasks and kept for predetermined time intervals on a mechanical shaker at 30 °C. The reactor was a jar cell with a double cylindrical jacket in which the temperature was controlled by circulating water through the jacket and stirring speed was kept 720 rpm to keep the sorbent particles in suspension [37].

The pH was adjusted using sulfuric acid. Solutions were then filtered using filter papers and filtrate was analyzed for residual Cr(VI) ion using an atomic adsorption spectrophotometer (Varian, spectra-110-220/880) equipped with a Zeeman atomizer. The uptake of metal ion in the solution was calculated by the difference in their initial and final concentrations. Each experiment was repeated three times and the results reported are the average values. These data were used to calculate equilibrium Cr(VI) uptake capacity according to the following equation:

$$q_e = V(C_0 - C_e)/m \qquad (1)$$

where q_e (mg g^{-1}) is the amount of metal in the adsorbate phase at equilibrium, C_0 and C_e are the initial and equilibrium concentrations of metal ion (mg L^{-1}) in the aqueous solution, V is the volume of the solution (L), and m is the weight of sorbent (g) in the mixture.

The effect of different parameters, including adsorbent dosage (0–0.8 g for WS AC and 0–0.4 g for MWCNT), pH of solution (2–11), initial concentration (20–110 ppm), temperature (30–50 °C) and contact time (0–40 min), was evaluated.

Table 1 The amounts of surface functional groups on WS AC and MWCNTs

Functional groups	WS AC (mmol g^{-1})	MWCNTs (mmol g^{-1})
Basic	1.58	0.263
Carboxylic	0.1	0.25
Lactonic	0.72	0.365
Phenolic	0.18	1.07

Results and discussion

Characterization of adsorbents

Chemical and thermal treatment processing could affect the adsorption capability of adsorbents for the removal of chromium ions as these treatments result in some functional groups on the solid surface [38]. To study the effect of functional groups on the Cr(VI) adsorption, these groups were measured quantitatively for both adsorbents using the Boehm's titration method. The results obtained from the Boehm's method are presented in Table 1. As shown in the table, the amounts of acidic and basic groups on both adsorbents are in the following order:

Walnut shell AC: Basic > Lactonic > Phenolic > Carboxylic.

MWCNTs: Phenolic > Lactonic > Carboxylic > Basic.

Effect of temperature and contact time

Figure 1a shows the effect of operating time on the adsorption of Cr(VI) at different temperatures for a fixed dose of 0.3 g AC. The initial concentrations were kept constant at 110 mg L^{-1} for all different cases. The experimental data show that adsorption of Cr(VI) is enhanced by increasing temperature (30–50 °C). It confirms that adsorption process has an exothermic nature; therefore, the tendency of chromium molecules for adsorption on the solid surface would decrease with increasing temperature.

The adsorption of Cr(VI) is increased by increasing the contact time, due to higher contact between the chromium ions and adsorbent particle surfaces. The amounts of Cr(VI) adsorbed are increased during the first 10 min of adsorption and at the temperature of 30 °C as an example it reached up to about 75 % of its removal efficiency. Subsequently, the adsorption is enhanced gradually and reached nearly equilibrium after about 30 min. The results also indicate that there is not much differences among the amounts of Cr(VI) adsorbed at various temperatures. This is a reason for great adsorption potential between Cr(VI) and WS activated carbon.

Figure 1b shows the effect of operating time on the adsorption of Cr(VI) with a initial concentration of 100 mg L^{-1} at 30 °C for 0.15 g MWCNTs. The experimental results show enhancement of Cr(VI) ion adsorption by time. The rate of Cr(VI) removal is fast in the first 2 h reaching about 50 % of its final value and then gradually reduced. The equilibrium adsorption time is seen to be much shorter in the case of WS AC compared to that of MWCNTs. The shorter time needed to attain equilibrium could be attributed to high adsorption efficiency of WS AC and readily available basic sites on its surface.

Effect of Cr(VI) initial concentration

The effect of Cr(VI) initial concentration at different levels of 21, 61, 87 and 110 mg L^{-1} and constant AC dose of 0.3 g are presented in Fig. 2a. The results show that the Cr(VI) ions removal is concentration dependent and removal efficiency is increased by increasing Cr(VI) initial

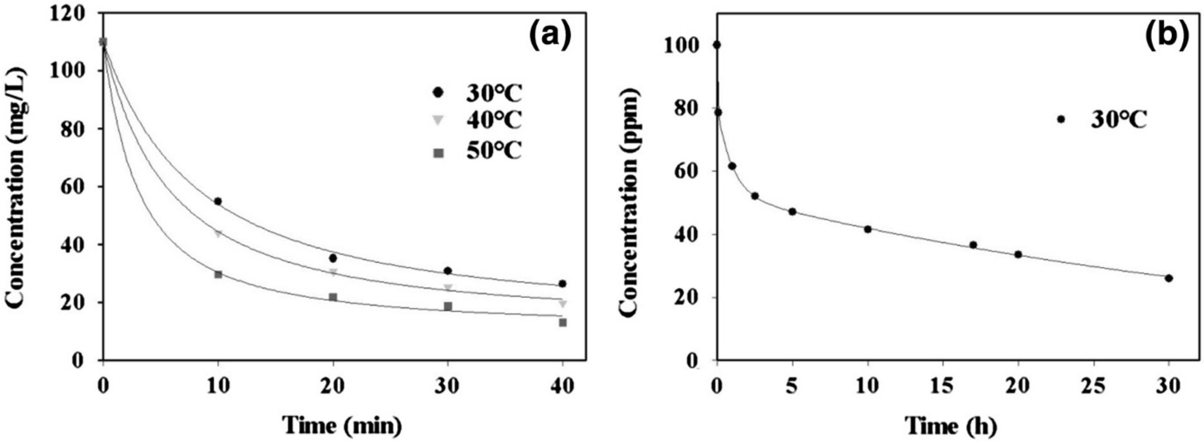

Fig. 1 Effect of contact time in Cr(VI) removal using **a** WS AC (dose = 0.3 g, $C_0 = 100$ mg L^{-1}, $T = 30, 40, 50$ °C) and **b** MWCNT (dose = 0.15 g, $C_0 = 100$ mg L^{-1}, $T = 30$ °C)

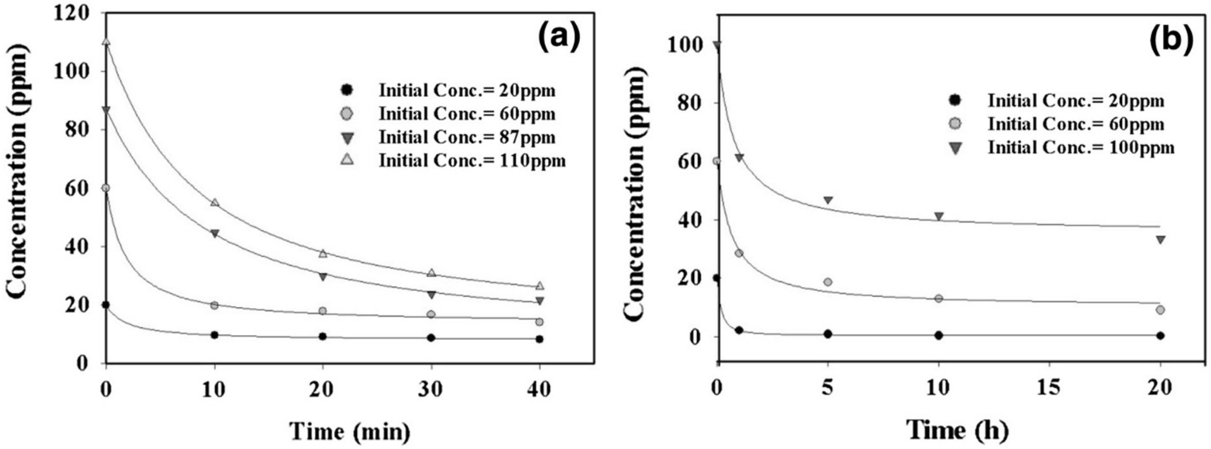

Fig. 2 Effect of Cr(VI) initial concentration on its adsorption using, **a** WS AC (dose = 0.3 g, $C_0 = 20, 60, 87, 110$ mg L^{-1}, $T = 30$ °C) and **b** MWCNTs (dose = 0.15 g, $C_0 = 20, 60, 100$ mg L^{-1}, $T = 30$ °C)

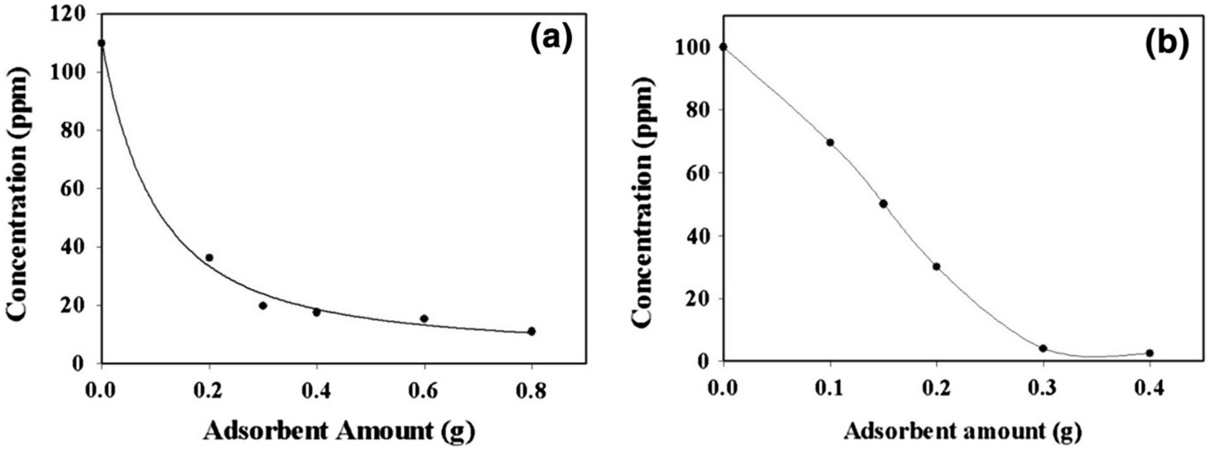

Fig. 3 Effect of sorbent dose on the removal of Cr(VI) using, **a** WS AC (dose = 0.2, 0.3, 0.4, 0.6, 0.8 g, $C_0 = 100$ mg.L^{-1}, $T = 30$ °C, contact time = 30 min) and **b** MWCNTs (dose = 0.1, 0.15, 0.2, 0.3, 0.4 g, $C_0 = 100$ mg L^{-1}, $T = 30$ °C, contact time = 5 h)

concentration (from about 50 to 73 %). The limited size of pore openings and the electrostatic repulsion between negative charges of adsorbate ions result in the reduction of adsorption percentage. Interestingly, the equilibrium times are found to be the same for all the concentration levels studied.

The effect of Cr(VI) initial concentration at 20, 60 and 100 mg L^{-1} levels and constant dose of 0.15 g with contact time of 30 min are seen in Fig. 2b for MWCNTs. Different behavior is seen for this adsorbent, i.e., the percentage of Cr(VI) removal is increased with decreasing the initial concentration from about 100 to 53 %. It should be noted that the time scale for adsorption in the case of MWNT is very high compared to that of AC. At long time and higher initial concentrations, the ratio of available adsorption sites of MWCNTs to chromium ions is less and the binding sites being saturated.

Effect of sorbent dose

The effect of sorbent dose was investigated by changing the amount of AC from 0.2 to 0.8 g at 30 min contact time, keeping the initial Cr(VI) concentration and temperature constant at 100 mg L^{-1} and 30 °C, respectively (Fig. 3). Our observations show that the remaining chromium ions in the solution (unadsorbed ions) decreased by enhancing the sorbent dose for a fixed initial concentration due to greater surface area available for adsorption and also more effective contact between the adsorbent and Cr(VI) ions. It is also found that there is an optimum value of sorbent for each initial concentration which gives maximum removal.

Similar results can be found in Fig. 3b for MWCNTs. The amounts of MWCNTs were 0.1, 0.15, 0.2, 0.3, and 0.4 g for the same initial concentration and temperature at 5 h contact time. Adsorption was enhanced by increasing

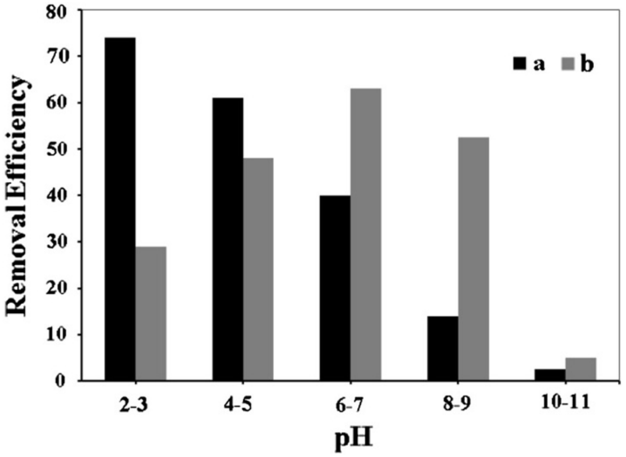

Fig. 4 Effect of pH on the removal of Cr(VI) ions using, **a** WS AC (dose = 0.3 g, $C_0 = 100$ mg L^{-1}, $T = 30$ °C, contact time = 30 min) and **b** MWCNTs (dose = 0.15 g, $C_0 = 100$ mg L^{-1}, $T = 30$ °C, contact time = 6 h)

the adsorbent dose until it reached to a constant value due to equilibrium.

Effect of pH

pH is one of the most important parameters controlling the metal ion adsorption. Figure 4 shows the effect of pH on adsorption of Cr(VI) with initial concentration of 100 mg L^{-1} at 30 °C for both adsorbents. For all different cases, the adsorbent amounts and contact times were kept constant at 0.3 g and 30 min for AC and 0.15 g and 6 h for MWCNTs. This figure shows that WS AC is more active at the lower pH range. The maximum adsorption of Cr(VI) is found in the pH range of 2–3 for AC and the removal percentage is almost negligible at pH values higher than 11. But in the case of MWCNTs, the best performance is seen in the pH range of 5–6.

The pH of system controls the adsorption capacity due to its influence on the surface properties of the adsorbent as well as ionic forms of the chromium solutions. The chromic acid predominates at pH values less than about 1.0, $HCrO_4^-$ at pH range of 1.0–6.0, and CrO_4^{2-} and $Cr_2O_7^{2-}$ at pH values above 6.0. In the case of AC, more adsorption at acidic pH indicates that lower pH results in an increase in H^+ ions on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and chromium ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0 may be due to the dual competition of two anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent, of which OH^- predominates. This is in accordance with earlier studies on the removal of Cr(VI) by different adsorbents [39]. It has also been suggested that, under acidic conditions, Cr(VI) could be reduced to Cr(III) in the presence of AC adsorbent.

The result of Boehm's test for WS AC shows that basic groups on the carbon surface are more than others. Therefore, by decreasing pH (or increasing H^+) of the solution, basic groups could adsorb chromium ions. In other words, by decreasing the negative charge density on the adsorbent surface, the electrostatic force of adsorption between Cr(VI) ions and surface increases.

The Boehm's test indicates that most of the functional groups on MWCNTs surface are phenolic. In the aqueous environment (especially at low pH), phenolic groups transform into C_xO. On the other hand, at low pH, both $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions coexist in the solution. In the presence of a reducing substrate (C_xOH), the Cr(IV) species are quickly reduced into Cr(III) ions as indicated by the following equations [40].

$$3C_xOH + Cr_2O_7^{2-} + 4H^+ \rightarrow 3C_xO + HCrO_4^- + Cr^{3+} + 3H_2O \quad (2)$$

$$3C_xOH + HCrO_4^- + 4H^+ \rightarrow 3C_xO + Cr^{3+} + 4H_2O \quad (3)$$

where C_x is the carbon. Cr(III) ions are not adsorbed or poorly adsorbed at these low pH values. Therefore, at $pH < 3.0$ the adsorption capacity is very low. Since the concentration of H^+ decreases at pH >3.0, the chemical reactions of (2) and (3) will not proceed. The adsorbent surface may become negative and adsorption operation does not happen anymore. One of the reasons for slow adsorption operation with MWCNTs is hydrolysis of phenolic group which is a slow reaction.

Adsorption isotherms

Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium of water and wastewater treatment applications. The linear form of Langmuir isotherm is given by the following equation [41]:

$$1/q_e = 1/q_m + 1/bq_mC_e \quad (4)$$

where q_e is the adsorbed amount at equilibrium (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), b is a constant related to the energy or net enthalpy of adsorption (L mg^{-1}), and q_m is the Langmuir constant related to maximum adsorption capacity. When $1/q_e$ is plotted against $1/C_e$, the straight line with slope of $1/bq_m$ is obtained, which shows that the adsorption of chromium on WS AC follows Langmuir isotherm. Langmuir constants, b and q_m, were then calculated and these values are given in Table 2.

The adsorption data are also analyzed by Freundlich model. The logarithmic form of Freundlich model is given by the following equation:

Table 2 Freundlich and Langmuir adsorption constants associated to adsorption isotherms of Cr(IV) on WS AC

Freundlich			Langmuir		
K_f (mg g^{-1})	n	R^2	q_m (mg g^{-1})	b (L mg^{-1})	R^2
1.45	1.13	0.98	166.5	0.007	0.98

Table 3 R_L values for Cr(VI) adsorption on to WS AC

C_0 (mg L^{-1})	100	150	200	250
R_L	0.588	0.487	0.416	0.363

$$\log q_e = \log K_f + 1/n \log C_e \tag{5}$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich parameters are also given in Table 2. The adsorption isotherms were determined at fixed temperature of 30 °C for Cr(VI) concentration range of 100, 150, 200, and 250 mg L^{-1}. All solutions contained fixed dose of 0.3 g adsorbent.

The good correlation coefficients showed that both Langmuir and Freundlich models are suitable for adsorption equilibrium of chromium ion.

R_L value indicates the type of isotherm. R_L values between 0 and 1 indicate favorable adsorption.

$$R_L = 1/1 + bC_o \tag{6}$$

where b is the Langmuir constant and C_0 is the initial metal ion concentration (mg L^{-1}). The results are presented in Table 3. R_L values for chromium were found to be between 0 and 1 for all concentrations at 30 °C, indicating favorable adsorption.

For comparison purposes, adsorption capacities of other adsorbents are collected from the literature and reported in Table 4. It is clear from the Table that the adsorption capacities of WS activated carbon for Cr(VI) ion are comparable with most other adsorbents.

Conclusion

Based on the present investigation, it can be concluded that the adsorption capacity of low-cost adsorbent (AC) from an agricultural based material is comparable with that of MWCNTs for chromium ion removal. In the batch adsorption technique studied, the ion removal was dependent on the adsorption time, metal ion concentration, adsorbent amount and pH of solution.

Table 4 Comparison of maximum adsorption capacity of WSAC and MWCNTs with other low-cost adsorbents or chromium removal

Adsorbents	pH	Temp.(°C)	Model	(mg g^{-1})	References
Bagass	6.0	25	Langmuir	0.0005	[42]
Soya cake	<1.0	20	Langmuir	0.00028	[43]
Raw rice bran	5	25	Langmuir	0.07	[44]
Maghemite nanoparticles	10	22.5	Freundlich	1.5	[45]
Almond shell (AS)	4	10	Langmuir	2.4	[46]
Almond	2	30	Langmuir	10.6	[47]
Beech (Fagus orientalis L.) Sawdust	1	25	Langmuir	16.1	[48]
Walnut shell (WS)	4	10	Langmuir	18.4	[49]
MWCNTs	5–6	30	Langmuir–Freundlich	24	This study
Carbon slurry	–	45	Langmuir	25.2	[50]
Walnut shell AC	2–3	30	Langmuir–Freundlich	35	This study
Activated carbon, CZ-105	3	–	Freundlich	40.4	[51]
Brown coal, YK	3	25	Langmuir	47.83	[52]
Carbon, F-400	2	30	Langmuir	48.5	[53]
Norit carbon (oxidized)	3.7	40	Langmuir	53	[54]
T. indica seed (TS)	6	50	Langmuir	80	[46]
Activated carbon obtained from black liquor lignin	3	25	Langmuir	80.0–92.6	[55]
Activated carbon (Acticarbone CXV)	3	25	Langmuir	124.6	[56]
Chitosan	4.0	25	Langmuir	154	[57]
Activated sludge	1.0	25	Langmuir	294.0	[58]

The experimental results indicated optimum operating conditions for each adsorbent. Chromium removal was found to be pH dependent and the efficiency was observed fairly high at pH = 2–3 for AC, in comparison with the pH = 5–6 for MWCNTs. Adsorption was increased by increasing the adsorbent dose and time at initial stages and then it became somewhat constant due to the attainment of equilibrium. The percentage of Cr(VI) removal was increased by enhancing the adsorbate concentration for WS AC and the opposite trend for MWCNTs (but at longer time).

The adsorption process can be modeled by Langmuir and Freundlich adsorption isotherms. The adsorptive capacity of WS activated carbon is comparable with other sorbents for chromium ion. This low-cost adsorbent with its rapid adsorptive ability would offer a promising technique for industrial wastewaters cleanup.

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