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Application of Water Hyacinth as a Benign Solid Phase Extractor for Selective Removal of Cr(VI) from Natural Water Samples: Equilibrium, Isotherm and Kinetics Studies

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ABSTRACT

Stem of Water Hyacinth (SWH) is a low-cost, friendly solid phase extractor was used to remove Cr(VI) from natural water samples. For obtaining its maximum removal, batch experiments were carried out at different parameters including hydrogen ion concentration, initial Cr(VI) concentrations, mass of the adsorbent and equilibration times. The FT-IR spectra of SWH before and after uptake of Cr(VI) were recorded to explore the nature of the functional groups responsible for its binding onto the adsorbent. Surface morphology was also explored in parallel, using Scanning Electron Microscope (SEM). The equilibrium characteristics of Cr(VI) adsorption was described and data well fitted by Langmuir isotherms with maximum uptake capacity (4.599 mg g^{-1}). The Cr(VI) adsorption was fast and completed within 7.5 min and the kinetics data was best fitted with the pseudo-second order type. Finally, Cr(VI) spiked natural water samples such as Doubly Distilled Water (DDW), Drinking Surface Water (DSW), Drinking Ground Water (DGW) were quantitatively recovered (>98.0%) using batch experiments.

Key words: Stem of water hyacinth, adsorption, Cr(VI), kinetic, isotherm, FT-IR, SEM

INTRODUCTION

Chromium is one of the chemical risks present in aqueous solution. It is mainly found in aqueous solution with two oxidation states [Cr(III) and Cr(VI)]. The trivalent form is an essential nutrient (Rojas *et al.,* 2005). The Cr(VI) is highly toxic, carcinogenic and mutagenic in nature (Araujo and Teixeira, 1997), it is highly mobile in soil and an aquatic system as well as it is a strong oxidant capable of being absorbed by the skin (Singh and Singh, 2002). Chromium in the hexavalent form is commonly used in the preparation of a great variety of industrial products, such as pigments for the manufacture of paints, inks, rubber, ceramics, corrosion inhibitors and fungicides (Langard *et al.*, 1986).

Health risks caused by Cr(VI) are the perforation of the nasal septum (Hughes *et al.*, 1994), lung cancer (Bidstrup *et al.*, 1983), skin ulceration (McCarron *et al.,* 2000) as well as kidney, liver and gastric damage. More recently, several medical studies have evidenced the capacity of Cr(VI) to produce cancer in workers who manipulate chromates (Radovic, 2000). One of the main reasons for this risk occurrence is the discharge of industrial wastes in to the aquatic system. Thus, these wastes must be controlled and limited according to standards defined by international organizations and governmental directives. According to WHO the maximum limit hexavalent

chromium is 0.05 mg L^{-1} in water destined for domestic consumption (WHO., 2003). Due to the great riskiness of hexavalent chromium several treatments occurred for its removal or reduction of Cr(VI).

Conventional methods are employed for removing metal ions include chemical precipitation, chemical oxidation and reduction, ion exchange, electrochemical treatment and evaporative recovery (Rawat and Singh, 1992). However, these high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal. So, environmentally friendly processes need to be developed to clean-up the environment without creating hazard waste by-products (Sen and Dastidar, 2010) as Solid Phase Extraction (SPE) technique. It has become known as a powerful tool for separation and removal of various inorganic and organic analytes (Ahmed, 2008; Soliman and Ahmed, 2010). SPE has several advantages over other techniques, including stability and reusability of the solid phase, easiness of separation and enrichment under dynamic conditions, no need for organic solvents and minimal costs due to low consumption of reagents. Recently some natural materials had been used as adsorbent for heavy elements from aqueous solutions such as wheat bran (Nameni *et al.*, 2008), *Aspergillus niger* (Munir *et al.*, 2010), potato peel waste (Abdullah and Devi Prasad, 2009), volcanic ash soil (Babel and Opiso, 2007), powder of potato peelings (Mutongo *et al.*, 2014), barks of *Acacia albida* and leaves of *Euclea schimperi* (Gebrehawaria *et al.*, 2015).

Water hyacinth (*Eichhornia crassipes* Mart. Solms) is growing abundantly in Egypt as well as in tropical and sub-tropical regions of the world (Ibrahim *et al.*, 2012). It was found that about 20 dry tons per hectare can be harvested from standing water hyacinth plants, whereas, 5-8 harvests can be collected per year (Hussein, 1992). Because of the rapid growth of this plant there has been a growing interest in the use of water hyacinth in treating polluted effluents during the last decade as effective phytoremediation tool (Skinner *et al.*, 2007; Ebel *et al.*, 2007). It was found that that plant biomass is effective tool for the removals of pollutants specially trace metals (Abdel-Ghani and Elchaghaby, 2007; Abia *et al.*, 2002). The aim of the present study is to investigate the ability of the powder of stem of water hyacinth to remove Cr(VI) from aqueous solutions under different parameters (pH, weight, time and initial concentration) using batch technique as well as kinetics and isotherm studies.

MATERIALS AND METHODS

Chemical and reagents: All the chemicals used were of analytical grade: potassium dichromate, hydrochloric acid, sodium hydroxide and 1, 5-diphenylcarbazide were purchased from E. Merck, India. Standard stock solution of 1000 mg L^{-1} of Cr(VI) was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in double distilled water and diluted to the required initial concentration (2.5-20 mg L^{-1}). 0.1 N HCl and 0.1 N NaOH solutions are used for pH adjustment. Water samples including: Nile River Water (NRW) as well as Drinking Surface Water (DSW) and Drinking Ground Water (DGW) were collected from El-Minia governorate, Egypt. Doubly Distilled Water (DDW) was obtained from our lab.

Instrumentation: Infrared spectra of water hyacinth before and after Cr(VI) adsorption were obtained using FT-IR Model 410 JASCO (Japan) in the range 4000-400 cm^{-1}. Scanning Electron Microscope (SEM) analysis obtained using JSM-5400 LV JEOL (Japan). Jenway pH-meter Model 3510 calibrated against three standard buffer solutions at pH 4.0, 7.0 and 10.0 was used for

all pH measurements. Flocculator lovibond instrument (Germany) which used for mix the material with a solution at 150 rpm for varied times. Biochrom Libra S12 spectrophotometer (England), which is used to determined Cr(VI) as the pink colored complex was formed, when 1, 5-diphenylcarbazide was added into Cr(VI) in acidic solution and concentration was determined spectrophotometrically at 540 nm (Park *et al.*, 2004).

Development of the adsorbent: The adsorbent in this study was stem water hyacinth [*Eichhornia crassipes*], which was collected from Minia governorate Egypt. The adsorbent was cleaned with double distilled water gently, dried at sun light then dried at 70°C for 3 h and finally ground in a mortar and sieved through 125-150 mesh.

Percentage extraction of SWH: The percentage extraction of Cr(VI) ions using stems of water hyacinth was determined in triplicate under static conditions by the batch equilibrium technique. About 0.5 g of the adsorbent was added to a mixture of 500 mL of 5 mg L^{-1} of Cr(VI) ion and a buffer solution of pH 1.0-10.0. This mixture was mechanically stirring for 10 min at room temperature to attain equilibrium. The adsorbent was separated by filtration, washed with DDW and the unretained Cr(VI) in the filtrate was determined. The equation of metal uptake capacity could be obtained as follows:

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

And the amount of metal adsorbed (Q, mg g^{-1}) was calculated as the following equation:

$$Q = (C_i - C_f) V/W$$

Where:
C_i = Initial concentration of Cr(VI) in mg L^{-1}
C_f = Final concentration of Cr(VI) in the filtrate in mg L^{-1}
V = Volume of the solution in liter
W = Mass of the adsorbent in gram

Moreover, the effect of contact time on Cr(VI) uptake was determined under the same batch conditions but at different shaking periods (2.5, 5, 7.5, 10, 12.5 and 15 min) and at the pH 1.0. The effects of Cr(VI) concentration (2.5-20.0 mg L^{-1}) and weight of adsorbent (0.25-2.50 g) on its percentage extraction were also systematically investigated (Ahmed, 2011).

RESULTS AND DISCUSSION
Characterization of materials
FTIIR spectroscopy: Functional groups in SWH powder was determined using FT-IR spectroscopy (Fig. 1a-b). The SWH is cellulosic materials mainly contains cellulose, hemi-cellulose and lignin. The FT-IR spectra of SWH before and after adsorption of Cr(VI) was performed to determine the vibration frequency changes in their functional groups within the range of 4000-400 cm^{-1}. The SWH powder spectrum showed numbers of major intense bands, around 3424.04, 2924.19, 1630.37, 1384.16, 1319.21, 1249.68, 1155.54, 1034.01, 780.87, 616.73 cm^{-1}. The broad band around 3424.52 cm^{-1} is attributed to the existence of free and intermolecular bonded hydroxyl groups. The peaks assigned at 2924.19 cm^{-1} represented aliphatic C-H stretching
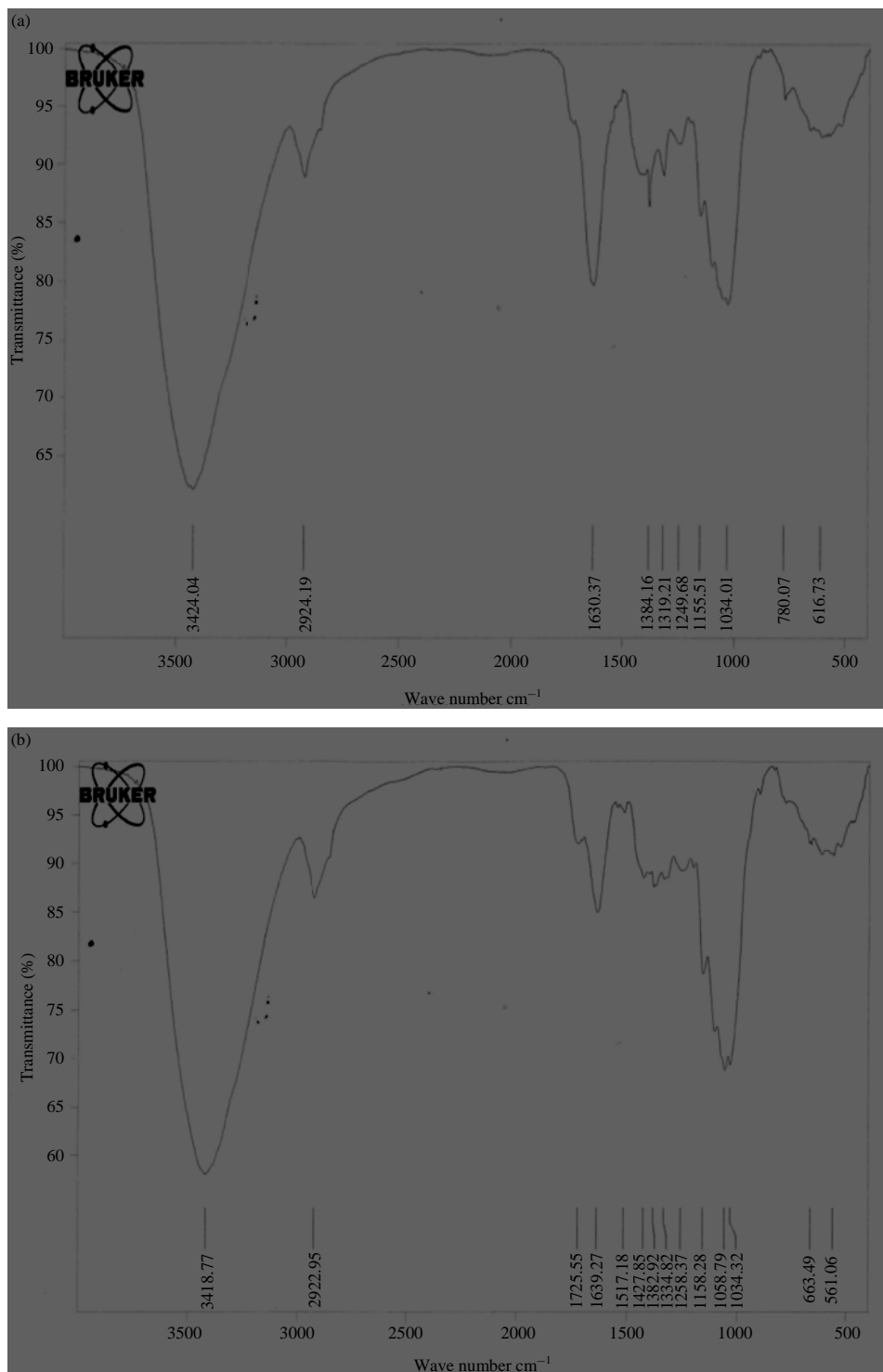
Fig. 1(a-b): FTIR of (a) SWH phase and (b) SWH- Cr(VI) phase

vibrations. The band at 1630.37 cm^{-1} was assigned to the asymmetric stretch mode of the COO- group. A characteristic band at 1384.16 cm^{-1} corresponds to the C = C linkages, which is

present in the guaiacyl ring of the lignin (Das *et al.*, 2015). The band at 1319.21 cm^{-1} can be imputed to the CH$_2$ present in the cellulose and hemi-cellulose (Sun *et al.*, 2008). The bands at 1247.35 cm^{-1} was attributed to absorption by C-O stretching in acetyl group in hemicelluloses, the vibrational modes of the -CH$_2$OH groups and the stretching of the IR spectra of the C-O bonds which are normally coupled with C-O bending of the C-OH functional groups of the carbohydrates can be responsible for the spectral bands at 1034.01 cm^{-1}. The small sharp band at 780.87 and 616.73 cm^{-1} are originated from the glucosidic linkages between the sugar units in hemicelluloses and cellulose.

Generally, the binding of metal ions to adsorbents may be proceed via complexation with functional groups, ionic exchange, surface precipitations and chemical reaction with surface sites. Regarding FT-IR for SWH after Cr(VI) adsorption, it was found that, oxygen containing functional groups vis, methoxy -OCH$_3$, carboxy -COOH and phenolic -OH groups are affected after uptake process. This is judging from shifts in their position, shape or band intensity from 3424.04, 1630.37, 1384.16, 1247.35, 1034.01, 780.87, 616.73 to 3418.77, 1639.27, 1382.92, 1258.37, 1034.02, 663.49, 561.06 cm^{-1} of ν(-OH), ν(-COOH) and ν(-O-C) for SWH before and after Cr(VI) sorption, respectively. The results indicate the participation of these groups via oxygen for Cr(VI) binding to SWH in agreement with Person principal for hard-soft acids and bases (Pearson, 1963).

Scanning electron microscopy: The surface morphology of SWH before and after Cr(VI) adsorption was analyzed using scanning electron microscopy (Fig. 2a, b). The microphotograph before Cr(VI) adsorption revealed the presence of pores and rough surface with highly order structure (Fig. 2a), which is an important factor facilitating the mass transfer rate of metal ions toward the polymer surface and consequently improving its sorption capacity (Yilmaz *et al.*, 2014). After Cr(VI) adsorption the micrograph revealed the presence of smooth surface with narrow thickness (Fig. 2b). These changes of the structure of SWH confirm the presence of Cr(VI) on the surface of SWH.

Effect of pH on Cr(VI) adsorption: pH is the important parameter for removal of metal ions from aqueous solutions, as it affects the surface charge of adsorbents, the degree of ionization and the species of adsorbate. Figure 3 showed the effect of the initial pH of solution of Cr(VI) percentage extraction. Percentage extraction was increased with decreased in the initial pH. At pH 1.0 the
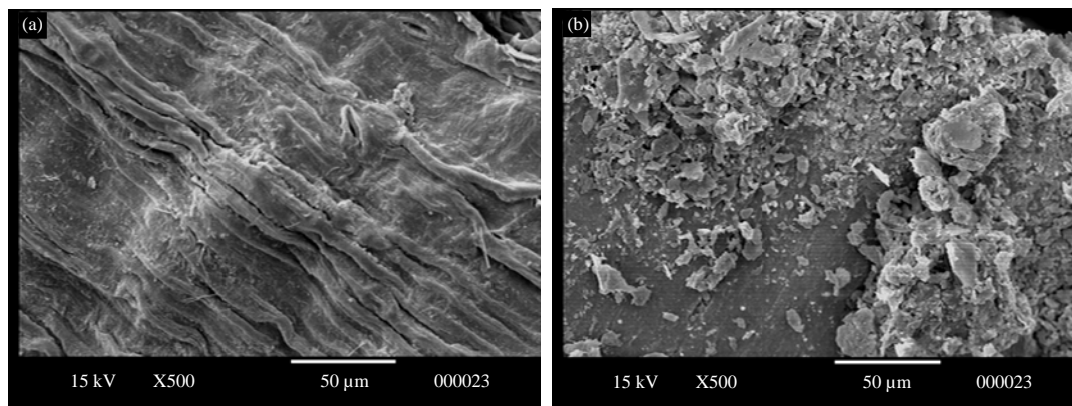

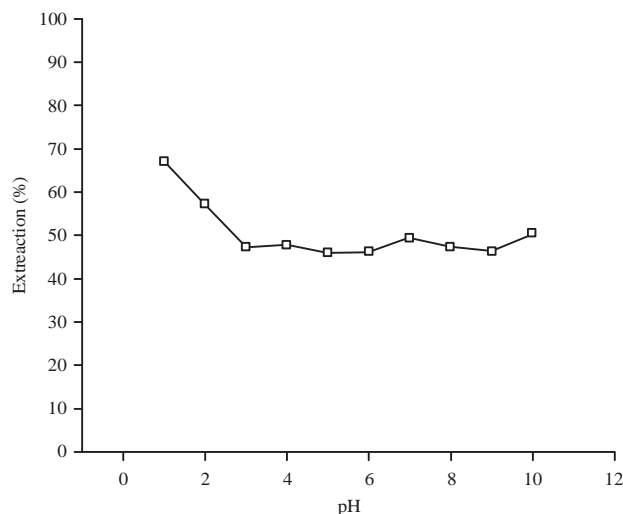Fig. 2(a-b): SEM of SWH (a) Before and (b) After adsorption of Cr(VI)

Fig. 3: Effect of pH on percentage extraction of Cr(VI)

percentage extraction is 67.29%, whereas, on increasing the pH (2.00-9.00) the percentage extraction is reduced to 46.29%. This phenomenon could be explained as Cr(VI) exists in different oxidation states and the stability of these forms depends upon the pH of the system. At low pH the surface of the adsorbent is positively charged. At pH> 2 therefore, electrostatic attraction occurred between the positively charged adsorbent and $HCrO_4^-$, which is predominant of Cr(VI) species at this pH (Dakiky *et al.*, 2002; Hamadi *et al.*, 2001). As the pH increases there was exponential decrease in the Cr(VI) adsorption this was due to dual competition of both the negatively species $Cr_2O_7^{2-}$, CrO_4^{2-} and hydroxyl group which is predominant at higher pH to be adsorbed on the surface of the adsorbent.

Effect of adsorbent weight: The weight of SWH was varied from 0.25-2.5 g keeping all the other experimental variables constant (Fig. 4). It was found that on increasing the adsorbent weight, the percentage extraction of Cr(VI) gradually increases from 54.6-99.98% at 2.0 g weight of the adsorbent. The Cr(VI) percentage extraction increases with increase in adsorbent weight until 2.0 g, since contact surface of adsorbent particles increased and it would be more probable for $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions to be adsorbed on adsorption sites. After 2.0 g, the percentage extraction was constant such behavior is expected due to the saturation level attained during an adsorption process (Dubey and Gopal, 2007).

Effect of contact time and kinetic study: Contact time is an important factor in the process of evaluation of the adsorbent. The batch experiments were carried out at different contact times 2.5-15 min using flocculator instrument with 2.0 g of adsorbent weight, Cr(VI) concentration equal 5 mg L^{-1} at a pH of 1.0 and 500 mL contact solution. The obtained results showed that the equilibrium is reached after 5 min and the percentage extraction was increased from 96.95-99.98%. The results showed that the adsorbent is acting fast in the adsorption process. In the beginning, the ions adsorbed, occupied the active sites on the phases. As the contact time increased the active sites on the sorbent were filled as shown in Fig. 5.

Kinetic study: The kinetics of Cr(VI) adsorption on SWH was studied using Lagergen kinetic model or pseudo-first-order, pseudo-second-order sorption equation, Elovich equation and the
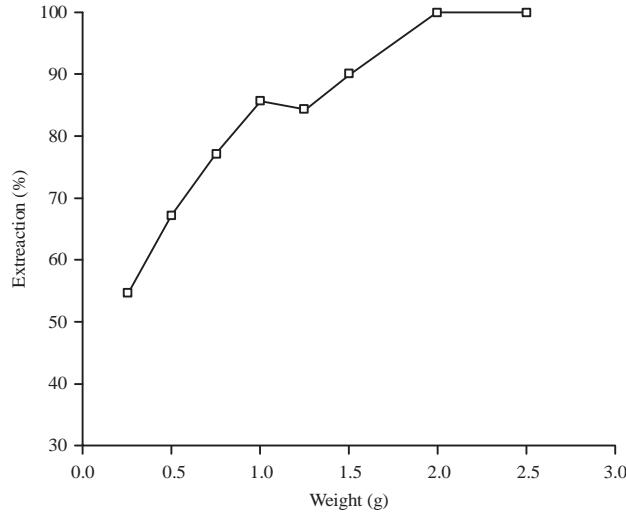
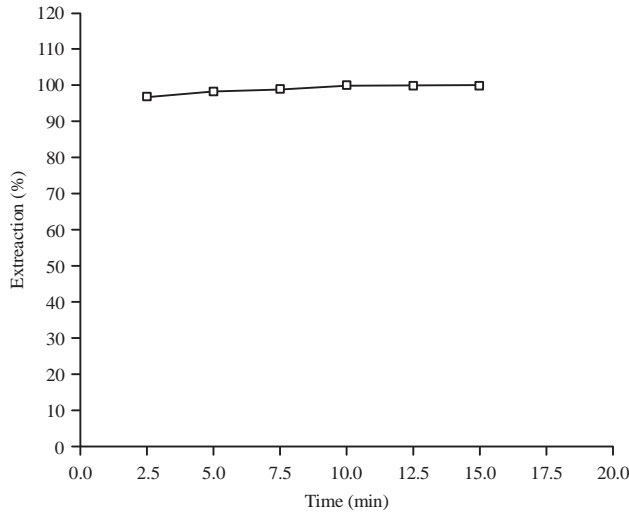Fig. 4: Effect of adsorbent weight on percentage extraction of Cr(VI)

Fig. 5: Effect of time on percentage extraction of Cr(VI)

intraparticle diffusion model. The adsorption kinetic for binding of Cr(VI) with SWH was determined by the batch technique at pH 1.0, solutions of Cr(VI) in the concentration is 5 mg L^{-1}, time stirred in the range (2.5-15 min) with a constant weight 2.0 g of water hyacinth.

Pseudo-first-order: Lagergen kinetic model or pseudo-first-order which it is the first equation for adsorption of liquid/solid system (Lagergren, 1898; Ho, 2004) and is usually written as follows:

$$\text{Log } (q_e\text{-}q_t) = \log q_e\text{-}(k_1/2.303) \, t \qquad (1)$$

where, k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption or Lagergen constant, q_e (mg g^{-1}) and q_t (mg g^{-1}) denote the amount of adsorption at equilibrium and at time t (min),

respectively. The plot of log (q_e-q_t) vs t should give a linear relationship. Which k_1 and q_e can be determined from the slope and intercept as show in Table 1.

Pseudo-second-order: Pseudo-second-order adsorption (Ho, 2006) (Eq. 2). Which can be expressed as:

$$dq_e/dt = k_2 (q_e -q_t)^2 \qquad (2)$$

By Integration of Eq. 2 and application of the conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, it will arrange obtained linear Eq. 3.

$$t/q_t=1/k_2 q_e^2+t/q_e \qquad (3)$$

where, k_2 (g mg^{-1} min) is the rate constant of adsorption, q_e (mg g^{-1}) is the amount of Cr(VI) adsorbed at equilibrium and q_t (mg g^{-1}) the amount of Cr(VI) on the surface of the sorbent at any time t (min). k_2 and q_e can be obtained from the intercept and slope of a plot of t/qt vs t as shown in Fig. 6 as well as regression coefficient (r^2) as shown in Table 1.

Table 1: kinetic parameters for the adsorption of Cr(VI) on SWH

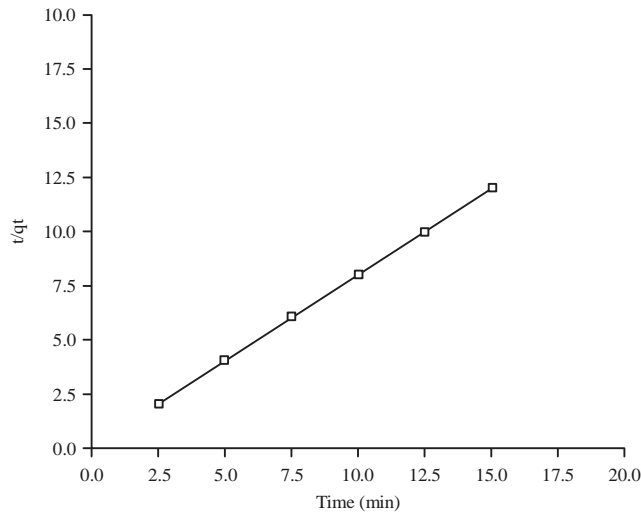| Kinetic parameters	Values
Pseudo-first-order	
R^2	0.756
q_e (mg g^{-1})	1.671
K_1 (min^{-1})	1.082
Pseudo-second-order	
R^2	0.999
q_e (mg g^{-1})	1.261
K_1 (min^{-1})	9.854
Elovich model	
R^2	0.952
α (mg g^{-1} min^{-1})	7.22×10^{21}
β (g mg^{-1})	45.45
Intraparticle diffusion model	
R^2	0.949
k_{id} (mg g^{-1} min^{-n})	1.244

Fig. 6: Pseudo-second-order kinetic plot for the adsorption of Cr (VI)

Elovich model: Elovich model (Chien and Clayton, 1980; Sparks, 1986) equation is generally expressed as Eq. 4:

$$Q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \tag{4}$$

where, α is the initial adsorption rate (mg g^{-1} min) and β is the desorption constant (g mg^{-1}) during any one experiment which related to the extent of surface coverage and activation energy for chemisorption. The plot of q_t vs ln(t) should give a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (α β) (Table 1).

Intraparticle diffusion model: The intraparticle diffusion model often the rate controlling step, is the possible method of movement of the ions from solution into the adsorbent (34) and is expressed (Khezami and Capart, 2005; Weber and Morris, 1963) as Eq. 5:

$$q_t = k_{id} t^{0.5} \tag{5}$$

A linearized form is Eq. 6:

$$Log\ q_t = \log k_{id} + 0.5 \log t \tag{6}$$

where, q_t is the amount Cr(VI) adsorbed, t is the contact time, k_{id} is the intraparticle diffusion coefficient. The plot of log q_t vs 0.5 log t it should give a straight line with a positive intercept for intra-particle diffusion controlled adsorption process.

From results in Table 1 the second order kinetic model provides the highest correlation coefficient ($r^2 = 0.999$) and the better agreement between calculated $q_e = 1.250$ mg g^{-1} and the experimental $q_e = 1.261$ mg g^{-1} value which indicates that the second order kinetic model is more suitable for the adsorption model and can be applied for the adsorption process of Cr(VI) using SWH as an adsorbent. As well as ($r^2 = 0.949$) for intraparticle diffusion model, this means that the intraparticle diffusion is indeed present in the adsorption of Cr(VI) but that it is not the rate controlling step.

Effect of Cr(VI) concentration and equilibrium isotherms: The effect of Cr(VI) concentration on its percentage extraction was studied at concentrations of 2.5-20 mg L^{-1} at fixed adsorbent weight of 2.0 g, pH 1.0 and contact time 7.5 min for SWH (Fig. 7). The results indicated that the percentage extraction of Cr(VI) initially increased with concentration of 7.5 mg L^{-1}. As the concentration was increased from 10-20 mg L^{-1}, the percentage extraction decreased with the adsorbent from 99.97-43.53%. This indicates that the percentage extraction is highly dependent on the initial concentration of Cr(VI) in solution. This phenomenon is attributed to a lack of sufficient surface area to the target metal ion present in the solution. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake. Uptake of the Cr(VI) also increased with increasing the initial metal concentration tending to saturation at higher metal concentrations (Malkoc and Nuhoglu, 2007).

To find out the mechanistic parameters associated with Cr(VI) sorption, the results obtained by the adsorption experiments were analyzed by the well-known models given by Freundlich, Langmuir and Temkin models. The adsorption isotherms for binding of Cr(VI) with water hyacinth,
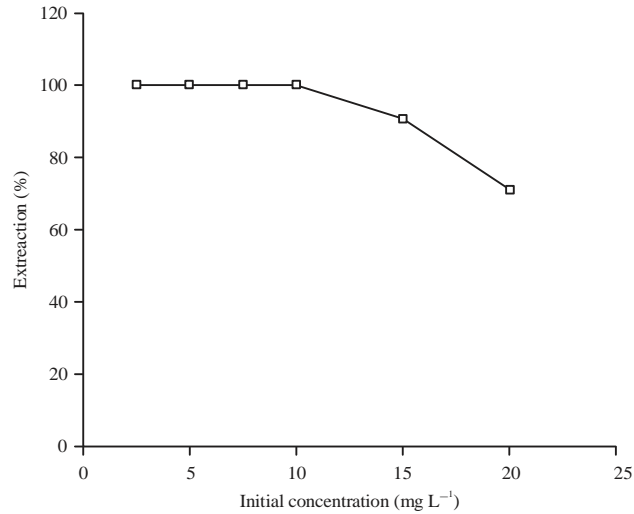
Fig. 7: Effect of initial concentration dosage on percentage extraction of Cr(VI)

was determined by the batch technique at pH 1.0. Thus, solutions of Cr(VI) in the concentration 2.5-20 mg L^{-1} was stirred for 7.5 min with a constant weight 2 g of water hyacinth.

Freundlich isotherm: The basic assumption of Freundlich isotherm is that if the concentration of the solute in the solution at equilibrium, C_e was raised to the power 1/n, the amount of solute adsorbed being q_e, then $C_e^{1/n} q_e$ was a constant at a given temperature. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the adsorption (Eq. 7). The non-linear form of Freundlish equation expressed as follows:

$$q_e = K_f C_e^{1/n} \text{ (non-linear form)} \tag{7}$$

where, K_f (mg g^{-1} (L mg^{-1})) 1/n and 1/n are Freundlich constants (indicators of the adsorption capacity and intensity, respectively). Taking logs and rearranging of Eq. 7, it can given the linear form of Freundlich model which expressed as:

$$\log q_e = \log K_f + 1/n \log C_e \text{ (linear form)} \tag{8}$$

The constants K_f and 1/n can be calculated from the intercept and slope of this linear equation, respectively (Table 2). It is clearly showed that the data is not fitting well to the Freundlich model.

Langmuir isotherm: The Langmuir equation (Langmuir, 1916) which uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate is given by the following equation:

$$C_e/q_e = (1/ Q_o) C_e = (1/ Q_o b), \text{ (linear form)} \tag{9}$$

where, C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phases in mg L^{-1} and mg g^{-1}, respectively. The Q_o and b are Langmuir constants, which are related to the maximum Cr(VI) mono layer adsorption capacity (mg g^{-1}) and affinity parameter (L mg^{-1}), respectively, it can be calculated from the intercept ($1/Q_ob$) and slope ($1/Q_o$) of the linear plot, C_e/q_e vs C_e given in Fig. 8, Table 2. The correlation coefficient ($r^2 = 0.963$) for the adsorption of Cr(VI) on water hyacinth and showed that the Langmuir model fitted the results better than Freundlich model. The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as follows:

$$R_L = 1/(1 + bC_o) \tag{10}$$

where, b is the Langmuir constant (indicates the nature of sorption and the shape of the isotherm accordingly) and C_o is the initial concentration of the analyte. The R_L parameter indicates the shape of the isotherm as follows:

$R_L > 1$, unfavorable, $R_L = 1$, linear, $0 < R_L < 1$, favourable, $R_L = 0$, irreversible. In our study, $R_L = 0.005$-0.038 is favorable.

Table 2: Equilibrium isotherm parameters for the adsorption of Cr(VI) on SWH

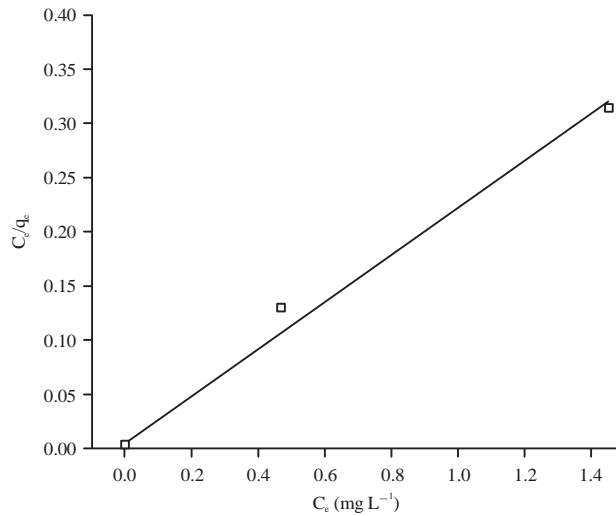| Isotherm parameters	Values
Freundlich	
R^2	0.781
$1/n$	0.110
k_F (L^n mg^{1-n} g^{-1})	4.110
Langmuir	
R^2	0.991
Q_o (mg g^{-1})	4.599
B (L g^{-1})	46.290
Temkin	
R^2	0.823
b_T (kJ mol^{-1})	3028.817
K_T (L g^{-1})	32245852.800

Fig. 8: Langmuir isotherm plot for the adsorption of Cr(VI)

Timken isotherm: Timken isotherm which developed by Temkin and Pyzhev (1940) and it is based on the assumption that the heat of adsorption decreases linearly with the increase of coverage of adsorbent (Hosseini *et al.*, 2003). This model can be shown by the equation:

$$q_e = RT/b_T \ln k_T + RT/b_T \ln C_e \tag{11}$$

where, K_T (L g^{-1}) is Temkin adsorption potential , b_T (J mol^{-1}) is heat of sorption, T is the absolute temperature, R is the universal gas constant (8.314 J mol^{-1} k). The linear plot of ln C_e versus q_e for the Cr(VI) ions for Temkin model, b_T and K_T can be evaluated from studies of adsorption isotherms we find that Langmuir isotherm model had the highest value of regression coefficient when compared to other models and this model is more suitable for the adsorption equilibrium of Cr(VI) and it was indicated that homogenous monolayer is adsorbed on the surface from the slope and intercept of the straight line, respectively shown in Table 2.

Comparison of adsorption of Cr(VI) using water hyacinth with alternative natural adsorbents: The proposed method was compared to a variety of recent adsorbents present in literature for adsorption of Cr(VI). The comparison is based on their maximum adsorption capacity (Q_{max}, mg g^{-1}), initial concentration of the metal ion, PH, time. In our study the Q_{max} of Cr(VI) using SWH is higher than other adsorbents present in Table 3, also the time required to equilibrium is shorter than in other adsorbents. The extraction of the adsorbent in this study is better than the other adsorbents present in the Table 4.

Application
Removal of Cr (VI) from natural water samples: Uptake experiments were carried out using different natural water samples: DSW, DGW. Two gram powder of SWH was conditioned with 500.0 mL of water sample spiked Cr(VI) at concentration of 5 mg L^{-1} (adjusted at pH 1.0 by fine addition of concentrated HCl) with stirring for 10 min. the solution (free from the suspended solid phase) were taken at the end of the experiment where the residual concentration of metal ion was determined via atomic absorption and Biochrom Libra S12. Although, the presence of anions such

Table 3: Comparison of adsorption of Cr(VI) using water hyacinth with alternative natural adsorbents

Adsorbents	pH	Time (min)	Initial concentration (mg L^{-1})	Maximum adsorption Qe (mg g^{-1})	References
Wheat bran	2	60.0	0-15	0.942	Nameni *et al.* (2008)
Aspergillus niger	5-6	-	25-100	6.97	Munir *et al.* (2010)
Isarong ash soil	2	60.0	0-15	0.864	Babel and Opiso (2007)
Potato peelings	2.5	148.0	20-120	3.25	Mutongo *et al.* (2014)
Barks of *Acacia albida*	2	60.0	0-20	2.983	Gebrehawaria *et al.* (2014)
Leaves of *Euclea schimperi*	2	60.0	0-20	3.946	Gebrehawaria *et al.* (2014)
SWH	1	7.5	0-20	4.599	This study

Table 4: Recovery of Cr(VI) spiked natural water samples with stem of water hyacinth using batch technique
Concentration of metal ion (mg L^{-1})

Samples	Ca (II)	Mg (II)	Fe (III)	Mn (II)	Cl^{-1}	SO$_4{}^{2-}$	Cr (VI)	Recovery (%)
DDW	-	-	-	-	-	-	0.0011	99.97
DSW	88	30	0	0	22	24	0.0150	99.70
DGW(1)	140	53	0.1	0.6	30	28	0.0400	99.20
DGW(2)	260	110	0.3	0.5	78	70	0.0800	98.40
DGW(3)	232	114	0.5	0.8	70	84	0.0800	98.40

DDW: Doubly distilled water, DSW: Drinking surface water, DGW: Drinking ground water

as Cl^-, SO_4^{-2} and cations Ca(II), Mg(II), Fe(III), Mn(II) with different concentrations in water samples, the percent recovery of Cr(VI) using SWH as adsorbent was very high. This indicate the suitability and selectivity of using stem of water hyacinth for extraction of Cr(VI) from natural water samples.

CONCLUSION

Stem water hyacinth is a good solid phase extractor for removal of Cr(VI) from aqueous solutions due to its advantages such as benign lignocellulosic material, highly available in Egypt, rich with functional groups and obtains good adsorption even at low concentration of target metal ion. The optimal conditions for Cr(VI) removal (percentage extraction is 99.97%) was studied. It was observed that the maximum removal occurs at an Initial Cr(VI) concentration of 7.5 ppm, at pH 1.0 with an adsorbent dosage of 2 g and maximum stirring time of 7.5 min . The adsorption isotherm was fitted well with Langmuir model ($r^2 = 0.991$, $R_L = 0.005$-0.038) and the maximum adsorption capacity (Q_o) was calculated to be 4.599 mg g^{-1}. The kinetic model obeying pseudo-second order type ($r^2 = 0.999$). The SWH was applicable for selective removal of Cr(VI) from different natural water samples (percentage recovery >98.0%) using batch techniques.

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