ISSN: 2469-9062 (print), 2467-9240(e)

Journal of Institute of Science and Technology, 2015, ***20(2):*** *145-152 , © IOST, Tribhuvan University*

Adsorptive Removal and Recovery of Aluminium (III), Iron (II), and Chromium (VI) onto a Low Cost Functionalized *Phragmities Karka* Waste

Shukraraj Regmi[1], Kedar Nath Ghimire*[1], Megh Raj Pokhrel[1] and Deba Bahadur Khadka[1]
[1]*Central Department of Chemistry*
Tribhuvan University, Kritipur, Kathmandu, Nepal
**E-mail:knghimire@gmail.com*

ABSTRACT

Chemically modified adsorbent based on *Phragmities* stem has been investigated by treating with concentrated sulfuric acid at 2:1 weight/volume ratio. The maximum loading capacity for Al(III) and Fe(II) onto phosphorylated charred *Phragmities* waste PCPW adsorbent was found to be 148 mg/g and 200 mg/g, while for Cr(VI) 200 mg/g, respectively, at their optimal pH. Similarly, it was 166.66 mg/g and 90.90mg/g for Al(III) and Fe(II) onto the charred *Phragmities* waste CPW, respectively. The adsorption process followed the Freundlich isotherm and pseudo-second order kinetic models.. The desorption of the loaded metal ions recovery was found to be to the extent of 82%, 91% and 100% for Al(III), Fe(II) and Cr(VI), respectively.

Key words: Adsorption, Charred *Phragmities* waste, Phosphorylated charred *Phragmities* waste

INTRODUCTION

Heavy metals are high density toxic pollutants mainly include transitional metal, metalloids, lanthanides and actinide (Homagai *et al.* 2010), viz Cr(VI), Cd(II), Pb(II), Fe(III), Fe(II), Al(III), Ni(II), Zn(II), Cu(II) (Sharma and Forster 1994). Industrialization mainly concerns to the exploration of chemical industries cause them to release heavy metal into aquatic ecosystem. Electroplating, leather tanning, cement, mining, dyeing, fertilizer and photography industries contributes an important role to dispose the heavy metals to the environment. Heavy metals are non biodegradable and may cause health problem to animal, plants and human being. .Hexavalent chromium is carcinogenic, may cause liver damage, pulmonary congestion and skin irritation resulting in ulcer formation (Chand *et al.* 1994).

The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mgL^{-1} and in potable water is 0.05 mg L^{-1}. But its concentration in industrial waste water ranges from 0.5-270 mg L^{-1}. Hexavalent chromium, Cr(VI) exists in the aqueous solution as oxyanions such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), ($HCrO_4^-$) and ($HCr_2O_7^-$) form (Mohan *et al.* 2006). Trivalent aluminum is non essential to the plants and animals. Excess solubility of Al(III) in water cause the destruction on of bone, lungs, spleen liver, and brain. It also causes alzehimers, clinically characterized by gradual loss of cognitive function. Chromium ingestion may cause dentalcaries, hepatic and renal dysfunction, neuromuscular disorders, Osteomalacia and blood cancer (Mohan *et al.* 2006). UN food and agricultural organization recommended its maximum level for irrigation water to 5 mg/L. In ground water, its concentration should be less than 0.1µg/L (Benefield *et al.*2007). Iron is also toxic if present in excess, which may cause anorexia, oliguria,, hypothermia, diphasic shock and metabolic acidosis and even death. In addition to these, patients experiences vascular congestion of the gastrointestinal tract and liver toxicity via lipid peroxidation and destruction of hepatic mitochondria. There are different methods of treatment of heavy metal contaminated water. They are chemical precipitation, lime coagulation, ion-exchange, reverse osmosis, solvent extraction, reduction, electrodialysis, evaporation, electrochemical precipitation and so forth. However, these methods are not widely acceptable due to high capital and operational costs and problem in disposal of residual metal sludge (Mohan *et al.* 2006). Biosorption is an effective and versatile method for removing of these heavy metals contaminated effluents. There are a number of biosorbents which have been investigated for the removal of different metals from aqueous solution (Ghimire *et al.* 2002). The chemically modified adsorbent is commonly used for removing Al(III), Fe(II) and Cr(VI) because of its effective adsorption capacity in trace level at low cost (Homagai *et al.* 2010). These chemically modified polymer of cellulose which are prepared from agriculture waste contain high percentage of carbon and have fairly high adsorption capacity for heavy metals including Al(III), Fe(II), Cr(VI). A great interest has been focused to understand the mechanism of adsorption of these metals in adsorbent prepared from agriculture waste.

The carbon prepared from agriculture waste can be activated by various method like chemical modification, steam activation, thermal activation etc. By means of such activation, the effective surface area of carbon increases and surface of the adsorbent gets modified due to formation of different functional groups (Mohan *et al.* 2006). In Nepal lots of biomaterial like, *Phragmities* stem, sugarcane bagasses, rice husk, maize barn, apple waste, orange waste and banana bark are easily available as waste material. *Phragmities* stem is one of the very popular in making roof and bar in agricultural farm and the waste produced is abundantly found in mountain and Terai region of Nepal, it is burnt as a less efficient fuel causing air pollution mainly in October season. Therefore, it is quite suitable to use as an adsorbent rather than wasting. In this research work, *Phragmities* stem collected from periphery of Tribhuvan University, Kritipur, Kathmandu has been explored to convert into cost effective environment friendly bioadsorbent for the removal of Al(III), Fe(II), Cr(VI) from aqueous solution.

MATERIALS AND METHODS

Chemicals

All chemicals, potassium dichromate, phosphoric acid, dimethyl formamide, 1,5 diphenylcarbazide (DPCI) , ferrous ammonium sulfate, potash alum , sulfuric acid, propanol employed were of reagent grade. Distilled water was used for the preparation of all solutions.

Preparation of bioadsorbent

Phragmities stem were collected from the periphery of Tribhuvan University. It was washed with distilled water and dried in sunlight and finally dried in oven at 70°C for 2h. It was cut into small pieces and grounded into powder and sieved to pass through 250 µm mesh size. The material was equilibrated in concentrated H_2SO_4 at 2:1 weight/volume ratio and allowed to soak for 24 hours at room temperature. The samples were then washed with distilled water till neutral and dried at 80°C for 3 hours (Ghimire *et al.* 2008).

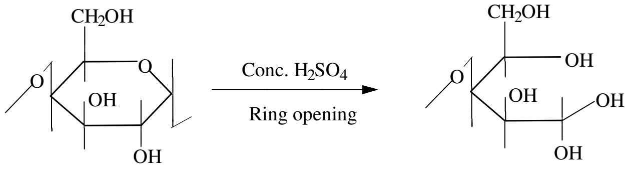

Fig. 1. Plausible reaction scheme for charring with sulphuric acid (Humagain *et al.* 2010).

Phosphorylation of charred adsorbents & reaction scheme

An amount of 20 g dried CPW adsorbent was soaked in 250 mL of DMF for overnight in 500 mL three naked flask. The flask was equipped with magnetic stirrer. Then 30 g of urea was added into the flask with constant stirring followed by the addition of 40 mL of H_3PO_4 drop wise with constant stirring. The mixture was refluxed for 3 hours at a temperature of 150 ^oC on paraffin bath. After cooling to room temperature, it was washed with 500 mL of 70% propanol followed by water till neutrality was obtained. The solid product was dried in sunlight and then in oven for 24 hours at 60^{o}C. Thus obtained dried bioadsorbent was termed as PCPW. The phosphorylation reaction can be expressed schematically (Ghimire *et al.* 2002) as:

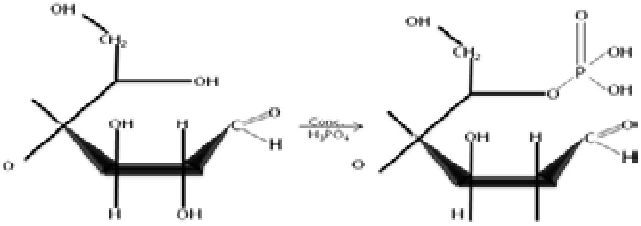

Fig. 2. Plausible reaction scheme for phosphorylation of charred adsorbent

Spectrophotometric determination of metal ions

Spectrophotomertric determination of aluminum ion was carried out using erichrome cyanine R as an complexing agent. With this reagent, dilute Al solution buffered to a pH of 6 produced red to pink color complexes that exhibit maximum absorption at 530 nm. The intensity of the developed color is influenced by the aluminium concentration, reaction time, temperature, pH, alkalinity and concentration of the other ions. The minimum and maximum concentration range detectable by this method in the absence of fluorides and complex phosphate is approximately 6-400 ppb. A pure reagent should be brick red in color, which fed to a pale yellow color in about two weeks. It appears that the form of the dye which reacts with Al ion is the strongly color one. Hence, it is most important for the optimization of the reagent that should be added in complex formation. Sensitivity and detection limit for the atomic absorption spectroscopy (AAS) methods, the ICP methods and the phenanthroline colorimetric procedure are almost similar and generally adequate for the analysis of natural and treated water (Mendham *et al.* 2003).

Thiocynate, dipyridine, tripyridine and 1, 10 phenanthroline are important indicators for the spectrophotometric determination of iron. The method consisting of red complex that forms between Fe(II) and 1,10 phenanthroline seemed to be more practical and sensitive. The orange red phenanthroline complex $(C_{12}H_8N_2)Fe^{2+}$ can be formed quantitatively in the pH range 2 to 9 with the suitable reagent concentration.

$$Fe^{2+} + 3\ phen \rightarrow Fe(phen)_3{}^{2+}$$

The molar extinction coefficient of the complex $(C_{12}H_8N_2)Fe^{2+}$, is 11,100 at 508 nm. The intensity of the color is independent of pH in the range of 3 to 9. The complex was very stable and the color intensity did not change appreciably over long period of time. Color standards were stable for at least 6 months.

The iron must be in ferrous state, and hence a reducing agent is added before the color is developed. Hydroxylamine hydrochloride can be used to reduce ferric ion to ferrous form.

$$2\ Fe^{3+} + 2\ NH_2OH + 2OH^- \rightarrow 2\ Fe^{2+} + N_2 + 4H_2O.$$

The pH was adjusted to 4.5 by using the acetate buffer. A more sensitive method for the determination of chromium(VI) is diphenylcarbazide indicator (DPCI) method, in which Cr(VI) forms a pink colored complex with 1,5-diphenylcarbazide in acidic medium and can be spectrophotometricaly analyzed ((Mendham *et al.* 2003).

Adsorption tests

Batch pH studies were performed by shaking 25 mL of 25 mg/L of Al(III), Fe(II) and Cr(VI) solutions with 25 mg of adsorbents in a mechanical shaker at room temperature for 24 hours over a wide range of initial pH values from 1.0 to 6.0. The concentration of all metal ions before and after adsorption was determined by suitable indicator using WPA Linton Cambridge UK, type S104 No 385 Spectrophotometer. Adsorption kinetic studies were carried out by shaking 25 mg of adsorbent with solution of Al (III), Fe(II) and Cr(VI) in 50 mL conical flask at room temperature. The removal kinetics of Al(III), Fe(II) and Cr(VI) was investigated by drawing the samples after desired contact time and the filtrate was analyzed for the residual metal ion concentration.

Adsorption isotherm studies were conducted by varying the initial concentration of Al(III), Fe(II) and Cr(VI) from 10 mg/L to 500 mg/L. 25 mL of metal ion solution having different concentrations were shaken using mechanical shaker for 24 hours with 25 mg of adsorbent for both CPW and PCPW at optimum pH respectively. The remaining metal ion concentration was determined after filtering the reaction mixture by using WPA spectrophotometer.

From the metal ion concentration measured before and after adsorption, amount of metal ion adsorbed onto adsorbent is determined by using following equation (1).

$$q_t = \frac{C_i - C_e}{W} \times V \qquad (1)$$

Where, C_i and C_e are initial & equilibrium metal ion concentrations in mg/L, respectively. q_t is the amount of metal ion adsorbed at time 't' in mg/g. V is the volume of metal ion solution in L. W is the weight of adsorbent in g.

Metal ion removal percentage is calculated by using the following equation (2).

$$A(\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (2)$$

This is the ratio of decrease in metal ion concentration before and after adsorption to the initial concentration.

RESULTS AND DISCUSSION

Effect of pH

The maximum adsorption of Al(III) was found at pH 6, afterwards the adsorption of Al(III) ion decreases due to the rapid precipitation of $Al(OH)_3$. It is believed that most of the metal ions including Al(III) is removed from aquous solution by cation exchange mechanism because at higher pH binding sites of the adsorbent start deprotonating and the metal ion uptake become difficult (Sud *et al.* 2008).

The pH of the aqueous solution is an important parameter in the removal of metal by adsorption. The metal removal capacity generally increases with the increase in pH. Fig. 3 shows that the % adsorption of Fe(II) increases up to optimal pH 2.7 and then decreased. It can be observed that % adsorption of Fe(II) is greater for PCPW than CPW, respectively.

The adsorption of Cr(VI) onto CPW decreases from 100 % to 26.66 % when the pH of the solution increased from 1 to 6 as shown in Fig. 3. It is obvious that pH determines the extent of the Cr(VI) removal as well as providing a favorable removal adsorbent surface charge for the adsorption to occur. At low pH, chromium exists as $HCrO_4^-$. From the batch pH studies it was found that the adsorption of Cr(VI) was found to be effective at pH 1 and 2 (Lal *et al.* 2010).

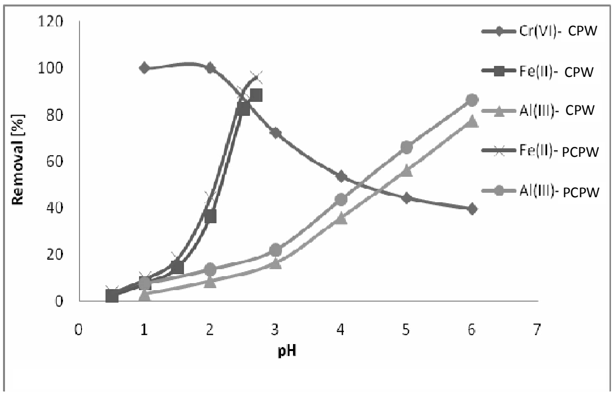

Fig. 3. Effect of pH in the removal of Al(III), Fe(II) and Cr(VI) as a function of pH

Effect of contact time

Fig. 4 shows the adsorption of Al(III), Fe(II) and Cr(VI) onto CPW and PCPW from 5 minutes to infinite time. The optimum time for the adsorption of Fe(II) onto CPW and PCPW was 3 hours. From this data, it can be concluded that PCPW is better adsorbent than others as it brings equilibrium quickly.

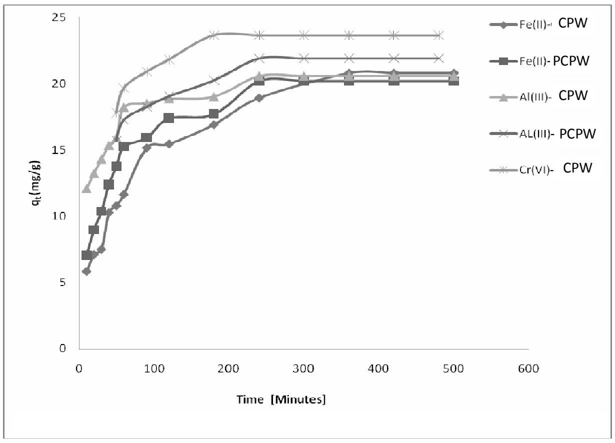

Fig. 4. Effect of contact time on the removal of Al(III), Fe(II) and Cr(VI) from aqueous solution

Adsorption Isotherms

The experimental data for the adsorptive removal of Al(III), Fe(II) and Cr(VI) from aqueous solution was analyzed by using Langmuir and Freundlich isotherm models. The respective metal ion adsorption isotherms of CPW and PCPW are shown in Figure 5 to Figure 9.

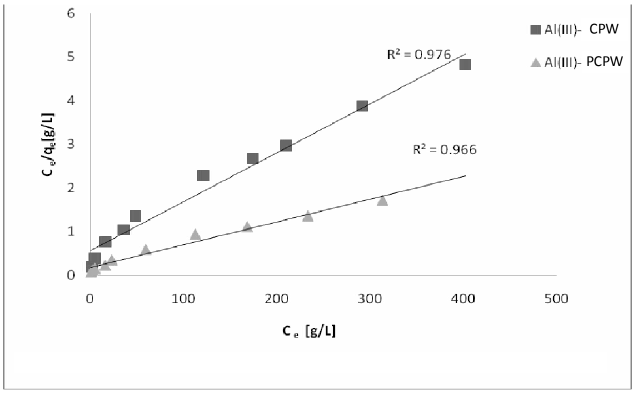

Fig. 5. Langmuir adsorption isotherm for the adsorption of Al(III) on to CPW and PCPW

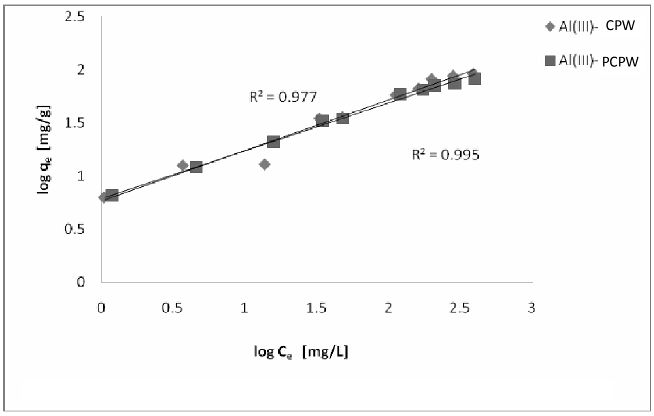

Fig. 6. Freundlich adsorption isotherm for the adsorption of Al(III) on to CPW and PCPW

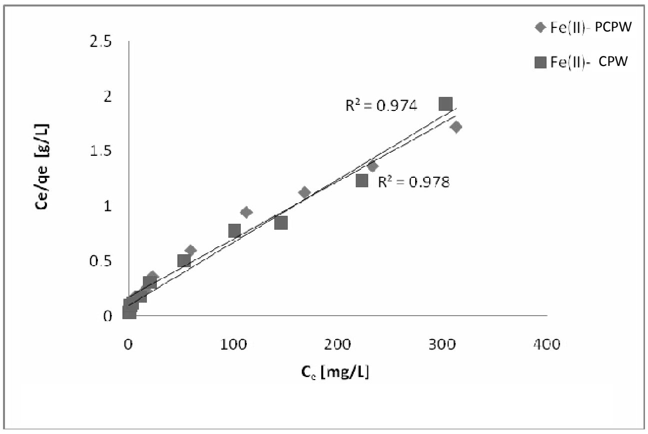

Fig. 7. Langmuir adsorption isotherm for the adsorption of Fe(II) on to CPW and PCPW

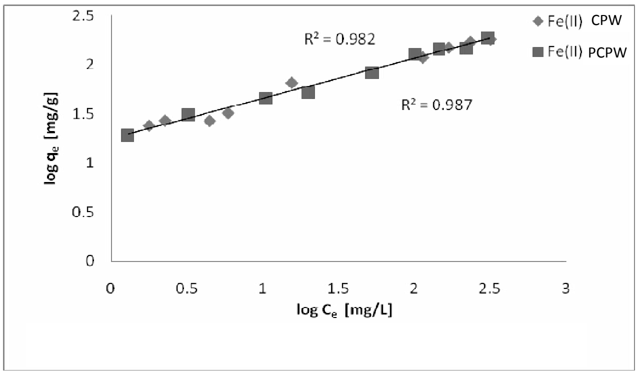

Fig. 8. Freundlich adsorption isotherm for the adsorption of Fe(II) on to CPW and PCPW

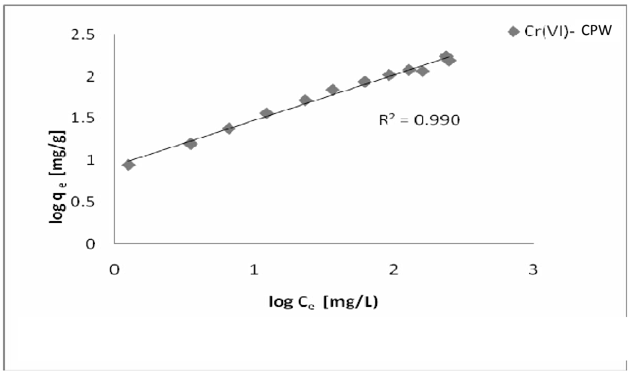

Fig. 9. Freundlich adsorption isotherm for the adsorption of Cr(VI) on to CPW and PCPW

Table 1. Langmuir and Freundlich adsorption parameters for the adsorption of Al(III) onto CPW & PCPW.

Adsorbent	q_m exp. (mg/g)	Langmuir Isotherm			Freundlich Isotheirm		
		q_m (mg/g)	b (L/mg)	R^2	K (mg/g)	1/n	R^2
CPW	82.00	90.90	0.019	0.976	5.78	0.475	0.977
PCPW	94.00	142.85	0.017	0.966	6.15	0.450	0.995

Table 2. Langmuir and Freundlich parameters for the adsorption of Fe(II) onto CNPW & PCPW.

Adsorbent	q_m exp. (mg/g)	Languir Isotherm			Freundlich Isotherm		
		q_m (mg/g)	b (L/mg)	R^2	K (mg/g)	1/n	R^2
CPW	165.00	166.66	0.028	0.974	10.59	0.527	0.982
PCPW	190.00	200	0.039	0.978	13.96	0.490	0.987

Table 3. Languir and Freundlich parameters for the adsorption of Cr(VI) onto CPW & PCPW.

Adsorbent	q_m exp. (mg/g)	Langmuir isotherm			Freundlich isotheirm		
		q_m (mg/g)	b (L/mg)	R^2	K (mg/g)	1/n	R^2
CPW	176.00	200	0.018	0.968	7.74	0.565	0.990

Langmuir and Freundlich parameters shown in Table 1 to Table 3 were determined from the slope and intercept of their respective plots. The values of Langmuir equilibrium parameters which lie between 0 and 1 indicated that equilibrium data fits well with Langmuir adsorption isotherm. The values of 1/n lie between 0 and 1 indicated that adsorption process is favorable.

Correlation coefficient values for Freundlich isotherms were found to be greater than that of Langmuir isotherms indicating that the adsorption process is better defined by the Freundlich adsorption isotherm model than by the Langmuir, which indicated the heterogenous distribution of active sites on the surface of adsorbent.. The higher values of q_m (both experimental and calculated from plots) for PCPW indicated that PCPW has higher adsorption capacity for Al(III), Fe(II) and Cr(VI) than CPW.

Kinetics

Kinetics studies for the adsorption of Al(III), Fe(II) and Cr(VI) onto CPW and PCPW were performed using pseudo-first order, pseudo-second order and second order models and the plots for pseudo-second order kinetic model are presented in Figure 10 to Figure 12.

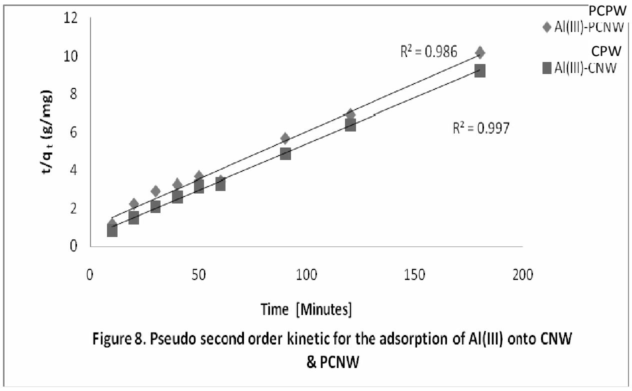

Fig. 10. Pseudo second order kinetic plot for the adsorption of Al(III) on to CPW and PCPW

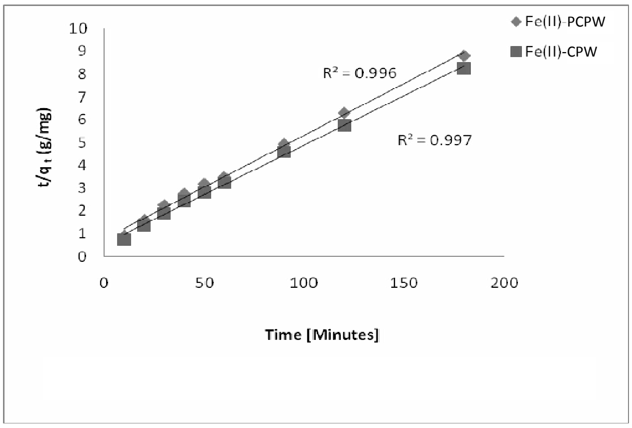

Fig. 11. Pseudo second order kinetic plot the adsorption of Fe(II) on to CPW and PCPW

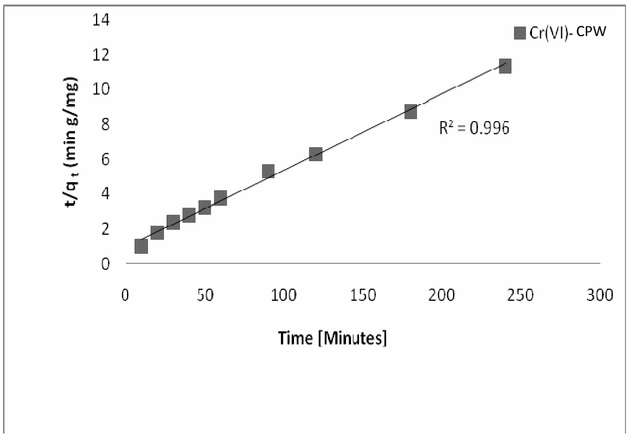

Fig. 12. Pseudo second order kinetic plot the adsorption of Cr(VI) on to CPW and PCPW

From the kinetic plots of adsorption of Al(III), Fe(II) and Cr(VI) onto CPW and PCPW it can be observed that the correlation coefficient (R^2) values for the pseudo second order were found to be higher than that of pseudo-first order and second order kinetic models.

The correlation coefficient (R^2) values of Al(III) for pseudo second order kinetic plots for CPW and PCPW were found to be 0.997 and 0.986 which are greater than the values for pseudo first order kinetic plots (0.884 and 0.898, not shown in Figure). Similarly, the correlation coefficient (R^2) values for Fe(II) for CPW and PCPW were found to be 0.964 and 0.969, while for Cr(VI) for CPW it was found to be 0.982. The overall correlation coefficient values for all metals regarding second order kinetics was not remarkable.

The correlation coefficient values for pseudo-second order kinetic plot for Al(III) and Fe(II) onto CPW and PCPW were found to be 0.997 ,0.986 and 0.997, 0.996, respectivly, while for Cr(VI) onto CPW it was 0.996. Thus the experimental results revealed that the adsorption process followed pseudo second order kinetics model with higher correlation coefficient value.

Desorption study and metal recovery

The efficiency of the absorbents was analyzed through the series of adsorption/desorption experiments. In this study, efficiency of the adsorbent was analysed by conducting desorption experiment up to three cycles and the percentage of metal ion recovery was analyzed. The data obtained showed that the adsorbent is efficient and can be used repeatedly for several times.

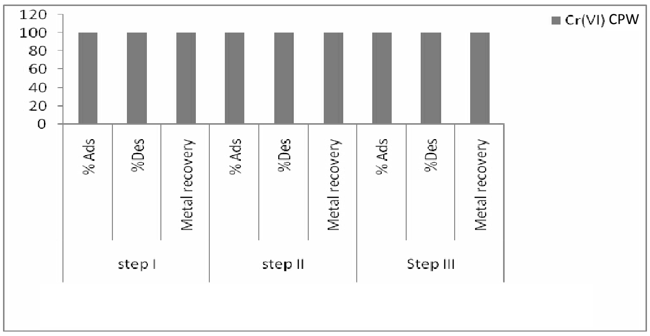

Fig. 13. Maximum adsorption, desorption and recovery of Cr(VI) onto CPW

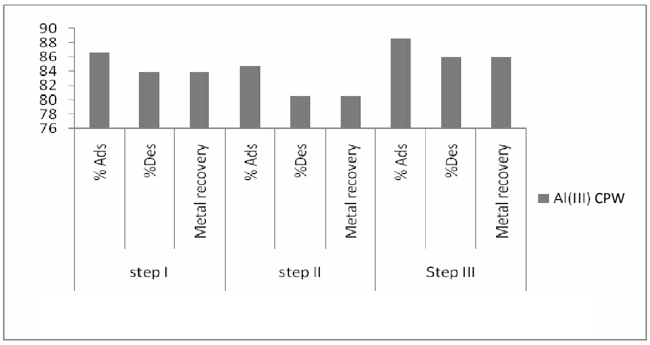

Fig. 14. Maximum adsorption, desorption and recovery of Al(III) onto CPW

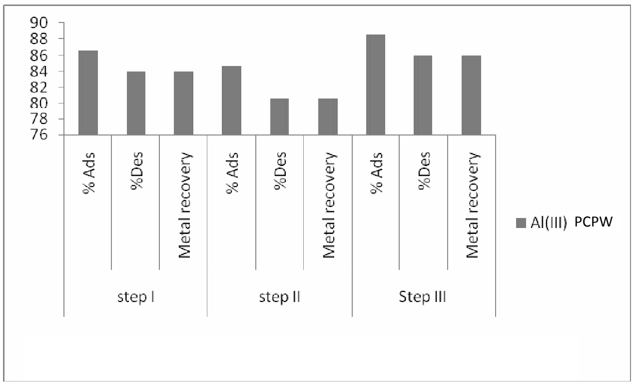

Fig. 15. Maximum adsorption, desorption and recovery of Al(III) onto PCPW

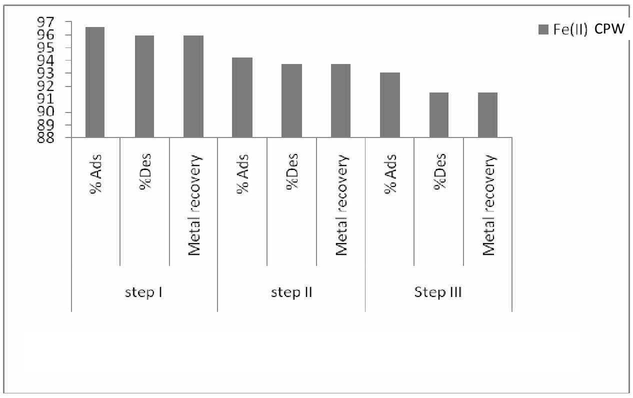

Fig. 16. Maximum adsorption, desorption and recovery of Fe(II) onto CPW

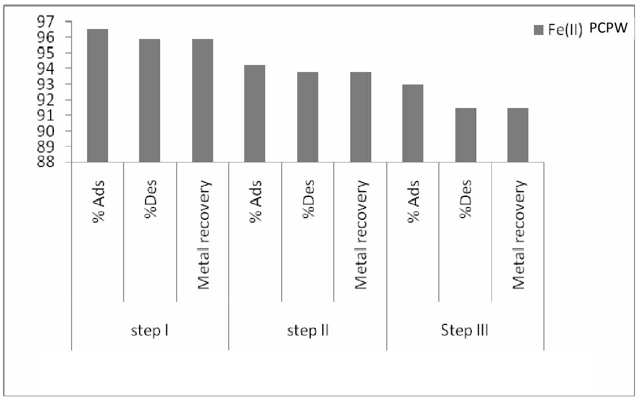

Fig. 17. Maximum adsorption, desorption and recovery of Fe(II) onto CPW

Plausible adsorption mechanism

After charring, the polymeric cellulose of *Phragmities* become chemically modified which provided the suitable site for the maximum possible adsorption of the metal. After phosphorylation, adsorbent consists of phosphoric group, which drastically alter the adsorption mechanism by many fold accordingly with cation exchange mechanism. The metal cations Al(III) and Fe(II) are considered to be adsorbed on the phosphoric group, while such adsorption of Cr(VI) onto phosphate group is not possible, due to the repulsion of same charge ions. Hence, adsorption takes place through complexation with polyphenolic group (Ghimire *et al.* 2002)

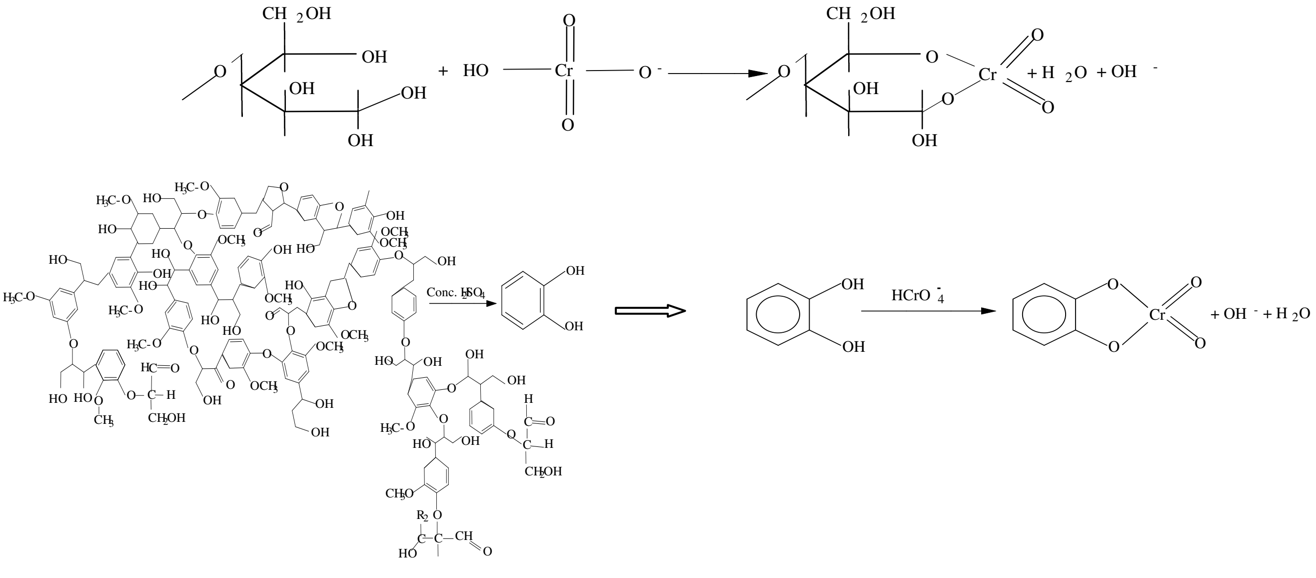

Fig. 18. Plausible adsorption mechanism of Cr(VI) onto CPW

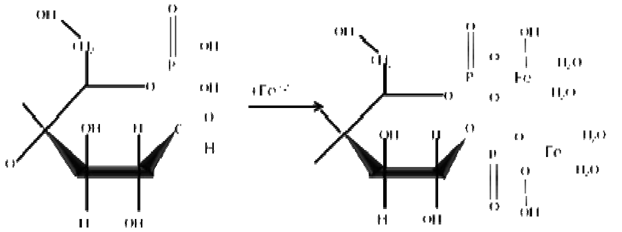

Fig. 19. Plausible adsorption mechanism of Fe(II) onto PCPW

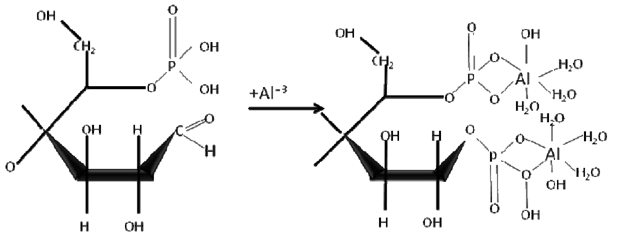

Fig. 20. Plausible adsorption mechanism of Al(III) onto PCPW

CONCLUSION

An effective adsorbent for the removal of the Al(III), Fe(II) and Cr(VI) has been investigated by making simple chemical modification of the *Phragmities* waste. The maximum Al(III), Fe(II) and Cr(VI) uptake capacity of the adsorbent prepared in our laboratory was found to be superior as compared to the previous reports. Thus it can be concluded that chemically modified *Phragmities* waste can be used for the separation /purification of Al(III), Fe(II) and Cr(VI) from waste water. The maximum adsorption capacity of Cr(VI) onto chemically modified *Phragmities* waste was found 200 mg/g at the optimum pH 1 and 2, for Al(III) it was found to be 90.90 mg/g and 148 mg/g for CPW and PCPW respectively at pH 6, and for Fe(II) it was found to be 166.66 mg/g for CPW and 200 mg/g PCPW at pH 2.7. The pseudo-first order, pseudo second order and second order model were used to analyse the kinetic data and it was found that the pseudo-second order model fitted well with the experimental data. Metal recovery after three cycles use of the adsorbents through desorption test shows that maximum recoveries of Al(III), Fe(II) and Cr(VI) were found to be 82%, 91% and 100% , respectively.

ACKNOWLEDGEMENTS

This research work was fully supported by University Grant Commission, Nepal under the scheme of Institutional Research Grants.

REFERENCES

Benefield, L.D., Jadneins, S. and Wend, J.F. 2007. *Process chemistry for water and wastewater treatment*, Prentice-Hall, Inc, Engle Wood Cliffs, New Jersey. **2(8):** 188-195.

Chand, S.A., Aggrawal, V.K. and Kumar, P. 1994. Removal of hexavelent chromium from the wastewater by adsorption. *Indian Journal of Environmental Health.* **36(3)**: 151-158.

Ghimire, K.N. 2007. Treatment of arsenic from aquatic environment on to Fe(III)-loaded orange waste. *Spectrum* **13:** 7-10.

Ghimire, K.N., Inoue, M.K.K. and Miyajima, T. 2002. Effectiveness of phosphorylated orange residue for toxic oxo-anion removal *Designed monomers and Polymers*, 4, 401-414.

Homagai, P.L., Ghimire, K.N. and Inoue, K. 2010. Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse. *Biosource Technology.* **101:** 2067-2069.

Kumar,U., Bandyopadhyay, M. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk Bioresource Technology ,97, 104-109.

Lal, J. and Sing, D.K.J. 1992**.** Removal of chromium (VI) from the aqueous solution using waste tea leaves carbon. Water Pollution Control Federation. **47:** 243-244.

Mohan, D., Sing, K.P.and Sing, V.P. 2006. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. *Journal of Hazardous Materials* **135**(1/3): 280–295.

Mendham, J., Denny, R.C., Barnes, J.D..,Thomas, .J.K. 2003. Vogel's Text book of quantitative chemical analysis, 6th edition, Pearson Educational Pvt. Ltd., New Delhi, India, 668.

Nasim, K. and Ahmad, M.H. 2001. Water and Waste Water Asia. *Journal of Chemical Engineering* **84:** 95-105.

Sandell. E.B. 1965. Colorimetric determination of trace metal from aquous medium. 3rd Edition, London, *Inter science Publishers*, Inc. New York.

Sharma, D.C. and Forster, C.F. 1994. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. Bioresource Technology **47(3): 257-264.**

Sud, D., Mahajan, S., Kaur, M.P. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions. *A Review, Bioresource Technology.* **99:** 6017-6027.