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## POLYPYRROLE–POLYANILINE-WATER HYACINTH LEAF PROTEIN CONCENTRATE COMPOSITE FOR THE REMOVAL OF Cr(VI) FROM AQUEOUS SOLUTION: KINETICS, ISOTHERM AND THERMODYNAMIC STUDIES

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**ABSTRACT**. This work focused on the extraction of "water hyacinth leaf protein concentrate" (WHLPC) and preparation of polypyrrole (PPy), polyaniline (PANI) and polypyrrole-polyaniline copolymer (PPy/PANI) coated WHLPC by in situ polymerization and investigate their application for the removal of Cr(VI) from aqueous solution. After optimizing the experimental conditions like pH, adsorbent dosage, contact time and initial concentration it was found that the kinetics and isotherm data were well fitted to the pseudo-second-order and Langmuir models, respectively. PPy/PANI/WHLPC was found to be an efficient material compared to the other polymer-coated adsorbents with maximum adsorption capacity of 230 mg/g. The presence of counter ions ( $(NO_3^-, CI^-, HPO_4^{-2}, SO_4^{-2})$ and  $HCO_3^-$  ions) slightly decreases the Cr(VI) removal efficiency PPy/PANI/WHLPC. The thermodynamic study reveals that the adsorption of Cr(VI) onto PPY/PANI/WHLPC is endothermic, thermodynamically feasible, and spontaneous. In addition, reusability of the material indicated high removal efficiency for two adsorption cycles.

KEY WORDS: Polypyrrole, Polyaniline, Protein concentrate, Water hyacinth, Chromium

## INTRODUCTION

In aqueous solution, chromium commonly exists in trivalent Cr(III) and hexavalent Cr(VI) states. Cr(VI) which is known to be 100-fold more toxic than Cr(III) is of great concern and is listed as class A human carcinogen by US Environmental Protection Agency [1]. WHO recommends that a maximum allowable Cr(VI) concentration for surface water be 0.1 mg/L while the permissible level of Cr(VI) in drinking water 0.05 mg/L [2]. But, chromium is continually being released into the environment as hazardous waste mainly because of its immense applications in paints and pigments, in metal plating [3], in leather tanning industry [4], in steel industry, as catalyst and as wood preservative [5]. Hence, detoxifying the hazardous wastes before being released into the environment is continuing to be a serious challenge and many researchers are investigating different methods. Such methods include adsorption [6], membrane filtration[7], photocatalytic degradation [8, 9], ion exchange [10], coagulation [7], and oxidation/reduction [11].

Among these methods, adsorption is found to be easier, convenient and particularly cheaper if one employs cheap and abundantly available adsorbent materials. This approach is going to be even more promising and rewarding if one uses other environmental pollutants and wastes as an adsorbent material. In this regard, water hyacinth (WH) which is one of the worst invasive weeds causing serious problems in irrigation, navigation and power generation in many tropical and

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subtropical countries [12, 13]. Water hyacinth leaf protein concentrate is a potential adsorbent of interest used for the removal of toxic metal such as chromium. Water hyacinth has been widely used for wastewater treatment as well as energy storage [14-18]. Some of the works were extensively investigated for effective management of the WH in wastewater treatment. This includes chemically modified dried water hyacinth roots [19], WH microspheres [20], ZnO supported nanoparticle on water hyacinth biochar [21] with their maximum adsorption capacity values of 1.28, 7.7, and 43.48 mg/g, respectively.

Conducting polymers like polypyrrole and polyaniline can be used for treating wastewater due to their popularity related to ease of synthesis, biocompatibility, redox, and ion exchange properties. Further coating of conducting polymer on the surface active substrate (biosorbents) improves their strength and processability [2, 22]. Conducting polymers like PANI, PPY, poly(3methylthiophene (P3MTh) and their composites with biopolymers have been also investigated to further improve the adsorption capacities of biosorbents. For instance, using PPy/wood sawdust [23], PPy/chitin [24], PPy/chitosan [25], poly(3-ethylthiophene)/chitosan [26], P3MTh/chitosan [27], PANI/humic acid [28], itaconic acid-PANI-copper(II)oxide nanoparticles [29], and PPy-PANI coated rice husk ash [22], reported the adsorption capacity values of 3.4, 28.92, 78.61, 127.6, 148.7, 150, 250, and 769.2 mg/g, respectively. Furthermore, other methods have been reported for management of WH weed for animal feed due to its high protein content especially in the leaves and its rapid growth [30-32]. However, to the best of our knowledge the water hyacinth leaf protein concentrate (WHLPC) extracted from the weed has not been used for removal of toxic metals. Hence, we report the adsorption characteristics of WHLPC coated with conducting polymers for detoxification of wastewater polluted with Cr(VI).

### **EXPERIMENTAL**

### Materials and method

Potassium dichromate, ferric chloride, sulfuric acid (96%), hydrochloric acid (37%), toluene, and acetone (HPLC grade > 99.9%), and pyrrole (Reagent grade, 98%), aniline (ACS reagent  $\geq$  99.5%), ammonium persulfate (APS) (Reagent plus<sup>®</sup>  $\geq$  98%), 1,5-diphenylcarbazide (ACS reagent grade) were purchased from Sigma-Aldrich and used as received. The fresh leaf part of the WH was used to extract water hyacinth leaf protein concentrate (WHLPC). The WHLPC was coated with PPy, PANI and PPy/PANI by chemically polymerizing pyrrole and aniline.

Adam PW 254 digital analytical balance, 2510 Bransonultrasonicator and 3510 Jenway pH meter were used for solution preparation. The UV-Vis absorption spectra were measured using Cary 60 UV-Vis, Agilent Technologies. FTIR study was carried out using Spectrum 65 FT-IR (PerkinElmer) in the range 400-4000 cm<sup>-1</sup> (resolution: 4 cm<sup>-1</sup>, number of scans: 4) and KBr pellets. The elemental percentage composition of WHLPC was determined by using Electron microscopeelectron dispersive X-ray spectroscopy (EDS). The crude fat, fiber and protein contents were determined using a Soxtec 8000 solvent extraction system, Fibertec 8000 auto fiber analysis system and Kjeldahl block digestion system, respectively. For adsorption studies, orbital shaker, GFL 3020 was used.

## Preparation of adsorbent materials

Water hyacinth was collected from Lake Tana, Bahir Dar, Ethiopia. The extraction of WHLPC was made based on previously established procedures [32]. Briefly, the WH leaves were soaked in distilled water at a 2:1(w/v) ratio for 30 min. A 0.1 M NaOH was added to the slurry until reaching pH 9.0 allowing the solubilization of leaf proteins. The tissue slurry was filtered using a clean cotton cloth and the filtrate collected. After addition of 0.1 M HCl into the filtrate at pH 2,

the protein was coagulated by heating at 80 °C for 5 min separated by decantation and filtration. The coagulated sample was then collected and oven-dried at 60 °C. Finally, the dried WHLPC was crushed into a fine powder to retain uniform particle size and kept in a dried vial.

The point of zero charge (pH<sub>PZC</sub>) was determined by batch equilibrium technique. A 50 mg of WHLPC was suspended in 50 mL of 0.1 M KNO<sub>3</sub> solution. The initial pH of the solution was adjusted to defined values from 2 to 12 using HNO<sub>3</sub> and KOH solutions. The suspension was allowed to equilibrate by shaking for 10 h with speed of 150 rpm at room temperature. The final pH of the potassium nitrate solutions was measured and plotted against their initial pH. The pH<sub>PZC</sub> was obtained from the plateau of constant pH to the ordinate in pH<sub>final</sub> versus pH<sub>initial</sub> plot [33] or from the abscissa value in which pH<sub>fina</sub>-pH<sub>initial</sub> is equal to zero from  $\triangle$ pH versus initial pH plot [34].

The polypyrrole-WHLPC composite, PPy/WHLPC, was prepared based on the previously established polymerization procedure [24]. PPy/WHLPC was prepared by adding 1.0 g of Py into 10 g of WHLPC dispersed in 100 mL deionized water under stirred condition between 0-5 °C. A 0.02 M APS was added drop wise into PPy/WHLPC suspension after 60 min under the same temperature. Then the result product was filtered after 12 h, washed with deionized water until the filtrate became colorless, and dried in the oven at 50 °C for 24 h.

Polyaniline WHLPC composites were synthesized by in-situ polymerization of aniline with WHLPC powder in the presence of APS [25, 35]. A 0.465 g WHLPC was dispersed in 60 mL of HCl (1 M) for 30 min and 9.12 mL aniline monomer was added to the WHLPC suspension, stirred for 30 min. A solution of HCl (1 M, 60 mL) containing APS (22.8 g) was added drop wise to the well-stirred reaction mixture over 1 h. After a few minutes, the dark suspension became green, the reaction system was kept in an ice bath and stirred for 24 h to complete the polymerization. Finally, the composite was collected by vacuum filtration washed with deionized water and dried in the oven at 50 °C.

Polypyrrol-polyaniline copolymer coated on the surface of WHLPC were prepared via in-situ copolymerization of pyrrole and aniline monomer in the presence of APS oxidant as described by Dutta *et al.* [22]. Initially 0.1 g WHLPC dispersed in 10 mL of deionized water in one beaker. Next, in separate beakers 0.3 mL of pyrrole and 0.15 mL of aniline monomers were mixed in 10 mL of deionized water and doped with 1 M HCl. The two monomer solutions simultaneously added into the WHLPC dispersed solution under continuous stirring for 5 to 6 hours at room temperature. Followed by the addition of 0.15 g of APS dissolved in deionized water into the above solution and kept the system in ice-bath for 12 h. The final product, PPy-PANI-WHLPC collected by vacuum filtration, was washed rapidly with excess amounts of water and dried in a vacuum oven at 60 °C for 12 h.

#### Adsorption experiments

Batch adsorption was used to evaluate the effects of pH (1-7), adsorbent dosage (0.025-3 g/L), contact time (30-660 min), initial concentration (50-1000 mg/L), and temperature (293–323 K). The expected pH value of the solution was adjusted by adding a very small amount of concentrated  $H_2SO_4$  or 2 M NaOH. The liquid and solid phases were separated via centrifugation at 4000 rpm for 5 min. Then the amount of Cr(VI) left in the filterate solution analysed after contacting with 1,5-diphenyl carbazide to form purpleviolet coloured complex, and determined by ultraviolet-visible (UV/Vis) spectrophotometry at 540 nm.

The reusability and stability of PPy/PANI/WHLPC was examined through one-step desorption experiments performed at the end of the adsorption experiments. For desorption experiment NaOH solution was used as an eluent to recover the absorbent material for Cr(VI) adsorption studies. The Cr(VI)-loaded PPy/PANI/WHLPC was undergo desorption, to select the optimal concentration of NaOH between 0.01 to 2 M. The concentration of Cr(VI) in the filtrate solution was analyzed and the adsorbent material was regenerated by treating with 2 M HCl

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followed by rinsing with double distilled water and dry in over at 60 °C. The reusability of the dry adsorbent material was used for five successive adsorption-desorption cycles by using 1 M NaOH as a desorbing agent. The effect of co-existing ions and their concentration (25-100 mg/L) on the adsorption of Cr(VI) by PPy/PANI/WHLPC was evaluated in the presence NO<sub>3</sub><sup>-</sup> SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> ions. The percentage removal of chromium(VI) from aqueous solution and adsorption capacity of the adsorbent material were calculated using Eq.(1) and (2), respectively.

$$\% R = \frac{(C_0 - C_e)}{C_0} X 100$$
 (1)

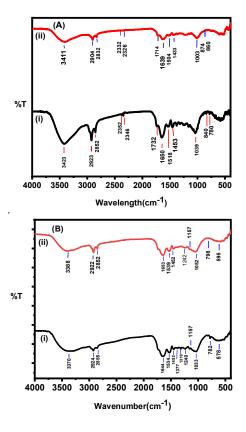
where  $C_0$  and  $C_e$  indicate the initial concentration of Cr(VI) and the equilibrium concentration, respectively. The  $q_e$  represents the equilibrium adsorption capacity and is calculated as given by Eq. (2) (C - C)V

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where the mass of the adsorbent is denoted by m (mg), and V (mL) is the volume of the Cr(VI) solution.

# **RESULTS AND DISCUSSION**

Characterization of the adsorbent material



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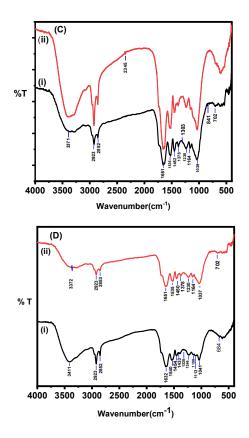


Figure 1. FTIR spectra of (A) WHLPC(B) PANI/WHLPC, (C) PPy/WHLPC and (D) PPy/PANI/WHLPC without Cr(VI) (i) and with Cr(VI) loading (ii).

The FT-IR spectra of the adsorbent materials with and without Cr(VI) loading, are shown in Figure 1. The broad and shallow band peak around 3400 cm<sup>-1</sup> indicates the presence of an amine functional group on the adsorbent materials. The small peak at 2900 cm<sup>-1</sup> exhibits the sp<sup>3</sup> C-H stretching of the adsorbent. The decrease in band peaks and minor shifting of band wavelengths were observed when Cr(VI) loaded on the adsorbent materials. The decrease in transmittance and shifting band wavelength could be attributed to the steric hindrance of Cr(VI) complex with adsorbent [33, 36].

The energy dispersive x-ray spectroscopy (EDS) was used to determine elemental percentage compositions of the WHLPC. Elemental compositions of carbon, oxygen, nitrogen and sulfur were found to be 71.87%, 21.67%, 6.24% and 0.47%, respectively. In addition, the crude protein, fat, fiber, ash and moisture percentages of WHLPC were evaluated and corresponding values were 42.23, 19.66, 4.62, 27.66 and 6.22%, respectively. Moreover, the crude protein content obtained is also in good agreement with values reported by others [32].

The point of zero charge,  $pH_{PZC}$  was employed to characterize the surface charge of the WHLPC and its value was found to be 4.2. Since the adsorption of Cr(VI) on the adsorbent was performed at pH 2.0, adsorbent surface charge remained positive ( $pH_{pzc}$  below 4.2). Consequently,

there is an electrostatic attraction between hexavalent chromium ( $HCrO_4^-$ ) and the adsorbent WHLPC which is reflected by higher adsorption capacities for solutions less than pH 4.

## Adsorption conditions

The effects of pH and adsorption dosage on adsorption capacity were investigated in the presence of 0.5 g/L of adsorbent dosage in 50 mg/L Cr(VI) at 240 min contact time and the results are shown in Figure 3. The solution pH greatly influences the adsorption capacities of unmodified WHLPC and polymer modified WHLPC for the removal of Cr(VI) and attain optimal value at pH 2 (Figure 2(A)). This can be attributed to the protonation of the adsorbent surfaces at lower pH, favoring the adsorption of the negatively charged chromate ions. With increasing pH, the equilibrium adsorption capacities ( $q_e$ ) decrease since the protonation decreases as the concentration of hydronium ions decreases.

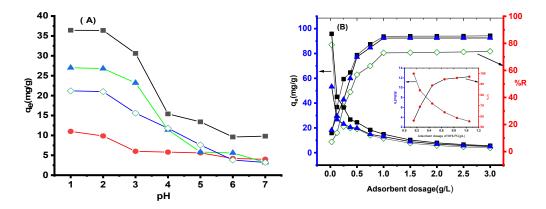


Figure 2. Effect of pH (A) and adsorbent dosage (B) on the equilibrium adsorption capacity and percent removal of Cr(VI) at WHLPC(●), PANI-WHLPC(△), PPY-HLPC(▲), and PY-PANI-WHLPC(■). (Inset the respective adsorption properties on WHLPC).

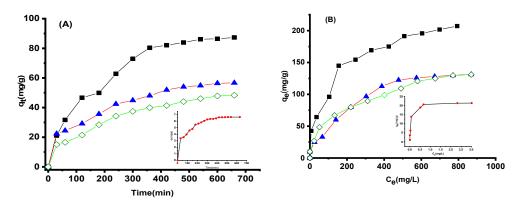


Figure 3. Effect of contact time (A) and concentration (B) on the adsorption capacity of Cr(VI) at WHLPC(●), PANI-WHLPC(♦), PPY-HLPC(▲), and PYY-PANI-WHLPC(■). (Inset the respective adsorption properties on WHLPC).

Figure 2(B) shows the effect of adsorbent dosage on equilibrium adsorption capacities and percent removal evaluated for 240 min contact time using 100 mg/L Cr(VI) as initial concentration at pH 2. The percent removal sharply increases with increasing adsorbent dosage at lower adsorbent dosage due to the availability of sufficient adsorbent sites. Both the adsorption capacities and percent removal reach saturation at higher adsorbent mass that causes agglomeration of adsorbent material. In order to minimize the mass of adsorbent without compromising the percent removal and adsorption capacity, an optimum dosage of 1.0 g/L was taken for further experiments

The effect of contact time and concentration of Cr(VI) ions on adsorption capacities are shown in Figure 3. The adsorption capacities initially increase with increasing contact time and concentration of Cr(VI) due to the availability of large active surface sites of the adsorbent. The adsorption capacities remain constant at higher contact time and concentration of Cr(VI). Hence, the optimum time was found to be 420 min for further experiments. Furthermore, the equilibrium adsorption capacity of PPY/PANI/WHLPC was higher than other polymer modified WHLPCs that could be attributed to the presence of more active adsorption sites per unit mass of the adsorbent.

From the experimental contact time data shown in Figure 4(A), the adsorption kinetics of Cr(VI) on the adsorbent materials were evaluated using the pseudo-first-order, and pseudo-second-order kinetics given by Eqs. (3) and (4), respectively.

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t$$
(3)

$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{t}{q_{e}}$$
(4)

where  $q_e$  and  $q_t$  are the amount of Cr(VI) ion adsorbed (mg/g) at equilibrium, and at time t, respectively, and  $k_1(min^{-1})$  and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>)are the rate constant of the adsorption of first and second orders, respectively.

The  $q_e$  and  $k_1$  values for the first-order kinetics are calculated from the intercept and slope of the linear plot of  $log(q_e-q_t)$  versus t. For the second-order kinetics, the  $q_e$  and  $k_2$  values are calculated from the linear plot of  $t/q_t$  versus t (Figure 4) and the values are listed in Table 1.

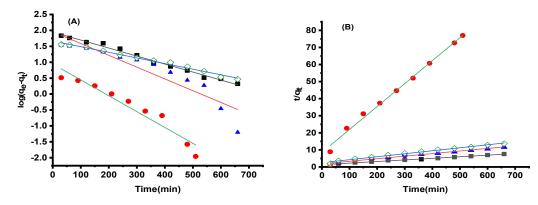


Figure 4. Pseudo-first-order (A) and pseudo-second-order (B) linear plots for the adsorption of Cr(VI) at WHLPC(●), PANI-WHLPC(♦), PPY-HLPC(▲), and PY-PANI-WHLPC(■).

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The parametric values of pseudo-first and pseudo-second kinetic models with their corresponding  $R^2$  value compared for WHLPC and the modified WHLPCs. The correlation coefficients ( $R^2$ ) in the pseudo-second kinetic model were higher than those of the pseudo-first kinetic model. The corresponding values were about 0.99 for all these adsorbents. The pseudo second kinetic model assumes that the adsorption of Cr(VI) ions on an adsorbent surface is controlled by a chemisorption mechanism. Hence, the primary removal of hexavalent chromium by the WHLPC was electrostatic adsorption.

Table 1. Kinetics parameters for adsorption of Cr(VI) onto different WHLPC based adsorbents

Adsorbent	Pseudo first-order			
	q <sub>e.exp.</sub>	q <sub>e.cal.</sub>	$k_1(x \ 10^{-3})$	R <sup>2</sup>
	(mg/g)	(mg/g)	$(\min^{-1})$	
WHLPC	6.65	8.75	1.15	0.9228
PPy/WHLPC	56.7	90.8	8.52	0.8464
PANI/WHLPC	51.2	46.2	4.12	0.9876
PPy/PANI/WHLPC	89.4	88.5	5.78	0.9873
	Pseudo second-order			
	qe.exp.	qe.cal.	k <sub>2</sub> (x 10 <sup>-3</sup> )	R <sup>2</sup>
	(mg/g)	(mg/g)	(g/(mg . min)	
WHLPC	6.65	7.44	2.13	0.9931
PPy/WHLPC	56.7	66.4	8.3	0.9892
PANI/WHLPC	51.2	57.2	0.184	0.9879
PPy/PANI/WHLPC	89.4	91.3	0.065	0.9949

The experimental data shown in Figure 4(B) were fitted to the Langmuir and Freundlich models given by Eqs. (5) and (6), respectively:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{5}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

where  $q_{max}$  is the maximum Langmuir adsorption capacity (mg/g), and  $K_L(L/mg)$  is the Langmuir adsorption constant associated with the rate of adsorption,  $[K_F[(mg/g)*(L/mg)^{1/n}]$  and n are the Freundlich constants associated with the adsorption capacity and degree of system heterogeneity, respectively.

The experimental results of equilibrium adsorption for Cr(VI) removal on the adsorbents were fitted to the two common isotherm models as shown in Figure 5. The correlation coefficients (R<sup>2</sup>) for Langmuir model were found to be 0.9433, 0.9834 and 0.9496 for PANI/WHLPC, PPY/WHLPC and PPY-PANI/WHLPC, respectively while the R<sup>2</sup> values for Freundlich model were 0.5096, 0.6680 and 0.7521. Moreover, the experimentally obtained adsorption capacities of 129, 130 and 199 mg/g for PANI/WHLPC, PPY/WHLPC and PPY-PANI/WHLPC, respectively, are in close agreement with the theoretical obtained values of 156, 174 and 230 mg/g for PANI/WHLPC and PPY-PANI/WHLPC.

In addition,  $\chi^2$  (Chi-square) values of Langmuir 95.10, 33.96 and 23.23 for PANI/WHLPC, PPY/WHLPC and PPY-PANI/WHLPC, respectively were much lower than that of Freundlich values (822.4, 924.3 and 1314). The results confirm that Langmuir isotherm is a suitable model for explaining the adsorption of Cr(VI) on the adsorbents, indicating the formation of a monolayer.

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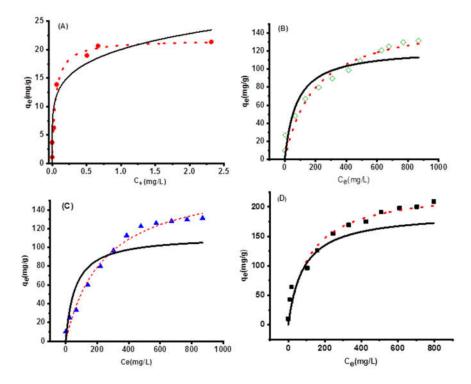


Figure 5. Langmuir (<sup>...</sup>) and Freundlich(—) isotherm models for the adsorption of Cr(VI) at WHLPC(●), PANI-WHLPC(♦), PPY-WHLPC(▲), and PPY-PANI-WHLPC(■).

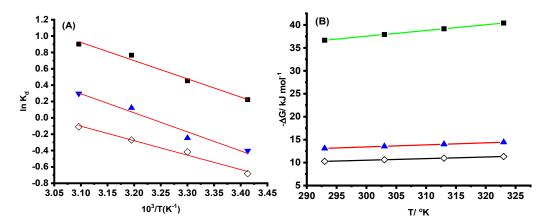


Figure 6. The plot of  $lnK_d$  versus 1/T (A) and the change in Gibbs energy with the variation of temperature (B) for Cr(VI) adsorption on PANI-WHLPC( $\diamondsuit$ ), PPY-WHLPC( $\blacktriangle$ ), and PPY-PANI-WHLPC( $\blacksquare$ ).

To investigate the adsorption thermodynamics, the three thermodynamic parameters, enthalpy ( $\Delta$ H), entropy ( $\Delta$ S) and Gibbs free energy ( $\Delta$ G), were calculated by first determing the distribution coefficient K<sub>d</sub> using Eq. (7) and ploting ln K<sub>d</sub> against 1/T according to Eq. (8):

$$K_d = \frac{q_e}{C_e} \tag{7}$$

$$\ell n K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$
(8)

allows us to determine  $\Delta H$  and  $\Delta S$  from the slope and intercept of the plot shown in Figure 6A.

The change in Gibbs free energy as a function of temperature was investigated as shown in Figure 6(B). The values of free energy change,  $\Delta G$ , for PANI/WHLPC, PPY/WHLPC and PPy/PANI/WHLPC were found to be in the range of -10.28 to -11.33 kJ/mol, -13.10 to -14.45 kJ/mol, -36.66 to -40.41 kJ/mol, respectively, as shown in Figure 6B. The negative sign of free energy change suggests that the adsorption of Cr(VI) onto adsorbents is spontaneous. The results also show that the adsorption of Cr(VI) onto PPy/PANI/WHLPC is more favorable than that of PPY/WHLPC and PANI/WHLPC.

Furthermore, the change enthalpies ( $\Delta$ H) were calculated to be 9.12 kJ/mol for PPY/WHLPC, 14.71 kJ/mol for PANI/WHLPC and 33.72 kJ/mol for PPy/PANI/WHLPC. The entropies were found to be 0.035, 0.015 and 0.125 kJ/mol K for PPY/WHLPC, PANI/WHLPC and PPy/PANI/WHLPC, respectively. These results indicate that the adsorption process is endothermic and an increase in randomness at the solid/solution interface.

Desorption and regeneration efficiencies of the PPy/PANI/WHLPC were further investigated to demonstrate its practical application. First, the concentration of desorbing solvent (NaOH) was optimized as shown in Figure 7(A), where the desorption efficiency initially increased with increasing concentration of NaOH and reached a limiting value with further increase in concentration. The optimum desorption concentration was found to be 1 M NaOH. As shown in Figure 7(B) using 1 M NaOH, the adsorbent was found to maintain excellent Cr(VI) removal efficiency with percent removal of 88%, 81 % and 68% in the first three consecutive cycles and then there were drastic reduction in the fourth, fifth and sixth cycles. The decrease in the Cr(VI) removal efficiency on the adsorbent on the latter cycles could be ascribed to the disintegration/deterioration of PPY-PANI composites [23].

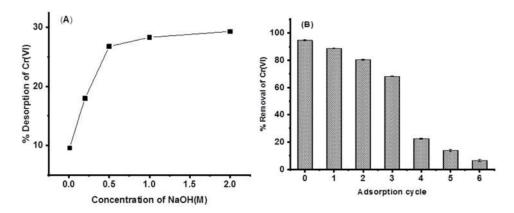


Figure 7. The effect of concentration of the desorbing agent (NaOH) (A) and adsorptiondesorption cycle (B) for the removal of Cr(VI) from PPy/PANI/WHLPC.

Figure 8 shows the influence of competing ions (NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>), and their concentration (25, 50, 75 and 100 mg/L) for the removal of Cr(VI) ions from aqueous solutions on PPy/PANI/WHLPC.

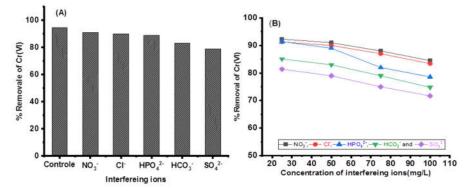


Figure 8. Effect of co-existing anions (A) and their concentration (B) on the removal of Cr(VI) onPPy/PANI/WHLPC.

Even if the  $SO_4^{2-}$  and  $HCO_3^-$  ions show an inhibiting effect on the removal efficiency of Cr(VI) compared to the other ions ( $NO_3^-$ ,  $CI^-$  and  $HPO_4^{2-}$ ), the percent removal still remains above 75%. This indicates that the adsorbent material can effectively remove Cr(VI) in the presence of competing ions. Finally the adsorbent material was compared with other similar materials reported in the literature in Table 2. The adsorption capacity of this material was much higher than most materials with intermediate contact time and easy method for preparing the adsorbents.

Table 2. Comparison of the performances of PPy/PANI/WHLPC and other adsorbents from literature for removing Cr(VI).

Adsorbents	q <sub>max</sub> (mg/g)	Optimal pH	Reference
PPy/wood sawdust	3.40	5	[23]
Chitosan/PPy composite	78.6	4	[25]
PANI/coated chitin	24.6	4.2	[37]
PPy functionalized chitin	28.9	4.8	[24]
PANI coated date seed	27.3	5	[38]
derived biochar			
Poly(2-ethylaniline)/chitosan-HCI	149	4.2	[27]
Composite			
PANI/humic acid composite	150	5	[28]
PANI-itaconic acid-CuOnanocomposite	250	2-6	[29]
Sodium aligate-polyaniline	73.3	2	[39]
PPY-PANI@ rice husk ash	789	2	[22]
Chitosan coated with	127	2	[26]
poly-3 methylthiophene			
Chitosan-grafted-PANI composite	166		[40]
Cross linked-chitosan-gafted-PANIcomposite	179	4.2	
PANI/WHLPC	157		
PPy/WHLPC	174		This work
PPy/PANI/WHLPC	230	2	

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## CONCLUSION

In this work, we have demonstrated that the WHLPC extracted from the highly invasive water hyacinth weed is an effective adsorbent for removal of toxic metals like chromium. Moreover, it is a good material for coating with conducting polymers like PPy and PANI. The PPy/PANI coated WHLPC showed a high adsorption capacity (230 mg/g) proving to be a cheap and scalable adsorbent material. The work also demonstrates a possible strategy for controlling the water hyacinth weed by using it as an adsorbent material for removal of pollutants.

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