

Treatment of liquid waste by sorption of toxic metal (Cr) using one-step steam pyrolysis corn cobs activated carbon

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Abstract: In the present study, a low-cost adsorbent is developed from the naturally and abundantly available biomass (corn cobs). The removal of Cr (VI) from synthetically prepared aqueous solutions and laboratories effluent of Nuclear Materials Authority was studied. The batch experiments were carried out to investigate the effect of type of the biomass and method of preparation, initial pH, contact time, temperature, adsorbent weight, and initial Cr(VI) concentration. The equilibrium data for the adsorption of Cr(VI) on steam pyrolyzed at 750 °C corn cobs activated carbon (CC-S75) was tested with various adsorption isotherm models; Langmuir, Freundlich and Tempkin equation. The Langmuir isotherm model is found to be the most suitable one with maximum adsorption capacity of 109.53 mg g⁻¹ at an initial pH value of 1. The adsorption process follows the second-order kinetics. Desorption of Cr(VI) from loaded CC-S75 using acid and base exhibited a higher desorption efficiency. The interference of other ions which are generally present in the laboratories effluent streams on the Cr(VI) removal was investigated. Finally, the prepared CC-S75 is applicable for treatment of wastewater and laboratories effluents containing toxic heavy metals.

Key words: Liquid waste; Chromium; Steam pyrolysis; Biomass; Corn cobs; Laboratories effluent.

1 INTRODUCTION

The increasing contamination of urban, industrial wastewaters and laboratories effluent by toxic metal causes significant environmental pollution [1-3]. All over the world, chromium is abundantly available in nature. The most common forms of chromium are trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] which are commonly used in various industrial processes. Cr(VI) is a metal particle that occurs naturally in rocks but is most commonly produced by industrial processes. It is present in many different compounds [NH₄)₂Cr₂O₇; CaCrO₄; CrO₃; PbCrO₄; K₂CrO₄; K₂Cr₂O₇; Na₂CrO₄; SrCrO₄; and ZnCrO₄] which has a variety of industrial applications. Cr(VI) is also used in various other industries such as electroplating, glass, ceramics, fungicides, rubber, fertilizers, tanning, mining, metallurgical, etc. [4-7]. Its ability to react with other elements makes hexavalent chromium a health hazard. Cr(VI) is highly mobile and is considered acutely toxic, carcinogenic and mutagenic to the living organisms, and hence more hazardous than other heavy metals. In addition, it also has an effect on human skin, liver, kidney, and respiratory organs. This results in a variety of diseases such as dermatitis, bronchitis, perforation of nasal septum, bronchogenic carcinoma, liver damage, ulcer formation, etc. [8-10]. Therefore, it is necessary to eliminate Cr(VI) from the environment, in order to prevent the deleterious impact of Cr(VI) on ecosystem and public health. Because of the stricter environmental regulations, a cost effective alternate technology for the treatment of Cr(VI) contaminated wastewater is highly desired by the industries [11]. There are various treatment technologies available to remove Cr(VI) from wastewater such as chemical precipitation, ion-exchange, membrane separation, electrocoagulation, solvent extraction, reduction, reverse osmosis, and adsorption [12-18]. These techniques are economically expensive and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or waste

products which require proper disposal without creating any problem to the environment [19,20]. Therefore, there is a dire need of a treatment method which is simple, effective and inexpensive [3]. Adsorption when combined with an appropriate step of desorbing the Cr(VI) from adsorbent and avoiding the problem of disposal of adsorbent is a cost effective and versatile method for the removal of Cr(VI) [21]. The advantages of the adsorption process prompted to extend the use of other materials with structural, compositional or chemical characteristics suitable to make this technique with high Cr(VI) retention values and thus it has a high potential for the Cr(VI) removal from wastewater streams [9]. It means that the selection of an adsorbent is a key factor for the use of adsorption as a treatment technique for Cr(VI) removal.

The cost associated with commercial adsorbents make adsorption process very expensive which has led to the search for new strategies for developing low-cost materials with a good capacity for Cr(VI) removal [22,23]. In the recent years, several studies have been reported on various low-cost adsorbents such as wool, used tyres, fungal biomass, green algae, maple sawdust, sugar industry waste, distillery sludge, soya cake, red mud, activated carbon derived from fertilizer waste, tea factory waste, Turkish brown coal, moss peat, hazelnut shell, coconut trees, lignocellulosic residues, rice bran [24-40], activated neem leaves [3], activated tamarind seeds [2]. However, many of these naturally available adsorbents have low chromium adsorption capacity. Thus, there is a need to develop or find innovative low-cost adsorbents which have a high adsorption capacity [5].

The objective of the present study is to investigate the possible use of corn cobs as an alternate adsorbent material for the removal of Cr(VI) from wastewater. Batch experiments are carried out for kinetic studies from liquid waste and laboratories effluents. The influence of various important parameters was investigated. The Langmuir, Freundlich and Tempkin,

equation models are used to fit the experimental equilibrium data obtained in this study. Pseudo first-order, second-order and Elovich kinetic models are used to evaluate the mechanism of adsorption. A feasible method for the desorption of Cr(VI) from the used adsorbent was proposed using acid and base treatment. Effect of the interfering of other ions present in the wastewater generated in electroplating, laboratories effluent and tanning industries on the removal of Cr(VI) was studied. One of the method was proposed to tackle the problem of disposal of the acid and base solution obtained during desorption process which contain high concentration of Cr(VI).

2. Materials and methods

2.1 Activated carbon

2.1.1 Preparation of one-step steam pyrolysis activated carbon from different precursors.

The major of raw materials used, are agricultural by-products. Although they have very high volatile content and hence give low yields of activated carbon, they are relatively inexpensive and economical starting materials. In Egypt abundant amounts of agricultural by-products including [Mango Stone (MS), Peanut Shell (PSH), Cotton Stalk (CSt), Charcoal (C), Date Pits (DP), Rice Husk (RH), Apricot Stone (AS), Corn Cobs (CC), Peach Stone (PSt), Saw Dust (SD), Olive Stone (OS), and Bagasse Pith (BP)] are available. The production of activated carbon from these sources is one of the most important phases of this study. Steam Activated carbon was obtained by heating 30 gm of the clean dry natural raw material to the specified temperature in a tube furnace. Different precursors were placed in the reactor to be situated in the hot zone of the tubular furnace in an inclined position with an angle of 70° , so as to allow flow of the pyrolysis products. The temperature was raised gradually ($50^\circ\text{C}/10$ min.), to allow free evolution of volatiles, up to around 350°C . Pure steam was then introduced through the heated mass, and heating was continued up to 750°C . The product was soaked at this temperature for 2hr, in the presence of steam, and then the product was cooled to room temperature and puted in a seal container. The produced sample take the following abbreviation; MS-S75, PSh-S75, CSt-S75, C-S75, DP-S75, RH-S75, AS-S75, CC-S75, PSt-S75, SD-S75, OS-S75, BP-S75 (where MS means Mango Stone, the letter S means Steam and the value 75 refers to the temperature of pyrolysis (750°C) and so on for other samples).

2.1.2. Characterization of prepared CC-S75 activated carbon

Particle size was determined using sieves of different particle size. Packed and apparent densities were determined by a tamping procedure using a 25 ml graduated glass cylinder. The texture characteristics were determined by the standard N_2 adsorption isotherms, followed by their analysis to evaluate the porous parameters. Nitrogen adsorption isotherms were conducted at liquid nitrogen temperature using a NOVA 1000 instrument (Chromatic). Thus, from the BET plots the "monolayer equivalent surface area" (S_{BET}) was obtained, the total pore volumes estimated from the volume of nitrogen adsorbed at $p/p^\circ = 0.95$ (V_f) and an average pore radius from $r = 2V_p/S_{\text{BET}}$. Methylene blue number was estimated by the extent of adsorption of milligrams of methylene blue adsorbed by 1 g of carbon in equilibrium with a solution of methylene blue. Fourier transformed infrared spectroscopy was used for analyses of surface functional groups. The activated carbon was analyzed for moisture content, ash content. Ultimate analysis was done by using CHNS analyzer (Cairo University, Micro-analytical Center) and TGA/DTA. Also, the FTIR of activated carbon (before and after adsorption of

Cr) was recorded. The surface topography of activated carbon samples and analysis of adsorbed metal were examined using SEM/EDX, (mode XL 30 ESEM) in Nuclear Materials Authority (NMA) at an accelerated voltage of 20 Kev.

2.2. Preparation of Cr (VI) solutions

All the chemicals used are of analytical grade. A stock solution of 1000 mgL^{-1} of Cr (VI) is prepared by dissolving 2.83 gm of 99.9% potassium dichromate (BDH) in 1000 mL of solution. This solution was diluted as required to obtain the standard solutions containing $50\text{--}500\text{ mgL}^{-1}$ of Cr (VI). pH adjustment was carried out using 0.5N HCl (Analar) and 0.5N NaOH (Sigma) solutions.

2.3. Batch experiments

The batch experiments were carried out in 100mL conical flasks. 0.02 gm of adsorbent was added in 20 mL of 50 mgL^{-1} Cr (VI) solution, and then stirred for a predetermined period at 25°C in water bath with mechanical shaker (GFL, germany). Afterwards, the resultant solution was filtered using a watman filter paper. Adsorption isotherm studies were carried out with different initial Cr (VI) concentrations ranging from 50 to 300 mgL^{-1} . The effect of initial pH of the solution was investigated at 25°C with 50 mgL^{-1} Cr (VI) concentration (using MANNA pH 211, Microprocessor pH meter). Influence of temperature on Cr(VI) adsorption was studied at 25, 50, 75°C . The effect of adsorbent amount was studied by varying it in the range of 0.005-0.030 gm with the Cr(VI) concentration of 100 mgL^{-1} at 25°C . The amount of Cr(VI) adsorbed and removal percentage were calculated using the following Eqs.: (1) and (2), respectively.

$$\text{Uptake } (q_e, \text{ mg.g}^{-1}) = (C_0 - C_e)V/W \quad (1)$$

$$\% \text{ Removal} = C_i - C_0 / C_i \times 100 \quad (2)$$

Where, q_e is the adsorption uptake in mg.g^{-1} , C_i , C_0 and C_e are the initial, outlet and equilibrium concentration of Cr(VI) in mg.L^{-1} , V is the volume of Cr(VI) solution in L and W is the amount of adsorbent used in gm.

2.4 Measurement of Cr(VI) concentration.

In the present study, di-phenyl carbazide method is used for the analysis of Cr(VI) in the solution which only measures the amount of Cr(VI). This method has been reportedly used in many studies for analysis of Cr(VI) at low pH [39]. The concentration of Cr(VI) ions in the effluent is determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as a complexing agent [41]. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min. To calculate the deviation of analytical method of Cr(VI) concentration, calibration curve is prepared from standard solutions.

2.5 Adsorption isotherm models

Adsorption isotherms are expressed in terms of a relationship between the concentration of adsorbate in the liquid and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. In the present study, as the adsorbent developed is new, it is essentially required to test the equilibrium data obtained for Cr(VI) removal using CC-S75 with different isotherm models available in the literature so as to know which one is the best suited out of all the reported isotherms. Various adsorption isotherm models such as Langmuir [42], Freundlich [43] and Tempkin [44] which are available in the literature are described in the following sections bringing out the differences among them and the significance of the characteristic parameters of each isotherm model.

2.5.1 Langmuir isotherm

The Langmuir isotherm is used to obtain a maximum adsorp-

tion capacity produced from the complete monolayer coverage of adsorbent surface. The isotherm equation is represented in term of the fractional coverage (θ) as given by Eq. (3):

$$\theta = q_e/Q_m = bC_e/1 + bC_e \quad (3)$$

where, b is adsorption equilibrium constant (Lmg^{-1}) that is related to the apparent energy of adsorption and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent ($mg\ g^{-1}$) and q_e is the amount adsorbed on unit mass of the adsorbent ($mg\ g^{-1}$) when the equilibrium concentration is C_e ($mg\ L^{-1}$). Eq. (3) can be rearranged to get the linear form, as given by Eq. (4):

$$C_e/q_e = 1/bQ_m + (1/Q_m)C_e \quad (4)$$

Which show that a plot of (C_e/q_e) versus C_e should yield a straight line when the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then yield the values of constants Q_m and b respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [47], also known as the separation factor, given by Eq. (5):

$$R_L = 1/1 + bC_e \quad (5)$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

2.5.2 Freundlich isotherm

For adsorption from solution, the Freundlich isotherm is expressed by Eq. (6):

$$q_e = K_f C_e^{1/n} \quad (6)$$

where, K_f ($mg^{1-1/n} L^{1/n} g^{-1}$) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and $1/n$ is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The Freundlich coefficients can be determined from the plot of $\log q_e$ versus $\log C_e$ on the basis of the linear form of equation as given by Eq. (7):

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

2.5.3 Timpkin isotherm

The non-linear form of Tempkin equation is given by Eq. (8) [49]:

$$q_e = RT/b_T \ln(A_T C_e) \quad (8)$$

Eq. (8) can be linearized as given by Eq. (11)

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (9)$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in K and R is the universal gas constant ($8.314\ Jmol^{-1}\ K^{-1}$). The constant b_T is related to the heat of adsorption, A_T is the equilibrium binding constant ($L\ min^{-1}$) corresponding to the maximum binding energy [50]. The slope and the intercept from a plot of q_e versus $\ln C_e$ determine the isotherm constants A_T and b_T .

2.6 Adsorption kinetics

The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption operation. The kinetics of removal of Cr(VI) is explicitly explained in the literature using pseudo first-order, second-order, and Elovich kinetic models [51-53].

2.6.1 Pseudo first-order kinetics

Lagergren showed that the rate of adsorption of solute on adsorbent is based on the adsorption capacity and followed a pseudo first-order equation [51,52]. The non-linear form of the pseudo first-order equation is given by Eq. (10):

$$dq_t/dt = k_{ad}(q_e - q_t) \quad (10)$$

where, q_e and q_t are the amounts of Cr(VI) adsorbed ($mg\ g^{-1}$) at equilibrium time and at any instant of time, t , respectively, and k_{ad} ($L\ min^{-1}$) is the rate constant of the pseudo first-order adsorption operation. The integrated rate law after application of the initial condition of $q_t = 0$ at $t = 0$, becomes a linear equation as given by Eq.(11):

$$\log (q_e - q_t) = \log q_e - \{k_{ad}t/2.303\} \quad (11)$$

The plot of $\log (q_e - q_t)$ versus t gives a straight line for the pseudo first-order adsorption kinetics, from the adsorption rate constant, k_{ad} , is estimated. Pseudo first-order kinetic equation differs from a true first-order equation in two ways: (i) the parameter k_{ad} ($q_e - q_t$) does not represent the number of available sites, and (ii) the parameter $\log (q_e)$ is an adjustable parameter and often it is found that it is not equal to the intercept of the plot of $\log (q_e - q_t)$ versus t , whereas in a true first-order model the value of $\log q_e$ should be equal to the intercept [52]. Hence, pseudo first-order kinetic model (Eq. (10) is used for estimating k_{ad} alone, which is considered as *mass transfer* coefficient in the design calculations.

2.6.2 Second-order kinetics

As pseudo first-order kinetic model gives only k_{ad} and as q_e cannot be estimated using this model, applicability of the second order kinetics has to be tested for the estimation of q_e with the rate equation given by Eq. (12):

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (12)$$

Where, k_2 ($mg\ g^{-1}\ min^{-1}$) is the second-order rate constant. From the boundary conditions, $t=0$ to t and $q_t = 0$ to q_t , the integrated form of the equation becomes Eq. (13):

$$1/(q_e - q_t) = 1/q_e + k_2t \quad (13)$$

Eq. (13) can be written in a linear form, as given by Eq. (14):

$$t/q_t = 1/h + (1/q_e) t \quad (14)$$

where, $h = k_2 q_e^2$ that can be regarded as the *initial sorption rate* as $t \rightarrow 0$. Under such circumstances, the plot of t/q_t versus t should give a linear relationship, which allows the computation of q_e and k_2 .

2.6.3 Elovich kinetic equation

Elovich equation is a rate equation based on the adsorption capacity commonly expressed as Eq. (15) [53]:

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (15)$$

Where, α ($mg\ g^{-1}\ min^{-1}$) is the initial adsorption rate and β ($mg\ g^{-1}$) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. Eq. (15) is simplified by assuming $\alpha \beta > t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, as given by Eq. (16):

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln t \quad (16)$$

The slope and intercept of the plot of q_t versus $\ln t$ result in the estimation of the kinetic constants, α and β .

2.7 Desorption study

Desorption studies are conducted by batch experiments. A known weight of loaded CC-S75 with Cr(VI) is treated with distilled water and 1N solution of NaOH, HCl, H₂SO₄ and HNO₃ to investigate which of these solution can be desorbs the adsorbed Cr(VI). After the treatment, CC-S75 is separated from the solution and the concentration of desorbed Cr(VI) was determined as mentioned above.

2.8 Interference studies

Batch experiments are conducted to investigate the influence of other ions such as iron (Fe), lead (Pb), uranium (U), cobalt (Co), phosphate (PO₄⁻³), chloride (Cl⁻), sulphate (SO₄⁻²), and nitrate (NO₃⁻) that are present in the industrial stream and laboratories effluent. These experiments are carried out by maintaining the initial Cr(VI) concentration, initial pH, and adsorbent amount constant at 50mgL⁻¹,

1, and 0.02g respectively. Experiments are conducted for same concentration of other ions.

3. Results and discussion

The comparison of the adsorbent capacity of different low cost and commercially available adsorbents is shown in Table 1.

Table 1: Maximum uptake of various commercial and low-cost adsorbents.

S No.	Adsorbent	Uptake, q_m (mg g ⁻¹)	Optimum pH	Ref.
1	Activated neem leaves	62.97	2	[3]
2	Activated carbon (Filtrisorb-400)	57.7	-	[57]
3	Bentonite clay	49.75	3.0	[58]
4	sawdust	41.52	1.0	[71].
5	Activated tamarind seeds	29.7	2.0	[2]
6	Coconut husk fiber	29	2.05	[59]
7	Tea factory waste	27.24	2.0	[7]
8	Leaf mould	25.9	2.5	[60]
9	Pine needles	21.50	2.0	[24]
10	Coconut shell based activated carbon	20	2.5	[61]
11	Sugar beet pulp	17.2	2.0	[62]
12	Palm pressed-fibers	15.0	2.0	[59]
13	Maize cob	13.8	1.5	[62]
14	Sugar cane bagasse	13.4	2.0	[62]
15	Activated charcoal	12.87	2.0	[63]
16	Almond	10	2.0	[24]
17	Polymer grafted CC-S75	9.4	3.0	[64]
18	Maple CC-S75	8.2	4.0	[28]
19	Activated alumina	7.44	2.0	[63]
20	Cactus	7.08	2.0	[24]
21	Coal	6.78	2.0	[24]
22	Biomass residual slurry	5.87	2.0	[65]
23	Distillery sludge	5.7	2.5	[30]
24	Calcined bauxite	2.02	3.8	[70]
25	Fly ash impregnated with aluminum	1.8	2.0	[66]
26	Waste tea	1.55	-	[67]
27	Fe(III)/Cr(III) hydroxide	1.43	5.7	[65]
28	Walnut shell	1.33	-	[67]
29	Agricultural waste biomass	0.82	2.0	[45]
30	Rice husks	0.6	-	[68]
31	Soya cake	0.28	1.0	[31]
32	River bed sand	0.15	2.5	[69]
33	CC-S75	109.53	1.0	Present study

Various mechanisms such as electrostatic forces, ion-exchange, chemical complexation must be taken into account while discussing the mechanism of Cr(VI) adsorption on adsorbents. Adsorption also depends on various parameters such as initial pH, change in pH during adsorption, contact time, adsorbent amount, temperature and initial Cr(VI) concentration. Based on the results obtained in the present study, the effect of these parameters was studied and discussed in detail in the following section.

3.1 Effect of precursors type.

The type of precursor of physically prepared adsorbents has a significant effect on their uptake of Cr(VI) as shown in table 2.

Table 2: The effect of precursor types on the uptake of Cr(VI).

No.	Precursors	Abbreviation	Uptake (q_e , mg.g ⁻¹)
1	Mango Stone	MS-S75	26.1
2	Peanut Shell	PSH-S75	44.9
3	Cotton stalk	CSt-S75	12.04
4	Charcoal	C-S75	45.97
5	Date Pits	DP-S75	13.77
6	Rice husk	RH-S75	17.31
7	Apricot Stone	AS-S75	36.8
8	Corn Cobs	CC-S75	49.837
9	Peach Stone	PSt-S75	46.43
10	Sawdust	SD-S75	29.45
11	Olive Stone	OS-S75	37.75
12	Bagasse Bith	BP-S75	33.63

[C₀ = 50 mg/l, temp. = 25 °C, W = 0.02 gm, V = 20 ml, pH = 1.5 and Time = 24 hr.]

The results obtained indicated that there was a high variation in the efficiency of some type of prepared activated carbon (peanut shell, charcoal, apricot stone, peach stone and olive stone) toward Cr(VI). So, this type of activated carbon can be used in the treatment of liquid waste containing Cr(VI). The highest uptake of Cr(VI) was achieved by one step steam pyrolysis at 750 °C corn cobs based activated carbon (CC-S75). Consequently, CC-S75 with Cr(VI) were chosen as an adsorption system for further investigation.

3.1.1 Characterization of adsorbent.

The biomass consists of polysaccharides, proteins, and lipids, offering many functional groups which can bind ions such as carboxyl, hydroxyl, carbonyl and amino groups. The major constituents of the corn cobs raw material are carbonaceous material (approximately 80 %) and very low ash content (4.75) indicating that the corn cobs is very suitable precursor for activated carbon preparation. Some characteristics of raw materials and corn cobs based single step steam pyrolysis activated carbon CC-S75 are shown in table 3. The yield of corn cobs activated carbon used in this study was found to be 15 %. The yield here was calculated as final weight of activated carbon produced after activation, washing, and drying, divided by initial weight of raw material; both on a dry basis.

Pore characteristic of the activated carbon was determined by N₂ adsorption. The nitrogen adsorption/desorption isotherms of CC-S75 activated carbon is illustrated in Figure (1). The presence of micropores and mesopores in the activated carbon prepared from corn cobs was indicated by the pore size distribution as depicted in Figure (2). The pore characteristics, a proximate analysis (carried out using the recommended standard methods of analysis) and the physicochemical characterization of CC-S75 activated carbon and its precursor (corn cobs) are summarized in Table 3.

Table 3: Physicochemical characterization of CC-S75 activated carbon and chemical analysis of corn cobs.

Characteristics of corn cobs steam pyrolysis activated carbon.			
parameters	Values	parameters	Values
Carbon yield (%)	15	Iodine number (mg.g ⁻¹)	540
Ash content (%)	3.9	Particle size (mm)	1.0 - 0.25
Methylene blue number (mg.g ⁻¹)	220	Matter soluble in water (%)	1.10
Packed density (g.ml ⁻¹)	0.384	Matter soluble in acid (%)	1.42
Apparent density (g.ml ⁻¹)	0.17	Matter soluble in base (%)	1.31
BET surface area (m ² .g ⁻¹)	460.2	Moisture content (%)	6.9
Langmuir surface area (m ² .g ⁻¹)	669.3	C %	71.46
Average pore radius (Å)	10.96	H %	5.19
Micropore surface area (m ² .g ⁻¹)	670.6	N %	0.71
Total pore volume (cm ³ .g ⁻¹)	0.252	S %	0.71
Micropore volume (cm ³ .g ⁻¹)	0.240	O % (by difference)	13.24
Mesopores volume (cm ³ .g ⁻¹)	0.012	Ash	8.69
Phenol number (mg)	160	pH	8.2
Characteristics of corn cobs raw material [72]			
Real Density (g cm ⁻³)	0.637	Pentozans %	21.50
Apparent Density (g cm ⁻³)	0.301	Raisins and waxes %	6.25
Specific surface area (m ² g ⁻¹)	52.98	Proteins %	4.01
Medium radius pore (Å)	173	Ash %	4.75
Cellulose %	42.96	Humidity %	6.78
Lignin %	13.73		

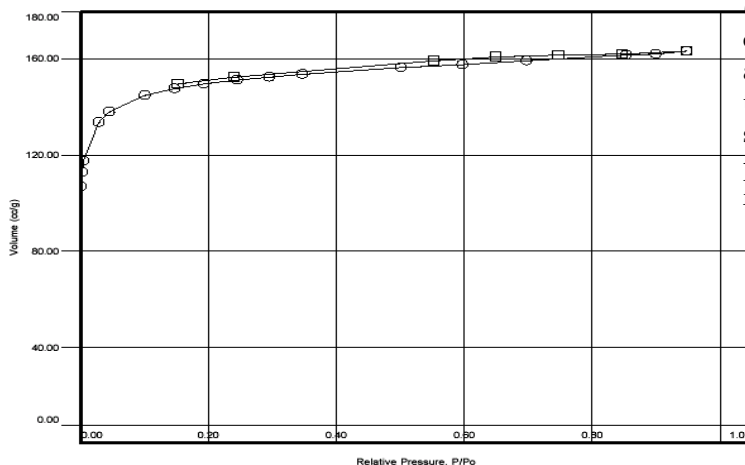


Fig.1: Nitrogen adsorption/desorption isotherm of CC-S75 activated carbon.

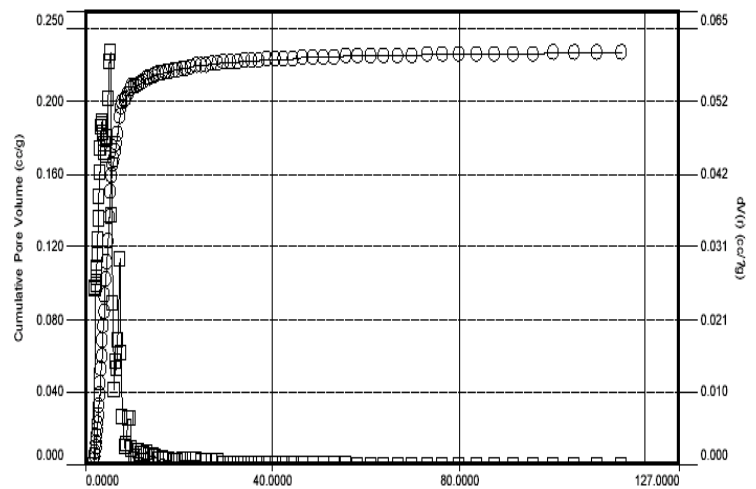
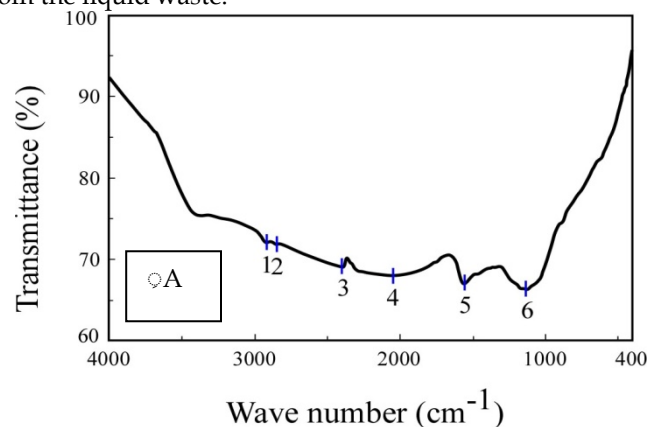


Fig.2: Pore size distribution of CC-S75 activated carbon.

The prepared adsorbent was characterized by FTIR (Perkin-Elmer System 2000) spectroscopy. The IR spectrum of the natural biomass reflects the increased complex nature of sample. Despite this complexity some characteristic peaks may be assigned. Taken into account the similarities presented in the literature, one may identify here the following functional groups[72]: Glycosidic C-O-C group presents characteristic absorption at 1163 cm⁻¹; C=O stretching of the acidic group has a peak at 1648 cm⁻¹; CH₃-COO- group has a peak at 1371 cm⁻¹; amino group (and may be also, bonded hydroxyl group) presents characteristic absorption at 3500-3000 cm⁻¹ (3420 cm⁻¹) and at 1250 - 1000 cm⁻¹; The strong band found at 1200 - 950 cm⁻¹ (1032 cm⁻¹) may be assigned to an alcohol stretching; Bending vibration of OH in phenols is 1255 cm⁻¹; Bending vibration of CH₃-CH₂- and CH₃-in lignine is 1460 cm⁻¹; Bending vibration of C=C in aromatic rings is 1430 cm⁻¹ and 1518 cm⁻¹; Bending vibration of -CH₂- is 2930 cm⁻¹.

The IR analysis showed that CC-S75 has functional groups (carboxyl, hydroxyl, carbonyl, and amino) that retain metal cations from aqueous solutions. The decrease of intensity or appear (or disappear) of some of these functional groups (in the range 400-800 cm⁻¹ due to C-metal bonds) presents at the surface of the carbon (as shown from the fig.3) confirms the participation of these groups in the interaction with Cr(VI) from the liquid waste.



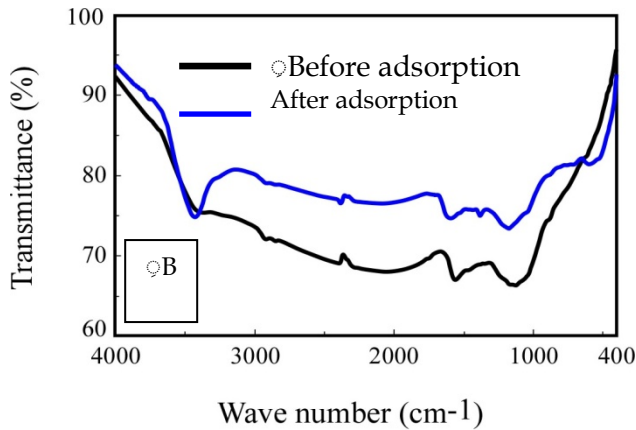


Fig. 3: FTIR spectroscopy of the CC-S75, (A) before adsorption and (B) after adsorption.

The pore structure and size vary depending on the conditions of activation. By using steam as the activating agent for thermal activation, the porous structure is enhanced according to the following reaction: $C + H_2O = CO + H_2$ [73]. The activation temperature was determined on the TG and DTG curves of the samples by heating in static air.

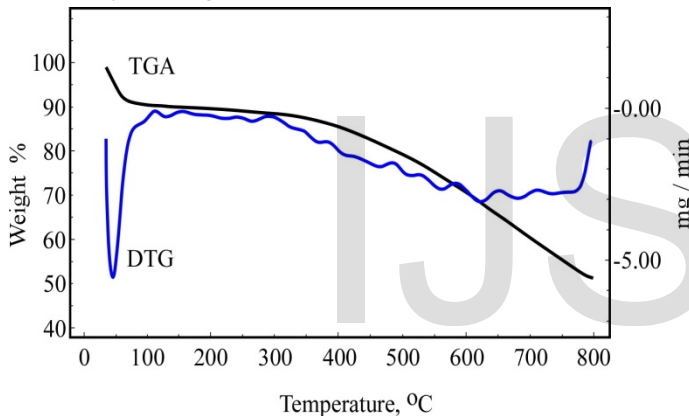


Fig.4: TGA and DTG of corn cobs sample by heating in static air to 800°C.

Generally, the reactivity of the sample is partly attributed to the change in surface area and increases with the O/C ratio of the precursor. Thus, the highest rate of reaction as observed on DTG curve (figure 4) was 630 °C for corn cobs sample. Since no great difference was observed after the temperature conditions of 750 °C, the activation temperature was set to 750 °C.

Fig. 5 shows the SEM photograph of the activated carbon obtained from corn cobs. Carbonization and activation of corn cobs result in porous with a considerable surface area. The corn cobs steam pyrolysis occurs rapidly with gas evolution at a higher temperature, thus destroying partially the original corn cobs structure. On the other hand, volatiles are gradually released at a lower and wider temperature range. Thus, the sample consists of particles that are partly porous, as shown in the SEM photographs of parts (a) and (b) of Figure 5, which illustrate the porosity of CC-S75 before and after adsorption of Cr(VI). Figure 5A and 5B presented the SEM analyses of CC-S75 before and after the sorption of Cr(VI) cations on CC-S75. Figure 5A represents a major modification porous structure of

activated carbon. The structure of sorbent is not uniform in pore size showing that some sort of chemical reaction occurred at the biomass surface.

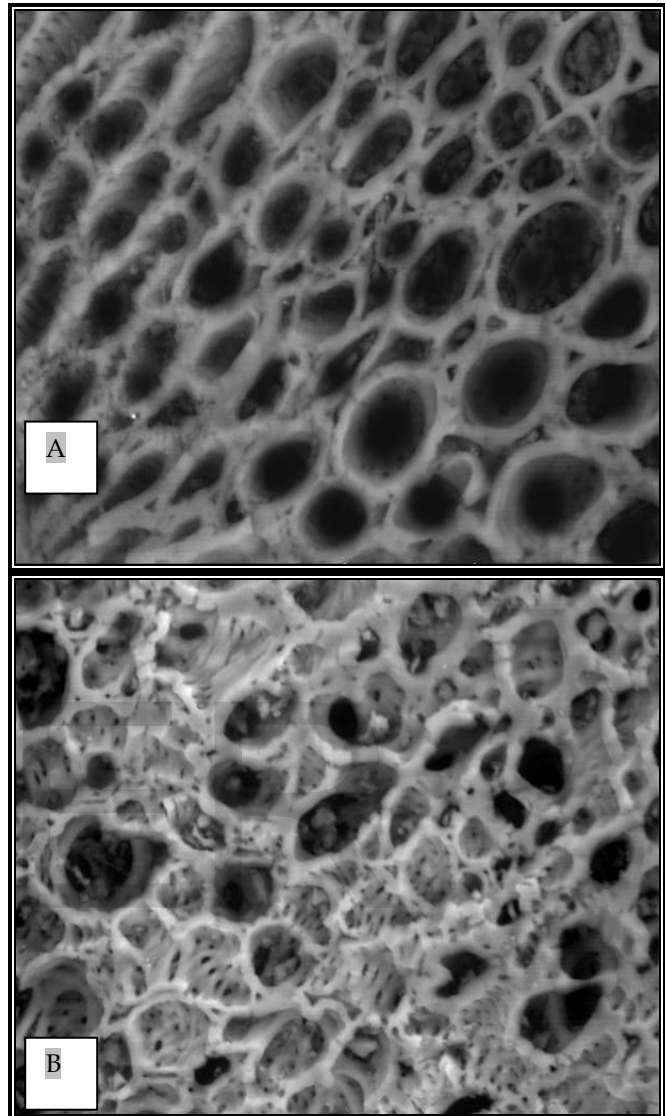


Fig.5: SEM of CC-S75, (A) before adsorption and (B) after adsorption of Cr(VI).

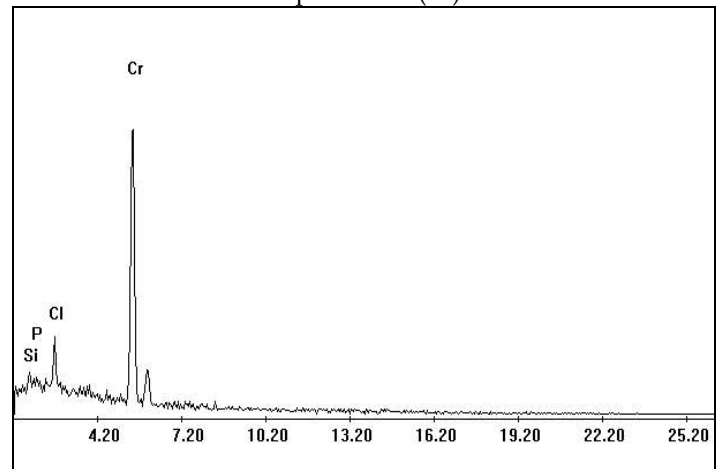


Fig. 6: X-Ray Spectrum after the sorption of Cr(VI) on CC-S75. Figure 6 shows the X-Ray Spectrum of CC-S75 brought in con-

tact with Cr(VI) synthetic solution proving that the CC-S75 retains a high amount of Cr(VI).

3.2 Effect of contact time

Figure 7 shows the percentage removal of Cr(VI) for the initial Cr(VI) concentration of 50 mgL⁻¹ at pH 1.

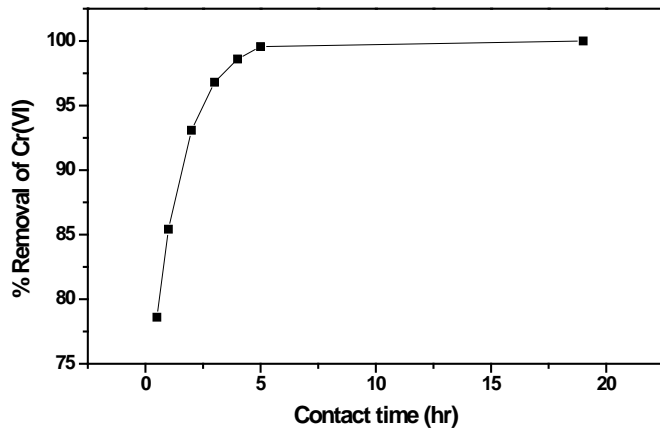


Fig. 7: Effect of contact time on the % removal of Cr(VI) using CC-S75.

It is evident that the contact time is an important parameter for the adsorption of Cr(VI) on CC-S75. While increasing the contact time, the percentage removal increases from 78.6 % at 0.5 hr to 98.6 % at 4 hr reaching 99.57 % at 5 hr. Hence the equilibrium time of 5 hr was selected for Cr(VI) adsorption. The rate of Cr(VI) removal using CC-S75 was increased rapidly till 5 hr. A further increase in the contact time has a negligible effect on the adsorption of Cr(VI).

The nature of adsorbent and the available adsorption sites affect the rate of adsorption of Cr(VI). The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. In the initial stages of adsorption, the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption of Cr(VI) is faster. The rate of adsorption decreases in the later stages due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

3.3 Adsorption kinetics

In order to understand the kinetics of Cr(VI) removal using CC-S75, pseudo first-order, second-order and Elovich kinetic models are tested with the experimental data.

3.3.1 Pseudo first-order kinetics

The plot of $\log(q_e - q_t)$ versus t gives a straight line as shown in Figure 8 which represents the pseudo first-order kinetics for the removal of Cr(VI) using CC-S75. The values of first-order rate constants, k_1 and q_e for the initial Cr(VI) concentration of 50 mg L⁻¹, by keeping the adsorbent amount constant (1g L⁻¹) and pH = 1, are calculated and listed in Table 4. The coefficient of determination (r^2) is found to be 0.996 which seems to be good and shows the applicability of pseudo first order kinetic model for the removal of Cr(VI) using CC-S75. The true value of q_e obtained was 49.78 mg.g⁻¹ which is not in agreement as expected (17.63 mg.g⁻¹) with the pseudo first-order model pre-

dicted values as given in Table 4.

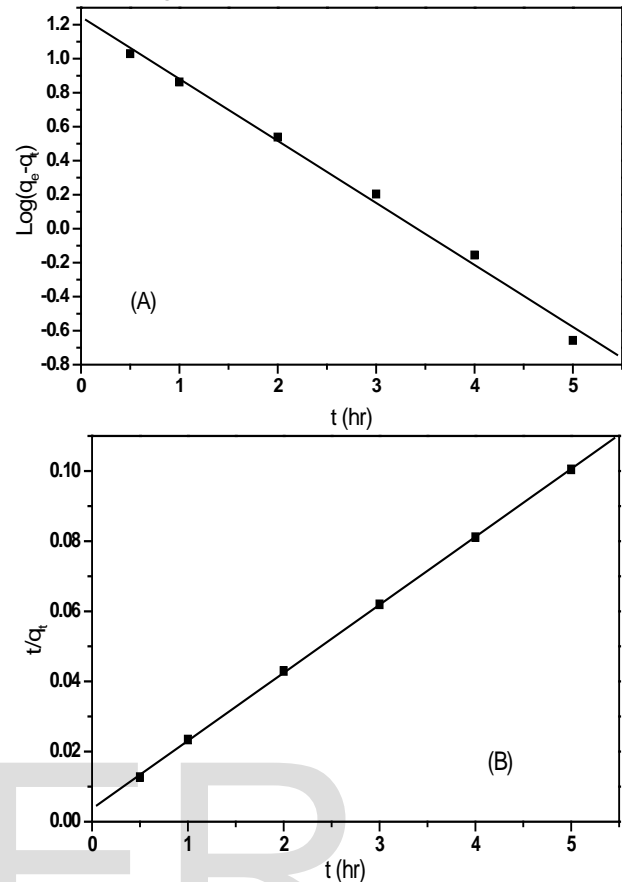


Fig. 8: (A) Lagergren plot and (B) Second-order plot for the adsorption of Cr(VI) using CC-S75.

3.3.2 Second-order kinetics

As a result of the non-applicability of pseudo first-order model, the kinetics for the adsorption of Cr(VI) on CC-S75 is tested with the second-order kinetic model. The application of the second order kinetics by plotting t/q_t versus t as shown in Figure 8, yielded the second-order rate constant, k_2 , estimated equilibrium capacity q_e , and the coefficient of determination (r^2) for the initial Cr(VI) concentration of 50 mgL⁻¹, which are reported in Table 4.

Table 4: kinetic parameters for the adsorption of Cr(VI) using CC-S75 as an adsorbent.

C_0 (mg.L ⁻¹)	q_e (mg.g ⁻¹) experimental		
50	49.87		
<i>First-order kinetic model</i>			
K_1	q_e	r^2	
0.84	17.6	0.9964	
<i>Second-order kinetic model</i>			
K_2	q_e	h	r^2
0.101	51.57	271	0.9999
<i>Elovich kinetic model</i>			
α	β	r^2	
0.695	0.2124	0.9952	

The calculated q_e values show a good agreement with the experimental values and the obtained values for coefficient of

determination (r^2) are more than 0.9999 which indicates that the second-order kinetic model describes well the removal of Cr(VI) using CC-S75 as an adsorbent.

3.3.3 Elovich kinetic equation

Figure 9 represents the application of linear form of Elovich kinetic equation which is a plot between q_t and $\ln t$.

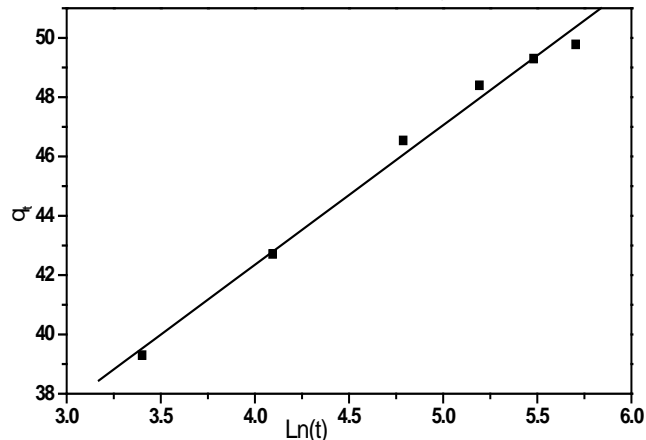


Fig. 9: Elovich kinetic model plot for the adsorption of Cr(VI) using CC-S75.

The Elovich kinetic constants α and β are obtained from the intercept and the slope respectively. The calculated initial adsorption rate α ($\text{mg g}^{-1} \text{min}^{-1}$) in the first hour of contact between Cr(VI) solution and CC-S75 was 41.745 mg.g^{-1} which is in a good agreement with the experimental value 42.71 mg.g^{-1} . The coefficient of determination (r^2) is obtained 0.9952 for Cr(VI) concentration of 50 mg L^{-1} which is found to be less than the value calculated using pseudo first-order and second-order kinetic model as shown in Table 4.

3.3.4 Clarification on kinetic studies

The value of coefficient of determination (r^2) for the second order kinetic model is more than that obtained using the pseudo first-order and Elovich kinetic models. Thus the kinetics of Cr(VI) adsorption using CC-S75 as an adsorbent can be better explained by the second order kinetic model. It is important to get the rate at which Cr(VI) was adsorbed onto the solid surface of CC-S75 which is important in designing of fixed-bed adsorption column.

3.4 Effect of pH

The metallic ions uptake on CC-S75 mainly depends on the ions concentration, and oxidation-reduction phenomena that simultaneously take place on the adsorbent surface [54,55]. In the present work, the effect of initial pH on the adsorption of Cr(VI) using CC-S75 was studied in the initial pH range of 1-10. The relation between the initial pH of the solution and the percentage removal of Cr(VI) is shown in Figure 10. The % removal of Cr(VI) was increased from 0.66 % to 100% with decreasing the initial pH from 10 to 1. At an initial pH value of 1, the percentage removal of Cr(VI) was 100% which shows almost the complete removal of Cr(VI).

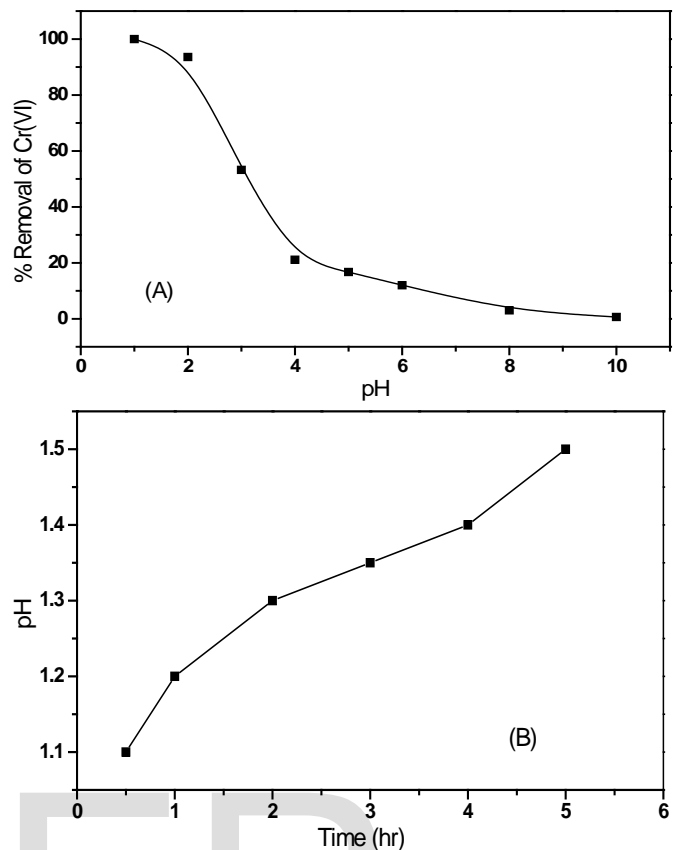
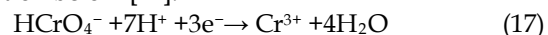


Fig. 10: (A) Effect of pH on the % removal of Cr(VI) (B) Change in pH of solution with time of adsorption of Cr(VI) using CC-S75 activated carbon.

Within the solution pH range of 1.0-6.0, chromium ions can exist in different forms, such as Cr_2O_7^- , HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- predominates [3]. At lower solution pH value (1-3), the increase in Cr(VI) adsorption is due to the electrostatic attraction between positively charged groups of adsorbent surface and the HCrO_4^- .

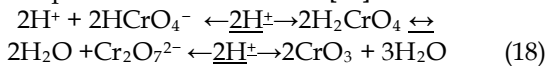
Another possible reason for the higher adsorption of Cr(VI) on CC-S75 could be the reduction of Cr(VI) to Cr(III) in acidic medium. At low pH, the presence of H^+ ions in the solution is high which causes the reduction of Cr(VI) to Cr(III) ions due to high redox potential (1.3V at standard state) as shown in the reaction below [21].



The oxidation product of this reaction is water. As the size of Cr(III) ions is small, they can be easily replaced by the positively charged ions present on the CC-S75 surface [25]. Though in principle, there is a possibility of reduction of Cr(VI) ion into Cr(III) at low pH, the earlier studies reported that the amount of total Cr(III) and Cr(VI) at low pH is approximately same [5] which indicates that the presence of Cr(III) in the final solution is insignificant. So in this study, the amount of Cr(III) is not determined. The mechanism of electrostatic attraction between CC-S75 surface and HCrO_4^- is found more appropriate for explaining the Cr(VI) adsorption onto the CC-S75.

The following reaction (Eq. 18) and the subsequent reaction mechanism for adsorption of Cr(VI) at different pH values are

used to explain the observed trend[71]:

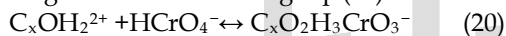


At a lower pH value (pH 1), the dominant form of Cr(VI) is HCrO_4^- while the surface of the adsorbent is charged positively. The stable forms of chromium such as H_2CrO_4 and CrO_3 exist as poly nuclear species at a high chromium concentration [75] and hence the low pH value of 1 results in a higher percentage removal. For the pH values above 2, the adsorption capacity decreases with increasing pH. Increasing the pH value shifts the concentration of HCrO_4^- to other forms (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$). The decrease in adsorption of Cr(VI) by increasing the value of pH may be due to the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates. The change in solution pH was observed with time at initial Cr(VI) concentration of 50mg L^{-1} by keeping the CC-S75 amount constant (1g L^{-1}) and shown in Figure10.

It is observed that the value of pH was increased from 1.1 to 1.5 with the increase in adsorption time from 0.5 to 5 hr. This may be due to the fact that the CC-S75 is a carbonaceous materials. Generally, oxo groups (C_xO and C_xO_2) are present on the surface of adsorbent which when come in contact with water, hydrolyze water molecules as shown in Eq. (19) [71]:



Thus the equilibrium pH of solution was increased in the presence of hydroxyl ions. When Cr(VI) ions are introduced into the system, they are adsorbed onto the positively charged surface as given in the following Eq. (20):



Combining Eq. (19) and (20) gives Eq. (21):



Hence every mole of HCrO_4^- adsorbed results in the release of two moles of hydroxyl ions into the solution which increases the solution pH.

3.5 Effect of adsorbent dose

Study of the effect of CC-S75 amount is important to get the trade-off between the adsorbent capacity and the percentage removal of Cr(VI) resulting in an optimum CC-S75 amount. The influence of CC-S75 amount, varying from 0.16 to 1g L^{-1} is shown in Figure 11. The percentage removal of Cr (VI) increases from 24.57% to 88.82% with an increase in the CC-S75 amount from 0.16 to 1g L^{-1} respectively. However, the adsorption capacity decreases from 147.42 to 88.82mgg^{-1} by increasing the adsorbent amount from 0.164 to 1g L^{-1} . It may be noted that though the increase in percentage removal is from 24.57% to 88.82% (from 0.16 to 1g L^{-1} for the above percentage removal range) which appears to be out of control, in order to find out the optimum amount of adsorbent (from 0.16 to 1g L^{-1} for the above percentage removal range), the trade-off between the adsorption capacity (147.42 to 88.82mgg^{-1}) and the percentage removal has to be studied. From figure (11), the increase in Cr(VI) removal with an increase in the CC-S75 amount is due to the increase in surface area and adsorption sites available for adsorption. The drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption

process. For the adsorbent amount of 0.417g L^{-1} , the optimum values of Cr(VI) removal and the adsorption capacity are found to be 45.65 % and 111.69mgg^{-1} , respectively.

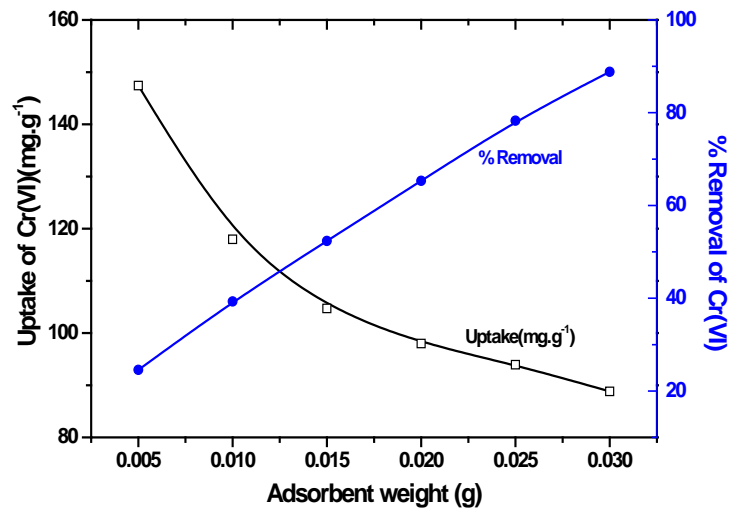


Fig. 11: Effect of weight of CC-S75 on adsorption of Cr(VI).

3.6 Effect of initial Cr(VI) concentration

Cr(VI) adsorption is significantly influenced by the initial concentration in aqueous solutions. In the present study, the adsorption experiments were performed to study the effect of initial Cr(VI) concentration and obtained results are presented in Fig. 12. Once the equilibrium is reached between the solid phase and the aqueous phase, the pH value of solutions are measured. It is found that the final value of solution pH increases from 1.13 to 1.49 with an increase in the initial Cr(VI) concentration from 50 to 300mg L^{-1} . This indicates that there is not a significant change in the final value of solution pH which confirms the higher acidic medium in solution after the adsorption of Cr(VI). The results show that with an increase in the Cr(VI) concentration from 50 to 300mg L^{-1} , the percentage removal decreases from 98.32% to 36.38% and the adsorption capacity increases from 49.16 to 109.15mgg^{-1} . The decrease in the percentage removal of Cr(VI) can be explained with the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration.

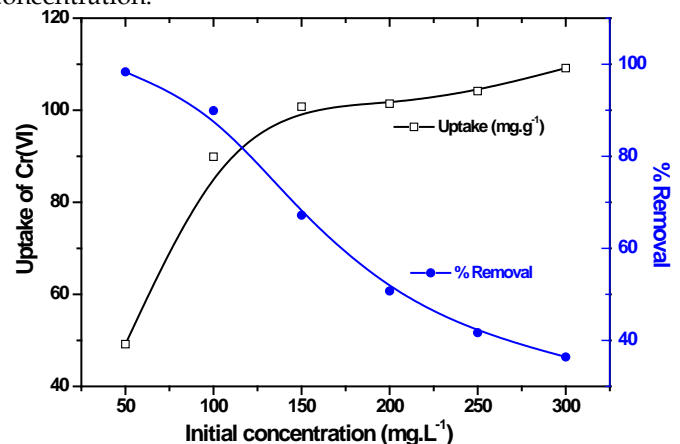


Fig.12. Effect of initial concentration on adsorption of Cr(VI).

The increase in adsorption capacity with an increase in the Cr(VI) concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. For an initial Cr(VI) concentration of the 116.63mg L⁻¹, the optimum values of Cr(VI) removal and the adsorption capacity are found to be 82.15% and 91.64 mgg⁻¹ respectively.

3.7 Adsorption isotherm study

Adsorption isotherms are important to describe the adsorption mechanism for the interaction of Cr(VI) on the adsorbent surface. The equilibrium studies are useful to obtain the adsorption capacity of CC-S75 for Cr(VI) removal. An adsorption isotherm is characterized by certain constants that express the surface properties and the affinity of the adsorbent towards Cr(VI). The equilibrium data for the adsorption of Cr(VI) using CC-S75 fits into various isotherm models which results in a suitable model that can be used for the design of an adsorption process. In the present study, three equilibrium models are analyzed to investigate the suitable adsorption isotherm, as the adsorbent developed is new.

3.7.1 Langmuir isotherm

The isotherm data has been linearized using the Langmuir equation and is plotted between C_e/q_e versus C_e which is shown in Figure 13(a). The Langmuir constant q_m was obtained as 109.53mgg⁻¹ in the equilibrium pH value range of 1.20-1.52. The Langmuir constant, b , was found to be 0.222 Lmg⁻¹. The high value of coefficient of determination ($r^2 = 0.999$) obtained indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Cr(VI) onto the CC-S75 surface. The dimensionless parameter, R_L , was found to be 0.030 ($0 < R_L < 1$) which confirms the favorable adsorption process. The value of R_L was near to zero which favors the irreversible adsorption. Though the r^2 value obtained is reasonably high (0.999), in order to find out if a better fit is possible with other isotherms, the results are analyzed with other two isotherms available in the literature.

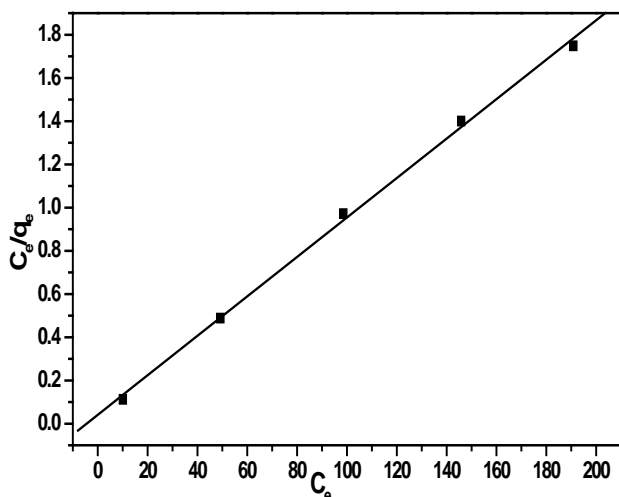


Fig.13 (a): Langmuir isotherm models for Cr(VI) adsorption onto CC-S75.

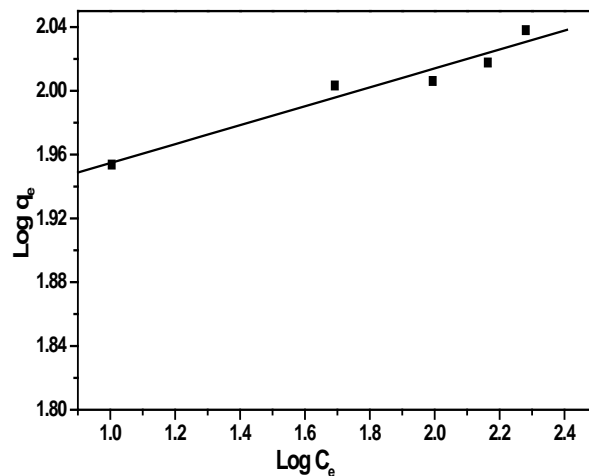


Fig.13 (b): Freundlich isotherm models for Cr(VI) adsorption onto CC-S75.

3.7.2 Freundlich isotherm

The Freundlich constants, K_f and n are obtained by plotting the graph between $\log q_e$ versus $\log C_e$ as shown in Figure 13(b). The values of K_f and n_F are 78.6 and 16.85 respectively. It was found that the coefficient of determination obtained was 0.973 which is lower than that for Langmuir isotherm model as given in Table 5. Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity. The obtained result indicates that the equilibrium data is not fitted well with the Freundlich isotherm model.

3.7.3 Tempkin isotherm

A plot of q_e versus $\ln C_e$ at a constant temperature is used to calculate the Tempkin isotherm constants, A_T and b_T which is shown in Figure 14. The constants A_T and b_T , obtained for Tempkin isotherm model are 500.82 Lmin⁻¹ and 424.8 and also tabulated in Table 5. The obtained coefficient of determination (r^2) for Tempkin isotherm model is 0.969 which confirms the better fit of equilibrium data as compared with the Freundlich isotherm model. But Tempkin isotherm model is not as good as Langmuir isotherm model as can be seen from the reported values of coefficient of determination (r^2) in Table 5.

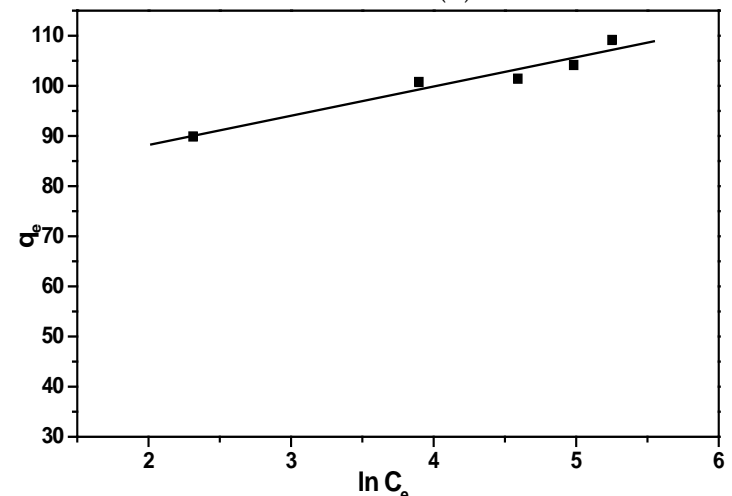


Fig.14: Timken isotherm model for Cr(VI) adsorption onto CC-S75.

Table 5: Isotherm constants for adsorption isotherms of Cr(VI) on CC-S75.

Adsorption isotherm	Isotherm parameters	Values	r ²
Langmuir	q _m	109.53	0.999
	b	0.222	
	R _L	0.030	
Freundlich	K _f	78.6	0.973
	1/n	0.059	
	N	16.85	
Tempkin	A _T	500.82	0.969
	B _T	5.83	
	b _T	424.8	

3.8 Effect of temperature

Adsorption experiments were carried out for Cr(VI) of 100 mg/L at three different temperatures (25, 50 and 75 °C) in order to observe the effect of temperature on the adsorption capacity. It was observed that with an increase in temperature, adsorption capacity increased, indicating better adsorption at higher temperatures (fig. 15).

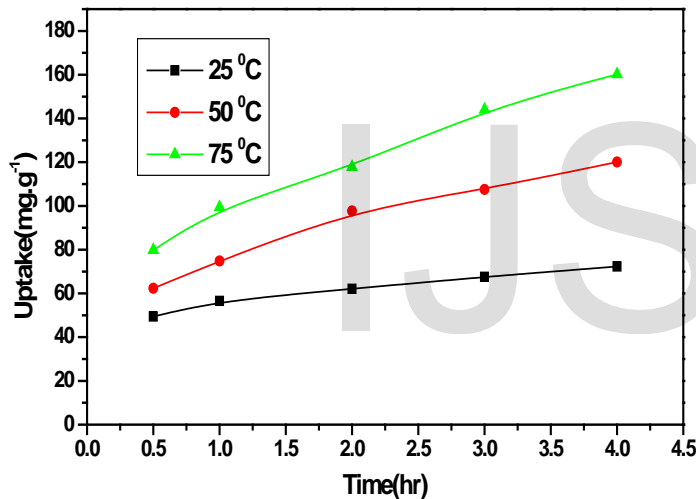


Fig. 15: Effect of temperature on the removal of Cr(VI) using CC-S75 adsorbent.

The increase in the amount of Cr(VI) adsorbed may either be due to acceleration of some originally slow adsorption steps or to the creation of some new active sites on the adsorbent surface. The enhanced mobility of Cr(VI) from the bulk solution towards the CC-S75 surface should also be taken into account [76]. Adsorption interaction in this case must involve some type of specific interaction at higher temperature i.e. probable bond cleavage (endo-process) to result in smaller entities feasible to certain pore size. Alternatively, such behavior may be ascribed to "activated" adsorption, which accelerates diffusion into certain pores in the adsorbent [76]. In the present investigation, the adsorption experiments were performed at a temperature of 25, 50 and 75 °C. It was found that, according to the adsorption isotherm, the amount of Cr(VI) adsorbed on CC-S75 activated carbon increases with the solution temperature. The Langmuir parameters for the adsorption obtained from different temperatures were calculated from the C_e/q_e versus C_e plots, and the results are given in Table 6. It was

observed that the value of Q_m increases with increase in temperature. The results also showed that b is an increasing function of the solution temperature for CC-S75 activated carbon.

Table 6: Langmuir constants at different temperature.

Parameters	25 °C	50 °C	75 °C
Q _m (mg.g ⁻¹)	17.94	37.64	65.66
b (L.mg ⁻¹)	0.021	0.034	0.0686
r ²	0.9935	0.986	0.980
R _L	0.3226	0.2272	0.1272

The increase of b with temperature indicates that the affinity of Cr(VI) ions for adsorbent is favored at high temperature, and therefore, this adsorption process is endothermic in nature and this phenomena is confirmed with decrease of the R_L (dimensionless equilibrium parameter, which is a measure of adsorption favorability) values indicating the irreversibility of the adsorption of Cr(VI) using CC-S75 activated carbon. The increase in capacity with respect to temperature indicates that some kind of chemical interaction may take place during the adsorption process [76]. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in increased adsorption capacity. The results of the present investigation support the conclusion that Cr(VI) sorption is controlled by pore diffusion. The thermodynamic parameters ΔG⁰, ΔS⁰ and ΔH⁰ have been determined using the following equations [76].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (22)$$

$$\log (q_e/C_e) = \Delta S^0 / 2.303R + (-\Delta H^0) / 2.303RT \quad (23)$$

Where q_e is the maximum amount of Cr(VI) adsorbed per unit mass of CC-S75 activated carbon (mg.g⁻¹). C_e is equilibrium concentration (mg.L⁻¹) and T is temperature in Kelvin. It may be noted that the experimental data considered here for the calculation of the thermodynamic parameters (ΔG⁰, ΔS⁰ and ΔH⁰) are in the linear range of the equilibrium adsorption isotherm. Therefore, Equation (23) can be used to evaluate entropy of adsorption ΔS⁰ and enthalpy of adsorption ΔH⁰ from a plot of log (q_e/C_e) versus 1/T.

The results of these thermodynamic calculations were shown in Table 7. The negative value for the Gibbs free energy shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature.

Table 7: Thermodynamic parameters for the adsorption of Cr(VI) onto CC-S75 activated carbon.

ΔH ⁰ (kJ mol ⁻¹)	ΔS ⁰ (Jmol ⁻¹ k ⁻¹)	ΔG ⁰ (kJ mol ⁻¹)		
		298 K	323 K	348 K
33.219	0.1125	- 0.300	- 3.112	- 5.924

Table 7 shows that the ΔS⁰ value is positive (i.e., that entropy increases as a result of adsorption). This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Adsorption is thus likely to occur spontaneously at normal and high temperatures because ΔH⁰> 0 and ΔS⁰>0. Also, as shown from Table 7, numerically the higher value of ΔH⁰(33.219 KJ.mol⁻¹) obtained in the studied systems than usually reported [76] for physical adsorption or ion exchange

adsorption (having the ΔH° value of $8.4 \pm 12.6 \text{ kJ mol}^{-1}$) clearly suggests to us that the overall process of adsorption of Cr(VI) does not proceed only via ion exchange mechanism. This indicates the possibility of surface complex formation in the system (i.e. chemisorption), which is in agreement with the results reported earlier [41]. This data confirm the result obtained from the equation of second order reaction and FTIR spectra of CC-S75 before and after adsorption process.

3.9 Effect of interfering ions.

The interference of other ions such as iron (Fe^{2+}), lead (Pb^{2+}), uranium ($\text{U}^{4+}, \text{U}^{6+}$), cobalt (Co^{2+}), phosphate (PO_4^{3-}), chloride (Cl^-), sulphate (SO_4^{2-}), and nitrate (NO_3^-) that are present in the industrial, tannery and laboratories effluents wastewater streams was plotted in Figure 16. The percentage removal of Cr(VI) is marginally decreased as shown in Figure 16 by the presence of U^{4+} , Pb^{2+} , Fe^{2+} and Co^{2+} ions. Hence, it can be inferred that the adsorption of Cr(VI) is not significantly affected by the presence of U^{4+} , Pb^{2+} , Fe^{2+} and Co^{2+} ions. This may be due to the higher ionic charge of the Cr(VI) which dominates in the adsorption as compared to the other divalent ions such as Pb^{2+} , Fe^{2+} and Co^{2+} ions (and tetra or hexavalent U) present in the laboratories effluent.

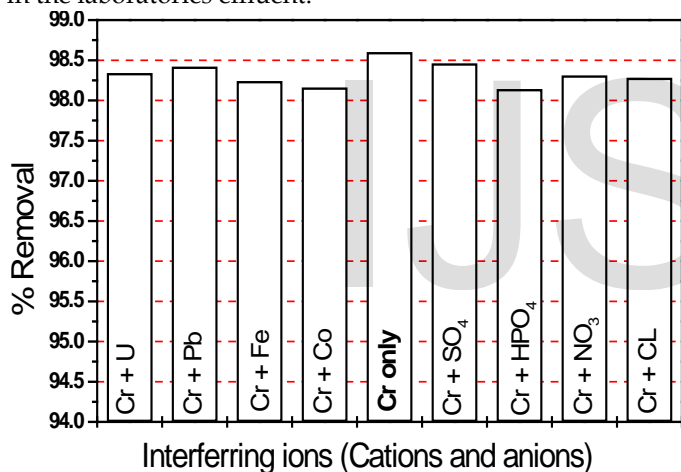


Fig. 16. Effect of other ions on the removal of Cr(VI) using CC-S75 activated carbon.

Also, in case of anions (such as phosphate), the decrease in the % removal may be due to the formation of soluble salts of chromium which prefers the aqueous phase than to be adsorbed on the solid adsorbent. The other co-existed ions such as Cl^- , NO_3^- have insignificant effect on the percentage removal of Cr(VI).

3.10 Desorption of Cr(VI) from loaded activated carbon.

Pre-concentration of adsorbate and reusability of an adsorbent is of crucial importance in application practice for metal removal from wastewater. In this study, the ability of different desorbing agents to desorb the Cr(VI) taken by CC-S75 was investigated. The adsorbent was loaded with the maximum amount of Cr(VI) ions and placed in 0.5 M desorbing agents and the amount of Cr(VI) desorbed in 5hr was measured.

Table 8: Desorption studies of Cr(VI).

Desorbing agent (0.5M)	% Desorbed	Desorbing with HCl	
	Cr	HCl concentration (M)	Desorbing percent
H ₂ O	0.00	0.5	29.21
NaOH	2.40	1.0	33.90
HCL	29.22	2.0	35.19
HNO ₃	9.70	4.0	36.01
H ₂ SO ₄	6.30	6.0	36.30

From table 8, only 2.4% of the adsorbed Cr(VI) is released from the carbon after five hours of contact between the loaded matrix and 0.5 M NaOH. No desorption occurred with double distilled water. Desorption in acid media was ordered as follows: HCl > HNO₃ > H₂SO₄. From the results obtained, it may be noted that the kinetic tests suggested that the reversibility of the adsorption process is only high in case of HCl medium. In this concern, various concentrations of HCl (0.5 - 6.0 M) were tested as shown in Table 8. The desorption of Cr (VI) reached 35.19 % at 2 M and increase slightly with further increase in acid concentration. This results confirm the irreversibility of adsorbed Cr(VI) using CC-S75. It has been postulated that the high concentration of H⁺ ions at low pH is responsible for the displacement of adsorbed Cr(VI).

3.11 Treatment of laboratories effluent of Nuclear Materials Authority wastewater: case study application.

The samples of the laboratories effluent of Nuclear Materials Authority (NMA) contain the digestion and experimental wastewaters. So, the laboratories effluents of NMA must be treated before discharge. Different elements, which are presents in the ores, have environmental hazardous because their initial concentrations are higher than the permissible levels according to the Egyptian Environmental Regulations [77]. So, we used the CC-S75 prepared sorbent to check its applicability for metal removal in wastewater treatment of this effluents. As shown in table 9, the percent removal for Cr(VI) at both best pH (pH=1) and real initial pH of solution is 85.10 % and 29.75 respectively at (V/M ratio = 1.5 L/g).. Also, the removal of other concerned interfering ions in the same wastewater were measured (using AAS) and their value are shown in table 9.

Table 9: The concentration of heavy metals before and after treatment (time=4 hr).

No.	Co (ppm)	pH	C _F (ppm)	Uptake (q _e , mg.g ⁻¹)	% Removal
1	13.73 ppm Cr	1	2.05	17.52	85.10
2	13.73 ppm Cr	Sol. (2.6)	9.65	6.13	29.75
3	32 ppm U	1	22.75	13.875	28.91
4	32 ppm U	Sol. (2.6)	28.63	5.055	10.53
5	2.66 ppm Pb	1	0.0951	3.84735	96.43
6	2.66 ppm Pb	Sol. (2.6)	2.06	0.9	22.56

From these results, the prepared CC-S75 is applicable for treatment of industrial wastewater and laboratories effluents and removal of toxic heavy metals.

4. Conclusions.

Utilization of agricultural by-products such as corn cobs as a

precursor of activated carbon for the removal of Cr(VI) from the laboratories wastewater streams was investigated. CC-S75 was found to be a better adsorbent for the removal of Cr(VI) as compared to many other low cost and commercially available adsorbents. The maximum percentage removal of Cr (VI) was obtained at pH 1. It was found from the kinetic studies that the adsorption rate of Cr (VI) was faster for the initial 240 min and then it decreases in the later part of adsorption and it was explained by the second-order kinetic model. The equilibrium time for Cr (VI) adsorption on CC-S75 is obtained as 300 min. The equilibrium data are best fitted with Langmuir isotherm model which confirms the monolayer adsorption of Cr(VI) onto the CC-S75 with maximum adsorption capacity of 109.53 mg g^{-1} , which is comparatively good adsorption capacity. With the increase of adsorbent amount, the percentage removal of Cr (VI) increases and the adsorption capacity decreases because of the availability of more unsaturated adsorption sites. The presence of other ions such as U^{6+} or U^{4+} , Fe^{2+} , Pb^{2+} , Co^{2+} , HPO_4^{2-} , NO_3^- , Cl^- and SO_4^{2-} in aqueous solutions are found to have insignificant effect on Cr(VI) adsorption. The saturated adsorbent is regenerated by acid, water and base treatment. 2 M HCl is sufficient to desorb 35.19 % of adsorbed Cr(VI) and increase slightly with further increase in acid concentration. From these results, the prepared CC-S75 is applicable for treatment of laboratories effluents (e.g., NMA) and industrial wastewater streams (electroplating and tannery) containing large amounts of toxic heavy metals Cr(VI).

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