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Kinetics of Cr(VI) Sorption/Reduction from Aqueous Solution on Activated Rice Husk

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Abstract

A carbonaceous sorbent was prepared from rice husk via sulphuric acid treatment. After preparation and washing, the wet carbon with moisture content 85% was used in its wet status in this study due to its higher reactivity towards Cr(VI) than the dry carbon. The interaction of Cr(VI) and the carbon was studied and two processes were investigated in terms of kinetics and equilibrium namely Cr(VI) removal and chromium sorption. Cr(VI) removal and chromium sorption were studied at various initial pH (1.6–7), for initial Cr(VI) concentration (100 mg/l). At equilibrium, maximum Cr(VI) removal occurred at low initial pH (1.6–2) where, Cr(III) was the only available chromium species in solution. Cr(VI) removal, at such low pH, was related to the reduction to Cr(III). Maximum chromium sorption (60.5 mg/g) occurred at initial pH 2.8 and a rise in the final pH was recorded for all initial pH studied. For the kinetic experiments, approximate equilibrium was reached in 60-100 hr. Cr(VI) removal data, at initial pH 1.6-2.4, fit well pseudo first order model but did not fit pseudo second order model. At initial pH 2.6-7, Cr(VI) removal data did not fit, anymore, pseudo first order model, but fit well pseudo second order model instead. The change in the order of Cr(VI) removal process takes place in the pH range 2.4-2.6 under the experimental conditions. Other two models were tested for the kinetics of chromium sorption with the data fitting well pseudo second order model in the whole range of pH. An increase in cation exchange capacity, sorbent acidity and base neutralization capacity was recorded for the carbon sorbent after the interaction with acidified Cr(VI) indicating the oxidation processes on the carbon surface accompanying Cr(VI) reduction.

Keywords : *kinetics, sorption, reduction, carbon, Cr(VI), Cr(III), rice husk*

1. Introduction

Chromium occurs in aqueous systems as both Cr(III) and Cr(VI). Cr(III) apparently plays an essential role in plant and animal metabolism when emitted in low levels in the environment. On the other hand, Cr(VI) is directly toxic to bacteria, plants and animals [1]. The US EPA [2] has set the maximum contaminate level (MCL) for Cr(VI) in domestic water supplies to be 0.05 mg/l due to its sever toxicity. Main industrial sources of chromium pollution are leather tanning, electroplating, paint and pigment, textile, dyeing, canning, metal finishing and chromate preparation.

Cr(VI) is typically present as anion and its direct precipitation is not usually practical. Instead, the anionic species are typically reduced to Cr(III) and then precipitated as chromic hydroxide by using lime. However, it is a process which can give an incomplete removal, has a high chemical requirement and produces a voluminous toxic sludge which may pose disposal problems [3]. Although ion exchange and activated carbon adsorption are other available treatment methods, they suffer from the need of higher capital investment. The problems associated with on-site regeneration and re-use has made the process less attractive.

Adsorption of Cr(VI) on activated carbon and other adsorbents has been the subject of various studies [3-9]. However the results which have been reported are variable, particularly in terms of the optimum pH for chromium removal. Reduction of Cr(VI) to Cr(III) was observed with different sorbents [4, 5, 9-13] at low pH values. Using activated carbon, Perez-candela *et al*. [7] found that Cr(VI) is reduced at $pH < 3$ while Huang and Wu [12], in their study, found that the reduction occurs at $pH < 6$.

In this paper, two processes were studied: Cr(VI) removal and chromium sorption. Cr(VI) removal from the aqueous solution occurs via reduction to Cr(III) and adsorption of Cr(VI) on the sorbent surface. The process is followed by analyzing Cr(VI) concentration in the aqueous solution. However, chromium sorption refers to the uptake of total chromium, Cr(VI) and evolved Cr(III), from the aqueous solution by the sorbent and the process is followed by analyzing total chromium in the aqueous solution. In this paper, both processes were investigated for the kinetics and equilibrium, using initial Cr(VI) concentration, 100 mg/l, in the initial pH range 1.6-7. Different kinetic models were examined.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. Rice husk was received from a local rice mill and washed with a stream of distilled water through a sieve of 16 mesh (Tyler Standard Screen Scale), to remove dirt, dust and any superficial impurities. The husk was put in trays and left to dry in open air at room temperature to constant weight. The sorbent was prepared as follows: Clean air-dried rice husk (20 g) was weighed in a clean dry beaker of capacity 500 ml. 100 ml of 13 M sulphuric acid were added to the rice husk and the mixture was heated to 180°C in 20 minutes with occasional stirring. The temperature was kept at 180 ± 2°C for 20 minutes. The resulting black mixture was allowed to cool, and then filtered using a Buchner funnel under vacuum. The black spent sulphuric acid (black liquor) was filtered off and the carbonized material was washed several times with distilled water and was stored under dilute acidic conditions (dilute sulphuric acid, pH 1.5-2) to avoid any bacterial growth. Before use for Cr(VI) sorption, a sample of the carbonized product was washed in Gooch crucible until the wash water did not show a change of methyl orange color and did not show a precipitate with barium chloride solution. The sample was washed again with a stream of distilled water between two sieves of 16 and 60 mesh (Tyler Standard Screen Scale) to remove fine particulates and to select a suitable size range for the experiments. The sample was transferred to a Gooch crucible and left under suction for 30 minutes. Suitable samples of the carbonaceous sorbent were then used in sorption experiments (as a wet sorbent) and a sample of 1 g was separated to measure the moisture content by oven drying at 120°C until constant weight. The wet sorbents used in this study possess ~85% moisture. For work under dry conditions, the carbonized wet product (acid free) was dried in an oven at 120°C to constant weight, transferred to a desiccator to cool and finally stored in a dry, clean and well-closed polyethylene jar. From preliminary experiments in addition to a previous study [14], if the carbon that was prepared via sulphuric acid treatment is dried, its efficiency for Cr(VI) removal and total chromium sorption decreases with a slower kinetics. This is probably related to shrinkage and compaction of the sorbent on drying giving narrower pores for the diffusion of the Cr(VI) ions [14] and accordingly, the wet sorbent (85% moisture) was selected in the present study for the sorption/reduction of Cr(VI). The dry sorbent was used for physico-chemical tests before and after the sorption/reduction processes.

2.2. Methods

A stock solutions of Cr(VI), 1000 mg/l, was prepared in distilled water using $K_2Cr_2O_7$ and all the working solutions were prepared by suitable dilution in distilled water. Kinetic and batch experiments were prepared by mixing ~0.67 g wet sorbent (equivalent to 0.12 g on dry basis) with 100 ml of Cr(VI) solution (100 mg/l) at required initial pH (1.6-7) at 25°C in a shaking water bath (100 rpm). The pH was adjusted by adding few drops of 0.1 M H_2SO_4 or 0.1 M NaOH prior to the addition of the sorbent.

For the kinetic experiments, at different periods of time, the pH of the reaction solution was recorded and aliquot of supernatant was withdrawn for the analysis of Cr(VI) and total chromium. For the batch experiments, after the equilibrium time was reached, the final pH was recorded and aliquot of supernatant was withdrawn and analyzed for Cr(VI) and total chromium.

For Cr(VI) removal that is based on the decrease in Cr(VI) concentration with time, two kinetic models were investigated: pseudo first order and pseudo second order models [15], (equations 1&2, respectively).

$$\log C_t = \log C_o - \frac{k_1}{2.303} \cdot t \tag{1}$$

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \tag{2}$$

where C_o and C_t are the concentration of Cr(VI) at equilibrium and at time t, k_1 (hr^{-1}) is the pseudo first order rate constant and k_2 ($l\ mg^{-1}\ hr^{-1}$) is the pseudo second order rate constant for Cr(VI) removal. For chromium sorption, which is based on the decrease in total chromium concentration with time, two kinetic models were tested: pseudo first order model and pseudo second order model [16, 17], (equations 3&4, respectively).

$$\log(q_e - q_t) = \log q_e - k_1' t/2.303 \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2' q_e^2} + \frac{t}{q_e} \tag{4}$$

Where q_e and q_t are the amount of chromium sorbed at equilibrium and at time t per unit weight of sorbent (mg/g), k_1' (hr^{-1}) is the rate constant for the pseudo first order model, k_2' ($g\ mg^{-1}hr^{-1}$) is the rate constant of the pseudo second order model. Here, the initial sorption rate $h = k_2 q_e^2$ ($mg\ g^{-1}hr^{-1}$).

Physicochemical properties of the dry sorbent were measured. ASTM standard methods were used to measure the cation exchange capacity (CEC) [18]. Sorbent pH (sorbent acidity) was measured as follows [19, 20]: a sample of sorbent (0.100 g) was mixed with distilled decarbonated water (20 cm^3) and two drops of acetone, to facilitate wetting of the sample, and refluxed for 15 min. After cooling, the pH of the sludge was obtained using a pH meter and combined pH electrode.

Base neutralization capacity was measured by Boehm titrations [21]. Neutralization of 0.1 M sodium bicarbonate and sodium hydroxide, and 0.05 M sodium carbonate, by the dry sorbent was studied by mixing 0.25 g sorbent portions with 50 ml of the respective solution in 100 ml Quickfit polyethylene bottles. The suspensions were flushed with nitrogen gas to remove oxygen present [22]. This step was essential to avoid the possibility of base-catalyzed auto-oxidation of carbonaceous sorbents in the presence of oxygen [23]. The suspensions were shaken mechanically for 72 hours covering the equilibrium time. The fall in concentration of each solution was determined by titration of an aliquot of the supernatant liquid against 0.1 M HCl.

Cr(VI) was analyzed spectrophotometrically using 1,5 diphenylcarbazide method [24] at λ max 540 nm (Unicam UV/VIS spectrophotometer UV2 5000). Total chromium was determined via Perkin Elmer 2380 atomic absorption spectrophotometer. The difference in concentration between the total chromium and Cr(VI) gives Cr(III) concentrations. Experiments and analysis were carried out at least 3 times and maximum analytical error was found to be less than 5%.

3. Results and Discussion

Rice husk, as a precursor material, possesses cellulose, hemicellulose and lignin as main components. Concentrated sulphuric acid behaves as an extremely strong dehydrating agent and a strong oxidizing agent because of its tendency to lose an atom of oxygen to form sulphurous acid, H_2SO_3, which readily decomposes to sulphur dioxide and water [25]. Under the preparation conditions of the sorbent, carbonization with partial oxidation took place to the cellulose and hemicelluloses in addition to partial fragmentation to the lignin components [26] resulting in a carbonaceous material loaded with function groups on the surface such as –COOH and –OH as examined later in the paper via physico-chemical tests. These functional groups act as ion exchange sites for metal cations. The carbonaceous material possesses sorptive and reductive properties [27]. Surface area of the dry sorbent was measured via nitrogen adsorption and was found to be 65 m^2/g.

3.1. Equilibrium Studies

In literature, optimum pH for Cr(VI) sorption was reported variable and this could be related to the variation in the experimental conditions including initial Cr(VI) concentration, sorbent type and reduction and sorption capabilities towards Cr(VI) for the different sorbents. Table 1 shows a summary of Cr(VI) adsorption capacities on various sorbents.

In the present study, using 100 mg/l (initial Cr(VI) concentration), a sorption maximum, 60.5 mg/g, appears at initial pH 2.8, Fig. 1. At initial pH < 2.8, Cr(VI) was barely detected in solution and Cr(III) was the main constituent of total chromium. A slight rise in the final pH was observed with low chromium sorption, (Table 2). The final pH was low enough that protons compete with evolved Cr(III) ions for

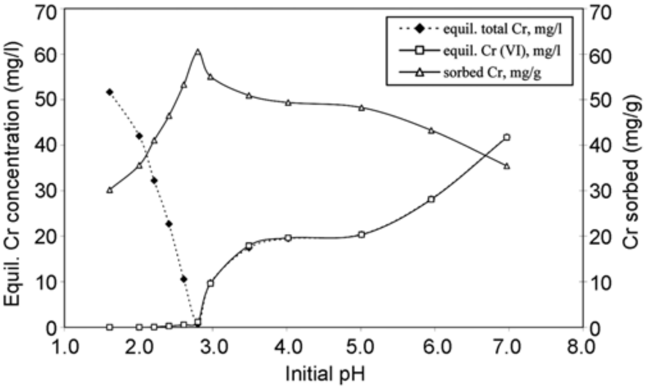

Fig. 1. A plot of equilibrium Cr concentrations and sorbed Cr at different initial pH values at 25°C. (Initial Cr(VI) concentration 100 mg/l).

Table 1. Summary of Cr(VI) adsorption capacities on various sorbents

Type of adsorbent	Maxi. Cr conc. used (mg/l)	Optimum pH	Cr sorbed (mg/g)	Reference
Coconut shell based activated carbon	20	2.5	2.0	[28]
Coconut shell charcoal	25	6.0	2.18	[29]
Nitric oxidized coconut shell charcoal	25	4.0	10.88	[29]
Sawdust	50	6.0	3.3	[30]
Leaf mould	1000	2.0	43.0	[5]
Commercial activated carbon	1000	3.0	145.0	[9]
Granular activated carbon (filtrasorb 400)	207	6.0	57.7	[12]
Sphagnum moss peat	1000	1.5	119.0	[4]
Hazelnut shell activated carbon	300	1.0	170.0	[31]
Carbon from flax shive with sulphuric acid treatment (wet)	220	2.4	168.9	[27]
Carbon from flax shive with sulphuric acid treatment (dry)	220	2.2	123.7	[27]
Carbon from rice husk with sulphuric acid treatment (wet)	100	2.8	60.5	Present study

Table 2. Initial and final pH for Cr(VI) sorption

Initial pH	1.6	2.0	2.2	2.4	2.6	2.8	3.0	3.5	4.0	5.0	6.0	7.0
Final pH	1.7	2.2	2.6	3.0	3.7	4.7	5.3	6.2	6.4	6.5	6.8	7.5
Cr sorbed (mg/g)	30.2	35.6	41.0	46.5	53.3	60.5	55.0	50.0	49.4	48.3	43.3	35.5

sorption at ion exchange sites on the sorbent surface, such as -COOH and -OH [14].

At initial pH 2.8, total chromium at equilibrium was minimal constituting Cr(VI) mostly with little or no Cr(III) with a large increase in the final pH that apparently allowed most of the evolved Cr(III) to be sorbed via ion exchange and complexation.

At initial pH 3-7, as the initial pH increases, sorption capacity decreases, with a rise in the final pH, however, no Cr(III) was detected in equilibrium solution. Applying such high pH values, Cr(VI) reduction is expected to decrease due to the lack of protons, and, thus, little Cr(III) are evolved in solution. Accordingly, low chromium sorption is achieved even with an expected extent of physico-chemical adsorption of Cr(VI) within this pH range [27, 32].

Nakano *et al*. [33], in their study of Cr(VI) adsorption on condensed tannin gel, found that Cr(VI) was reduced on tannin gel and the evolved Cr(III) was sorbed via ion exchange on carboxyl and hydroxyl groups with sorption maximum at pH 2. Sorption capacity decreased below initial pH 2 due to the elution of Cr(III), and above initial pH 2 due to the insufficiency of protons to produce Cr(III).

The molar ratio of initial concentrations of protons and Cr(VI), [H$^+$]/[Cr(VI)], at maximum sorption was 0.82. According to Kim and Zoltek [34], the optimum removal of chromium occurs when the initial concentrations [proton: chromium (VI)] ratio is 1 : 1, however, Sharma and Forster [9] found that, at optimum chromium removal, such ratio ranged from 2.6 at initial Cr(VI) concentration 20 mg/l to 0.16 when the initial concentration was 1000 mg/l. In the present study, the range of [H$^+$]/[Cr(VI)] ratio, at maximum sorption, was found to be nearer to the 1 : 1 ratio than that reported by Sharma and Forster [9]. The variation in the [H$^+$]/[Cr(VI)] ratio at sorption maxima is perhaps related to the difference in the reactivity of the sorbents towards Cr(VI).

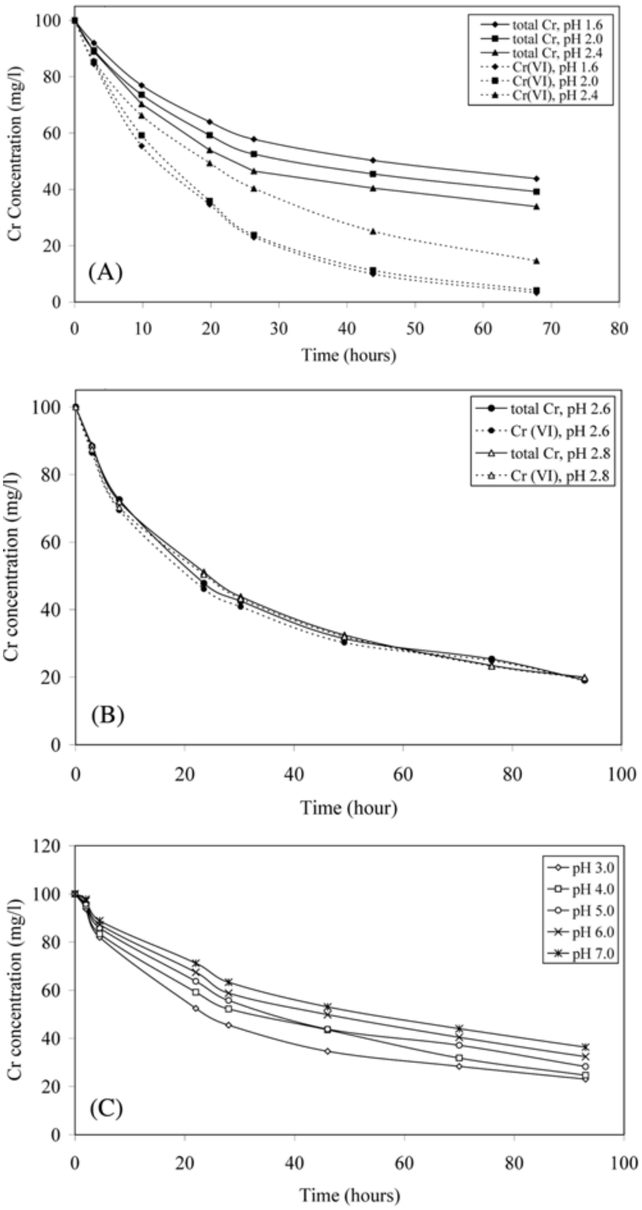

Fig. 2. Concentrations of Cr(VI) and total chromium versus time at different initial pH values. (a) pH 1.6-2.4. (b) pH 2.6 & 2.8. (c) pH 3.0-7.0.

3.2. Kinetics of Cr(VI) Removal

Kinetics of Cr(VI) removal and chromium sorption in the pH range 1.6-7 is relatively slow reaching equilibrium in 60-100 hr, (Fig. 2a-2c). Investigating the concentrations of Cr(VI) and total chromium with the progress of time showed a decrease in both concentrations. At initial pH 1.6-2.4, Cr(VI) was found to decrease faster than total chromium (Fig. 2a). The difference between total chromium and Cr(VI) is apparently unadsorbed Cr(III) which was produced as a result of Cr(VI) reduction. Under such low initial pH conditions, it is unlikely that Cr(VI) is adsorbed without being reduced to Cr(III) and the rate of Cr(VI) removal is clearly higher than that of total chromium sorption (Fig. 2a).

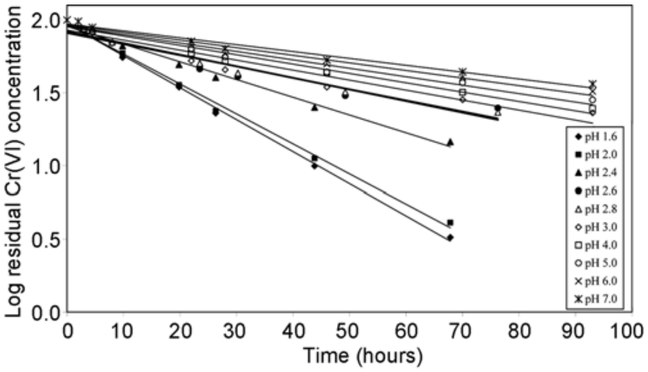

Fig. 3. Application of pseudo first order model for Cr(VI) removal at different initial pH values.

Accordingly, Cr(VI) removal in the pH range 1.6-2.4, refers to Cr(VI) reduction. By approaching equilibrium, the concentration of Cr(VI) further decreases and Cr(III) concentration increases, and at equilibrium, Cr(III) was the most abundant chromium species in solution, clearly identified by its greenish color.

At initial pH 2.6 and 2.8, the difference in concentration between Cr(VI) and total chromium decreases as time proceeds and, by approaching equilibrium, both concentrations overlap, (Fig. 2b). In the pH range 3-7, there was no difference in concentration of Cr(VI) and total chromium, and Cr(III) was not available in solution during the kinetic experiments, (Fig. 2c). Within that pH range (pH 3-7), as the initial pH increases, the extent of Cr(VI) reduction decreases, due to protons insufficiency, and an extent of physico-chemical adsorption of Cr(VI) is expected to take place [27, 32]. In addition, any evolved Cr(III) at such high initial pH are most probably sorbed fast on the sorbent surface before being released in solution.

Cr(VI) removal data were found to fit well pseudo first order model (equation 1) at initial pH 1.6-2.4 and deviates from fitting at initial pH 2.6-7, as shown in Fig. 3 and Table 3. Rate constants (k_1), at initial pH 1.6 and 2, are almost similar being 0.0505 and 0.0473 hr^{-1} with R^2 values 0.998 and 0.996, respectively. However, k_1, at initial pH 2.4, decreases to 0.028 hr^{-1} with R^2 value 0.990.

Table 3. Modelling of Cr(VI) removal at different initial pH

Initial pH	Pseudo first order model		Pseudo second order model	
	k_1 (hr^{-1})	R^2	k_2 (l/mg hr)	R^2
1.6	0.0505	0.998	0.00282	0.885
2.0	0.0473	0.996	0.00221	0.909
2.4	0.0280	0.990	0.000504	0.978
2.6	0.0182	0.915	0.000426	0.987
2.8	0.0175	0.974	0.000427	0.999
3.0	0.0158	0.931	0.000354	0.994
4.0	0.0147	0.971	0.000317	0.993
5.0	0.0134	0.965	0.000262	0.992
6.0	0.0120	0.969	0.000217	0.996
7.0	0.0108	0.974	0.000185	0.998

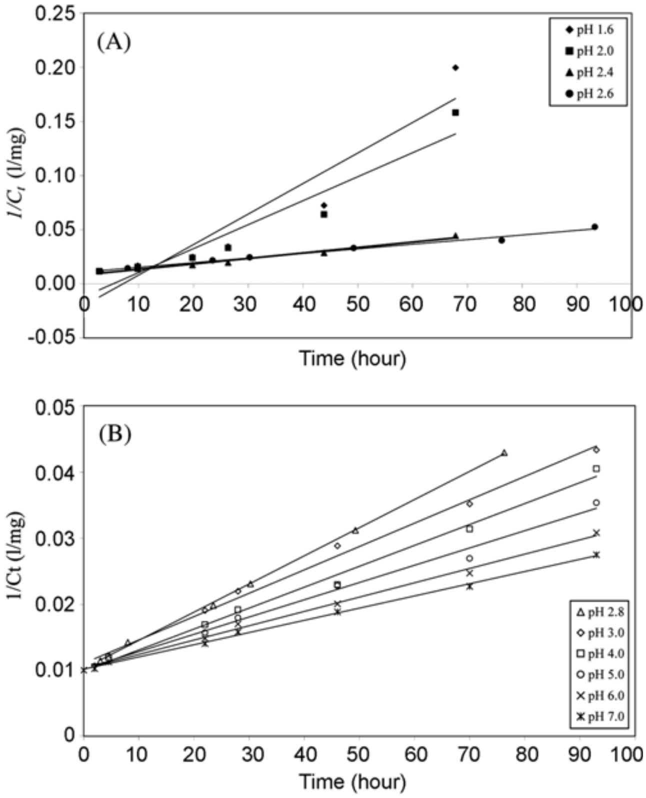

Fig. 4. Application of pseudo second order model for Cr(VI) removal at different initial pH values. (a) pH 1.6-2.6. (b) pH 2.8-7.0. (C_t : Cr(VI) concentration at any time t)

By examining the pseudo second order kinetic model (equation 2) for Cr(VI) removal, the data did not fit the model at initial pH 1.6-2.4, fit poorly at initial pH 2.6 and fit well at initial pH 2.8-7, Fig. 4a & 4b & Table 3. The change in the order of Cr(VI) removal process takes place at initial pH 2.4-2.6. Since all the other experimental conditions are the same, such change in the process order is clearly related to the initial pH or, in other words, the initial proton concentration.

Considering the carbon concentration during the kinetic experiment is constant, being a solid material, the order of Cr(VI) removal process depends on $[H^+]$ and [Cr(VI)] concentrations. Ratio of $[H^+]$/[Cr(VI)] at initial pH 1.6 and 2 and were 13.1, and 5.2, respectively, showing that $[H^+]$ is high enough during the kinetic experiment that it can be considered as constant. Thus, Cr(VI) removal follows pseudo first order model. At initial pH 2.4, the $[H^+]$/[Cr(VI)] ratio is 2.1. $[H^+]$ is almost double Cr(VI) concentration, however the process still shows a good fitting for pseudo first order model. $[H^+]$/[Cr(VI)] ratio at initial pH 2.6, 2.8 and 3 is 1.3,

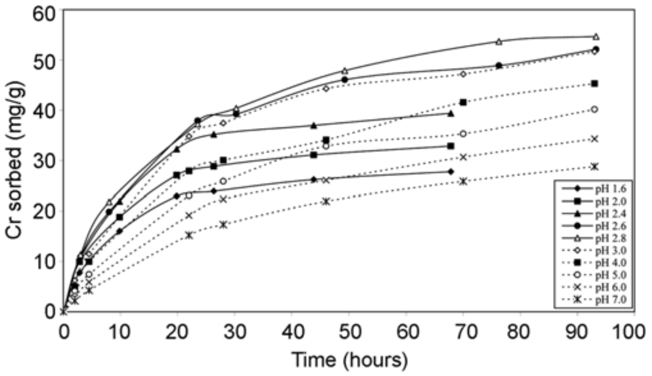

Fig. 5. Chromium sorption versus time at different initial pH values.

0.82 and 0.52, respectively and as the pH further increases until initial pH 7, the ratio $[H^+]/[Cr(VI)]$ further decreases. In that pH range 2.6-7, Cr(VI) removal is affected by both of [Cr(VI)] and $[H^+]$ and thus, the process follows pseudo second order model. In a previous study, the kinetics of Cr(VI) removal on a carbonaceous sorbent from flax shive prepared by sulphuric acid treatment [27] followed pseudo first order model (equation 1) at initial pH 1.5 and pseudo second order model (equation 2) at initial pH 4.5.

3.3. Kinetics of Chromium sorption

Fig. 5 shows that pH 2.8 is optimum for maximum chromium uptake and Fig. 6 shows the change of pH during the kinetic experiments. A drop in the pH value was observed in the early stages of the experiment (within the first few hours) followed by a pH rise with the progress of time. That pH drop is related to the sorbent acidity resulted from the preparation conditions of the carbonaceous sorbent, which produced functional groups such as -COOH and -OH on the sorbent surface [14]. It seems that the release of protons from the sorbent surface into the aqueous solution is faster than protons consumption in the reduction process causing a pH drop to values slightly lower than the initial pH.

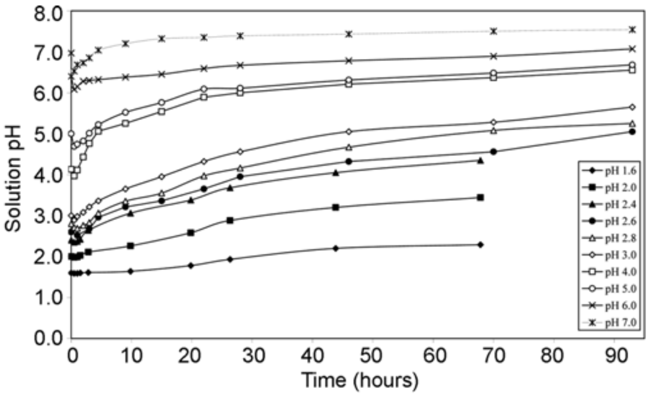

Fig. 6. Variation of solution pH versus time at different initial pH values.

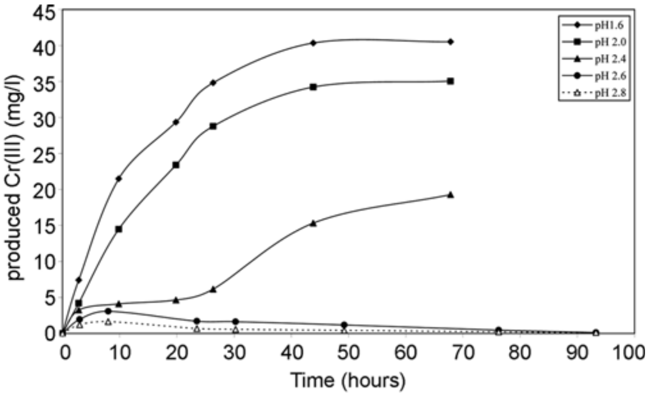

Fig. 7. Concentration of evolved Cr(III) in solution with time at different initial pH values.

Fig. 7 shows the variation in concentration of evolved Cr(III) in the pH range 1.6-2.8 versus time. With the progress of time, Cr(III) concentration increases at initial pH 1.6-2.4 until the equilibrium was reached. The low sorption of evolved Cr(III) at initial $pH < 2.4$ is clearly related to the high proton concentration that competes with evolved Cr(III) for binding sites on the carbon surface such as -COOH and -OH.

At initial pH 2.6 and 2.8, Cr(III) develops in the early stage of the sorption process and then slowly decreases almost to zero as equilibrium approaches. In the early stages of the kinetic experiments, the protons released due to the sorbent acidity compete with Cr(III) ions for ion exchange sites. As the reaction proceeds, more protons are consumed due to Cr(VI) reduction, and this allows most of evolved Cr(III) to be sorbed via ion exchange (Fig. 7) and, at equilibrium, almost no Cr(III) was available in solution.

At initial $pH > 2.8$, Cr(III) was not detected in solution during the experiment as a result of the rise in the pH, due to Cr (VI) reduction, allowing the evolved Cr(III) to be sorbed via ion exchange and complexation.

An important parameter in considering the adsorption of charged species from aqueous solution by the carbonaceous sorbent is the isoelectric point (IEP). This is the point at which the electrokinetic potential of the sorbent (zeta potential) equals zero [35]. IEP of the carbon under investigation represents the external surface charge of the carbon particle was detected at pH 1.2 while pH_{ZPC}, the point of zero charge, that represents the total surface charge of the particle was detected at pH 2.6. A decrease in the pH below the pH_{ZPC} value, both the surface charge of the sorbent and Cr(III) ions are positively charged and the uptake of metal ions is an exchange process of Cr(III) and protons [36, 37]. An increase in the pH value above pH_{ZPC} shows an increase in Cr(III) uptake in which the surface of the sorbent is negatively charged and the sorbate species are still positively

Table 4. Modelling of chromium sorption at different initial pH

Initial pH	Pseudo first order model		Pseudo second order model		
	k_1' (hr^{-1})	R^2	k_2' (mg/g.hr)	R^2	h (g/mg.hr)
1.6	0.0620	0.976	0.0038	0.999	3.729
2.0	0.0633	0.977	0.0034	0.999	4.636
2.4	0.0622	0.948	0.0025	0.998	5.048
2.6	0.0348	0.974	0.0012	0.998	4.072
2.8	0.0495	0.976	0.0010	0.998	4.058
3.0	0.0348	0.970	0.00092	0.998	3.406
4.0	0.0329	0.978	0.00086	0.993	2.533
5.0	0.0304	0.978	0.00082	0.995	2.023
6.0	0.0341	0.953	0.00078	0.997	1.522
7.0	0.0350	0.966	0.00072	0.999	1.111

charged [36, 37]. However, the sorption maximum that appeared at initial pH 2.8 is not only related to the value of pH_{ZPC} but mainly to the extent of Cr(VI) reduction together with the rise in the final pH that allows the evolved Cr(III) to be sorbed via ion exchange. Additionally, the oxidation process of the carbon by acidified Cr(VI) continues until equilibrium is reached. This perhaps leads to a change in the values of IEP and pH_{ZPC} of the sorbent during the kinetic experiments. Thus, a full study of electrophoretic mobility and pH titration of the carbonaceous sorbent during the reaction with acidified Cr(VI) at different conditions will be carried out in the near future.

Data of chromium sorption were found to fit well the pseudo second order model (equation 4) in the whole pH range studied, Table 4. However, those data did not fit the pseudo first order model (equation 3), Fig. 8, Table 4. This indicates that sorption of total chromium complies very well with pseudo second order reaction and an activated sorption mechanism, and the rate depends on both of the sorbent and sorbate concentrations [16]. In literature, Cr(VI) sorption varies in model fitting. In some studies [6, 38-40], Cr(VI) sorption followed pseudo first order model while, other studies found that the process followed pseudo second order model [4, 5, 9, 11, 41]. Such variation in the sorption process order is probably related to the variation in the experimental conditions, sorbent type and the difference in the reactivity of the sorbents towards Cr(VI).

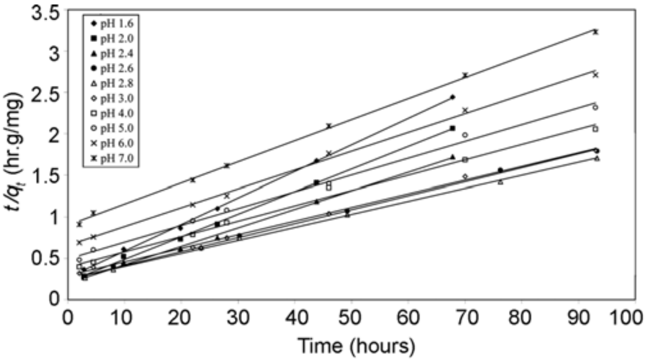

Fig. 8. Application of pseudo second order model for chromium sorption at different initial pH values.

3.4. Physico-chemical characterization of the carbon sorbent

Physicochemical properties of the dry sorbent before and after the reaction with 100 mg/l of Cr(VI) at initial pH 1.6 are shown in Table 5. Sorbent acidity (the pH of the aqueous slurry of the carbonaceous sorbent) that provides a convenient indicator of the surface groups on carbon sorbent has increased after the reaction with Cr(VI) at initial pH 1.6. The pH of the carbon is mainly related to the concentration of carboxylic groups [42]. CEC which is a measurement of the total amount of exchangeable cations that can be held by a sorbent, was found to increase for the sorbent after the reaction with acidified Cr(VI) indicating the presence of more acidic groups on the sorbent surface, such as -COOH, Table 5. The differences of surface functionalities developed by the preparation method and further surface oxidation after the reaction with acidified Cr(VI) were determined by Boehm titrations [21, 22, 42]. The three bases used in titration are considered as approximate probes for acidic functionalities: $NaHCO_3$ (carboxylic), Na_2CO_3 (carboxylic and lactonic), NaOH (carboxylic, lactonic and phenolic). The surface functionalities are listed in Table 5. An increase in the concentration of carboxylic and lactonic groups on the carbon surface was found after the reaction with acidified Cr(VI), as a result of the oxidation processes occurring on the carbon surface. However, phenolic groups concentration decreases after the oxidation reaction which could be attributed to their further oxidation to either lactonic or carboxylic groups. Generally, the increase in carbon acidity, cation exchange capacity and base neutralization capacities after the reaction

Table 5. Physico-chemical properties of the carbon sorbent

Dry sorbent	pH	CEC (meq/g)	Surface acidic functionalities based on weight (meq/g)		
			Carboxyl*	Lactone*	Phenol*
Before reaction	2.64	1.35	2.17	0.42	2.01
After reaction	2.53	1.49	2.71	0.73	1.23

*$NaHCO_3$ (carboxyl), Na_2CO_3 (carboxyl and lactone), NaOH (carboxyl, lactone and phenolic)

with acidified Cr(VI) indicates the oxidation processes on the carbon surface accompanying Cr(VI) reduction. Redox processes include Cr(VI) reduction (equation 5) and carbon oxidation to carbon oxygen functionalities (equations 6-8).

$$CrO_4^{2-} + 8\ H^+ + 3e^- = Cr^{3+} + 4\ H_2O\ (+1.350\ V) \quad (5)$$

$$\begin{aligned}&\sim\text{C-H} + \text{Cr (oxidized)} + H^+ \\ &\quad = \sim\text{C-OH} + \text{Cr (reduced)} + H_2O\end{aligned} \quad (6)$$

$$\begin{aligned}&\sim\text{C-H} / \sim\text{C-OH} + \text{Cr (oxidized)} + H^+ \\ &\quad = \sim\text{C=O} + \text{Cr (reduced)} + H_2O\end{aligned} \quad (7)$$

$$\begin{aligned}&\sim\text{C-H} / \sim\text{C-OH} + \text{Cr (oxidized)} + H^+ \\ &\quad = \sim\text{COOH} + \text{Cr (reduced)} + H_2O\end{aligned} \quad (8)$$

4. Conclusion

The carbon prepared by sulphuric acid treatment is efficient sorbent with high capability of Cr(VI) reduction. Sorption of Cr(VI) at different initial pH shows a maximum value at initial pH 2.8. At pH < 2.8, sorption decreases because of the protons competition with evolved Cr(III) for ion exchange sites while at initial pH > 2.8, sorption decreases due to proton insufficiency where the extent of Cr(VI) reduction decreases. Cr(VI) sorption maxima appears when reasonable reduction of Cr(VI) to Cr(III) occurs (and, as a result, generation of more ion exchange groups on the sorbent surface) with a significant pH rise that allows the sorption of most of the evolved Cr(III) via ion exchange.

Cr(VI) removal data at initial pH 1.6-2.4 fit well pseudo first order model while at pH 2.6-7, those data did not fit the pseudo first order model but fit pseudo second order model instead. The initial proton concentration between initial pH 2.4 and 2.6 seems responsible for the process order change. At pH 1.6-2.4, proton concentration is high enough to be considered as constant during the kinetic experiment, thus, Cr(VI) removal follows pseudo first order model. However, at pH 2.6-7, concentration of protons is low and the change in both concentrations (protons and Cr(VI) ions) during the experiment affects directly the rate of the process and thus, the process follows pseudo second order model.

Sorption of total chromium follows pseudo second order process in the pH range (1.6-7) showing that the rate of the process depends on sorbent and sorbate concentrations and the process follows an activated sorption mechanism.

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