Waste printing paper as analogous adsorbents for heavy metals in aqueous solution

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ABSTRACT

Waste printing paper (WPP) is an abundant local waste material that requires end-use channelling to reduce environmental pollution. In the present study, removal of cadmium (II) (Cd^{2+}), copper (II) (Cu^{2+}), nickel (II) (Ni^{2+}) and lead (II) ions (Pb^{2+}) from aqueous solution by WPP at varying incubating period, metal dosage and chemical modification with hydrogen peroxide were studied. In addition, desorption capacity of three solvents, distilled water (dil.H_2O), 0.1M nitric acid, (HNO_3), and ethylenediaminetetracetic acid (EDTA) was evaluated for possible recovery of Pb^{2+}. The results showed WPP has adsorption efficacy of >90.0% and metal uptake of ≤ 25 mg/g for the assessed metal ions. There was high effect of metal dosage and contact time on WPP adsorption efficacy for the metal ions. Hydrogen peroxide treatment has negative effect on the WPP adsorption efficacy for Cd and Ni (II) ions, necessitating FTIR of WPP for possible functional groups distortion. The eluents used could recover <50 % adsorbed Pb^{2+} from WPP. WPP has potential as good adsorbent for heavy metals uptake from aqueous solutions but the recovery efficacy as economic and environmental concern requires further investigation.

Keywords: Adsorption efficacy, desorption efficacy, lead (II) ions, metal ions, waste printing paper.

INTRODUCTION

The increase in industrial activities during recent decades is greatly contributing to the increase of heavy metals in the environment, mainly in the aquatic system[1]. Wastes containing metals are directly or indirectly discharge into the environment with rapid development of many industries such as fertilizer, pesticide, metallurgy, electro-osmosis, leather, electric appliance, metal surface treating, aerospace and atomic energy installations, thereby, causing serious environmental pollution and even threatening human life[2]. Nickel, cadmium, mercury, zinc, lead, copper and chromium are examples of metals that are content of harmful wastes produced by industries, which pose risk of contaminating groundwater and other water resources[3, 4]. According to World health Organization[5], the metals of most immediate concern are aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. Heavy metals have harmful effects on human physiology and other biological systems when they exceed the tolerance level. In particular, cadmium and cadmium compounds are especially dangerous and highly toxic contributing to large number of health conditions, such as heart disease, cancer and diabetes[6]. The removal and recovery of heavy metals from wastewater are important to protect public health and the environment[7, 8, 9, 10].

Several methods have been employed to remove heavy metal ions from wastewater, such as chemical precipitation, reverse osmosis, ion exchange, electrochemical technique and biological process.[11. 12. 13, 14, 2, 15]. Biosorption is considered as the most attractive method due to its simplicity, convenience and high removal efficiency. Utilization of agricultural wastes materials for removal of heavy metals have been explored [16,17,18,19] but those that are cellulosic-based is underexplored [20]. Waste paper contains cellulose fibres and constitutes 27 % of solid municipal waste in US (EPA, undated). In Nigeria, waste printing paper (WPP) is indiscriminately dumped at dumpsites and burnt over time or carried away by wind to close vicinity as pollutants in Nigeria,. The use of WPP for biosorption of heavy metals as an alternative channel for waste paper use is underexplored. In addition, recovery of heavy metals from adsorbents is necessary so as not to defeat the major goal of environmental remediation. This present study evaluated the biosorption efficiency of chemical treatment and untreated WPP for uptake of nickel, copper cadmium and lead, (II) ions from aqueous solution as an alternative channel for its uses. In addition, desorption efficacy of H_2O, EDTA and HNO_3 were assessed for possible recovery of Pb (II) ion.

MATERIALS AND METHOD

Chemicals and reagents

The entire chemicals used in this work were of analytical grade and the metal salts were obtained from Sigma Aldrich. Stock solution of 1000mg/L nickel II (Ni^{2+}), copper II (Cu^{2+}), cadmium II (Cd^{2+}) and lead II (Pb^{2+}) ions were prepared by dissolving 4.5g nickel II sulphate hexahydrate, 3.9g copper II sulfate pentahydrate, 2.3g cadmium II Sulfate octahydrate and 1.6g lead II nitrate salt, respectively, in deionized distilled H_2O and made up to 1000 ml. The 1000 mg/L stock solutions was used for serial dilutions to 50mg/L, 250mg/L and 500mg/L of each metal ions and the pH of the aqueous solution was adjusted to pH 6 with conc. HCl.

WPP samples and treatment

The paper waste samples were obtained from a printing press in Ijebu-ode. The paper waste samples were rinsed with deionized water to remove the particulate matter and dried at room temperature and then cut into smaller size of about 2mm with scissor. Portions of 50g WPP samples were chemically pre-treated by soaking in 400ml 10% hydrogen peroxide (H_2O_2) for 1hr and filtered. The paper samples were then washed many times with deionized water to remove surface bound H_2O_2 and dried at room temperature.

Batch Biosorption experiments for effect of time-course and initial metal dosage

The biosorption experiments for the removal of single metal of Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous solution were carried out at a constant temperature of 25^{o}C, pH 6 using 1g of WPP in 50 ml concentrate for varying initial metal dosage of 50mg/L, 250mg/L, 500mg/L and at contact times of 60 and 180 min with intermittent shaking. All sets of experiments were carried out in triplicates. At the end of appropriate contact time, the mixtures were filtered and filtrate collected to determine residual metal ions in WPP.

Determination of metal ions

The residual metal ions in filtrates were determined by atomic absorption spectrometer (AAS) using single hollow cathode lamp (Buck scientific, USA). The stock reference of the metals were also from Buck scientific (1000mg/L in HNO_3) and standard solutions were according to BUCK handbook.

Estimation of biosorption efficacy, metal uptake and metal adsorbed

The biosorption efficacy of the chemically modified and unmodified paper wastes was calculated using eqn. 1:

$$Adsorption\ efficacy, AE\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{(Eqn.1)}$$

Where C_i is initial metal dosage and C_f is residual final metal concentration

Metal uptake, q_t, is the concentration of metal adsorbed per unit mass of adsorbent at time t, equation 2:

$$Qt\ (mg/g) = \frac{(C_i - C_f) \times V}{W} \qquad \text{(Eqn. 2)}$$

Where V, is the total volume of the solution and W is the weight of adsorbent

The amount of metal adsorbed, qe, is the concentration of metal adsorbed per unit mass of adsorbent at equilibrium, equation 3:

$$Qe\ (mg/g) = \frac{(C_i - C_e) \times V}{W} \qquad \text{(Eqn. 3)}$$

Where C_e is the concentration of metal in solution at equilibrium

Desorption experiment

Desorption capacity of three common readily available laboratory solvents: 0.1M EDTA, 0.1M HNO_3 and dil.H_2O as eluents were assessed for desorb of adsorbed lead (II) ion at various concentration and contact time from previous experiments for possible recovery of Pb^{2+} in solution and regeneration of the Pb^{2+}sorbed-WPP. Desorption efficiency for the chemically-modified and unmodified Pb^{2+}sorbed-WPP^{+} for each eluent was calculated using Eqn. 4:

$$Pb\ desorption\ efficacy, DE\ (\%) = \frac{C_d}{C_{fd}} \times 100 \qquad \text{(Eqn. 4)}$$

Where C_d is the amount of lead desorbed, C_{fd} is the amount of lead previously adsorbed.

Freundlich adsorption isotherm

The Freundlich adsorption isotherm is an empirical method with assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption with the given linearized model Eqn. 5:

$$\log qe = logk_f + {}^{1}/_{n}\, logC_e \qquad \text{Eqn. 5)}$$

Where k_f is adsorption capacity and n is related to adsorption intensity with no unit and when n is greater than unity, it is a favourable adsorption.

Data analysis

Adsorption efficacy, AE; amount of metal uptake, Qt; and amount of metal adsorbed, Qe by WPP was calculated using excel sheet and subjected to precision measures, analysis of variance (ANOVA) and Pearson correlation across metal dosage, contact time, eluents and specific metal ions using SAS 9.2 (SAS, 2002). Charts

and linear graphs were also generated from the results using excel sheets.

RESULTS AND DISCUSSION

Table 1 is an overall mean and precision measures of AE and Qe of WPP across contact time and initial metal dosage. The Table shows WPP to have AE > 90% for Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} assessed and as low as Qe $\geq$ 2.3 mg/g for Cu^{2+} and Pb^{2+} and high as Qe >20 $\leq$ 25 mg/g for the four metals. According to Table 1, equilibrium is reached at 60 min at various initial metal dosages for all the metals except for Cu and Pb at 180 min 50 mg/L. The present AE and Qe obtained for WPP is comparable with various efficient adsorbents reported so far such as carrot residue, commercial grade ion exchange resin, activated carbon, modified chitosan, crab shell, water hyacinth, saw dust rice husk and keratins [21, 13, 22, 23, 24, 25].

Effect of Contact time and initial metal dosage on AE and Qe of WPP

Batch biosorption was used to observe and estimate effect of Ci, and contact time on adsorption capacity of WPP. Effect of contact time was evaluated at 500 mg/L, pH6 using 1g of WPP while for various Ci, contact time was changed to 60 min. As observed in Fig. 1, there were little or no changes in AE and Qe of WPP between 60 and 180 min across Ci for Cu^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} except for a slight change observed for Cu^{2+} and Pb^{2+}, only at 500mg/L. Lower contact time of 15 and 30 min were reported for waste sludge and keratin [26, 25] which were not included in the present study and the present 60 min is long enough to attain equilibrium for all assessed metal ions with AE >90% higher than values obtained at the lower contact time. Also, the trend of AE across various Co of 50, 250, and 500 mg/L showed little or no changes while there was increasing Qe with increasing initial metal dosage and 500 mg/L was observed as the optimal initial metal dosage. The AE >90% at all the initial metal dosage means enough sites for the adsorbates with 1g WPP, giving large surface area, despite not assessing effect of adsorbent mass.

Effect of chemical modification with H_2O_2 on AE and Qe of WPP.

Chemical modification with 30% H_2O_2 caused a high significant reduction in AE and Qe of WPP for Ni^{2+} and Cd^{2+} but that of Cu^{2+} and Pb^{2+} increased slightly (Fig. 2) and is similar to some reported observation but in contrast to increase AE and QE reported for many various modifications[27, 28]. Perhaps, treatment of WPP with H_2O_2 led to loss of important functional group for effective biosorption [29, 30] necessitating FITR of WPP and modification using other treatments in future research.

Table 1: Mean and descriptive statistics for AE, Qt and Qe of WPP at contact time and Co for assessed metals

	Mean estimates					**Descriptive statistics**				
Time	**Co (mg/L)**	**AE (%)**	**Qt (mg/g)**	**Qe (mg/g)**	Adosrbtion	Mean	SE (±)	CV	Min	Max
	Cadmium II ion					Cd				
60	50	.	.	.	AE	99.96	0.03	0.06	99.87	100
180	50	.	.	.	Qe	18.74	3.6	38.46	12.5	25
60	250	99.988	12.4985	12.4985						
180	250	99.952	12.494		Cu					
60	500	99.93	24.9825	24.9825	AE	97.94	0.81	2.02	95.24	99.95
180	500	99.998	24.9995		Qe	13.22	4.14	76.66	2.38	24.99
	Copper II ion				Ni					
60	50	95.75	2.3938		AE	99.99	0.01	0.01	99.98	100.01
180	50	98.76	2.469	2.469	Qe	18.75	3.61	38.48	12.5	25
60	250	98.128	12.266	12.266						
180	250	97.752	12.219		Pb					
60	500	99.944	24.986	24.986	AE	96.73	1.55	5.56	81.12	99.96
180	500	74.659	18.6648		Qe	12.65	2.56	70.21	2.43	24.85
	Nickel II ion									
60	50	.	.	.						
180	50	.	.	.						
60	250	100.002	12.5002	12.5002						
180	250	99.691	12.4614							
60	500	99.981	24.9952	24.9952						
180	500	99.973	24.9932							
	Lead II ion									
60	50	98.5	2.4625							
180	50	99.38	2.4845	2.4845						
60	250	98.394	12.2993	12.294						
180	250	98.99	12.3738							
60	500	98.617	24.6543	24.6543						
180	500	86.52	21.63							

AE, adsorption efficacy; Qt, metal uptake per unit mass at time, t; Qe, mass adsorbed per unit mass at equilibrium; WPP, waste printing paper; Co, initial metal concentration

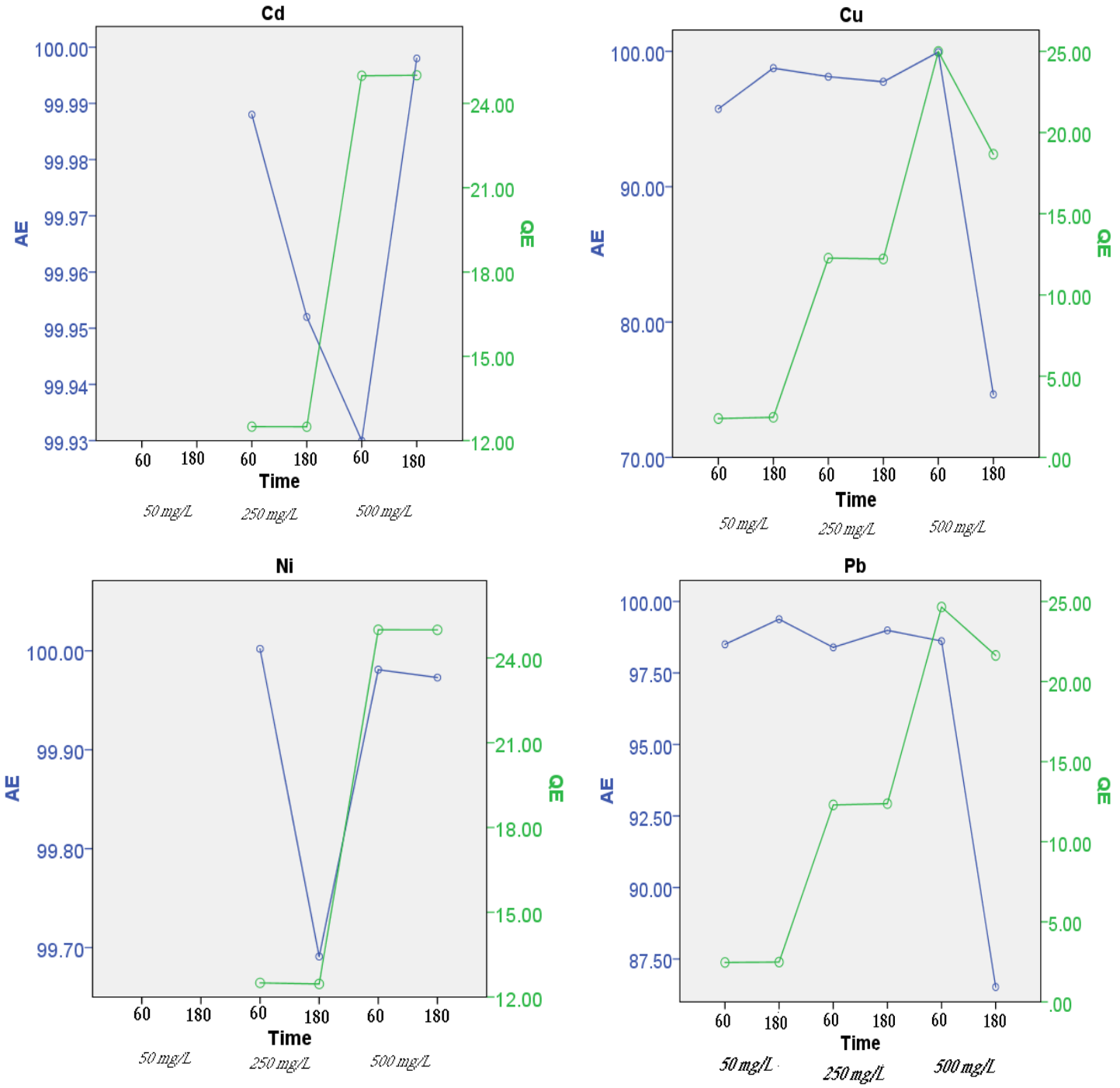

Fig.1 (x by 2y): Trend of AE and Qe for WPP over time at different concentrations for Ni, Cu, Cd and Pb (ii) ions

AE, adsorption efficacy, Qe, mass adsorbed per unit mass

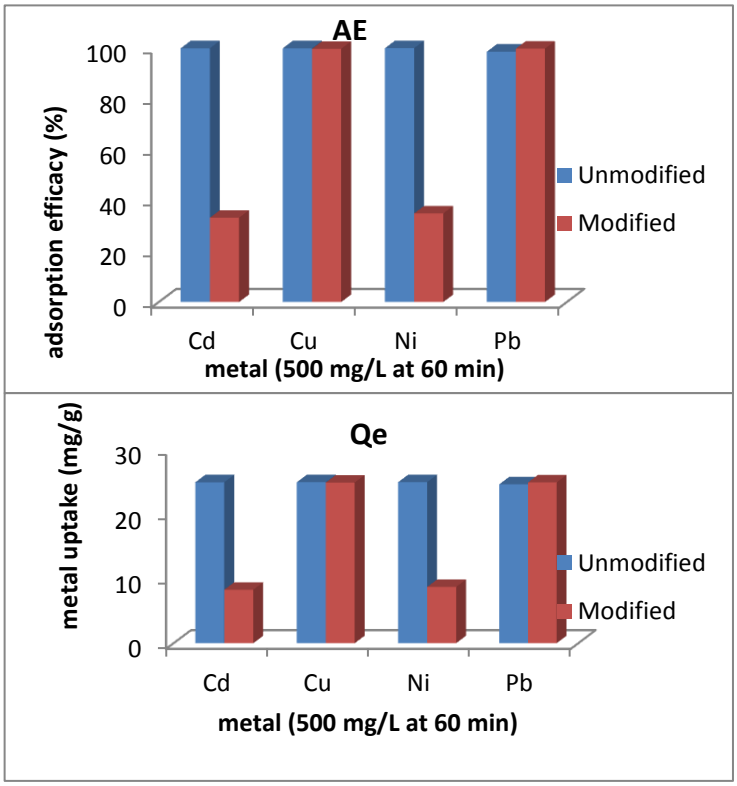

Fig. 2: Adsorption efficacy and amount adsorbed per unit mass by chemical modified and unmodified WPP for assessed metalsAE, adsorption efficacy, Qe amount of metal adsorbed per unit mass at equilibrium, modified, chemical modification with hydrogen peroxide

Analysis of variance

Analysis of variance (ANOVA) based on general linear model was used for estimation of significant differences for effects of initial metal dosage, contact time and chemical modification visualized in Figs. 1 and 2. ANOVA results showed no significant difference between contact time 60 and 180 min while there was high effect of Ci, chemical treatment and their interactions for AE and Qe, except for interaction between chemical treatment and Ci for AE (Table 2). Table 2 also shows a weak positive relationship between atomic number of metals and AE; treatment is directly related with Cf and inversed with AE and Oe, and Ci is strongly correlated with Qe but insignificant with AE. Therefore, Ci is an important factor for Qe of WPP, supporting previous reports on biosorption[31]. Importance of contact time has also been emphasized in previous studies and reviews, the present insignificance in contact time obtained, might be due to insufficient variables of assessed contact time used despite reaching equilibrium at 60 min, the future investigation should incorporate contact time such as 15, 20 and 120 min. Other parameters mentioned so far are pH and particle sizes and were also not included at present, for the study decided on unpulverized paper samples as obtainable for conveniences and lower cost of process.

Table 2: Estimates of analysis of variance and Pearson correlation for adsorption efficacy and amount of metal adsorbed per unit mass of WPP

Analysis of variance			***AE (%)***		***Qe (Mg/G)***			
Source	*DF*	*Type III SS*	*Mean Square*	*Pr > F*	*Type III SS*	*Mean Square*	*Pr > F*	
Treatment	*1*	*12663.18*	*12663.18*	***	*478.50*	*478.5*	***	
Time	*1*	*96.24*	*96.24*	*ns*	*5.00*	*5.00*	*ns*	
Metal	*3*	*6540.76*	*2180.25*	***	*38.08*	*12.69*	*	
Co	*2*	*2927.62*	*1463.81*	***	*2524.9*	*1262.5*	***	
Treatment*Metal	*3*	*16277.46*	*5425.82*	***	*646.14*	*215.38*	***	
Treatment*Co	*2*	*174.97*	*87.49*	*ns*	*71.11*	*35.56*	***	
Metal*Co	*6*	*3692.55*	*615.42*	***	*368.04*	*61.34*	***	
R-Square	*CV*	*Root MSE*	*Mean*		*R-Square*	*CV*	*Root MSE*	*Mean*
0.94	*7.93*	*6.74*	*85.03*		*0.95*	*17.31*	*2.06*	*11.91*

Pearson correlation

	Metal†	*Treatment‡*	*Time*	*Co*	*Cf*	*Ce*	*AE*	*Qe*
Metal	*1*	*0*	*ns*	*ns*	*ns*	*ns*	*0.29**	*ns*
Treatment		*1*	*ns*	*ns*	*0.34***	*-0.33***	*-0.46****	*-0.33***
Time			*1*	*ns*	*ns*	*ns*	*ns*	*ns*
Co				*1*	*0.37****	*0.84****	*ns*	*0.84****
Cf					*1*	*ns*	*-0.87****	*ns*
Ce						*1*	*0.38****	*1****
AE							*1*	*0.38****
Qe								*1*

†, metal is increasing atomic number according to the periodic table
‡ unmodified towards modified
Cf, final metal concentration,
Co, initial metal dosage
Ce, concentration of metal at equilibrium
Qe, amount of metal adsorbed per unit mass of sorbent
*P<0.05
** P<0.005
*** P<0.0005
ns not significant

Desorption efficacy of dil. H_2O, HNO_3 and EDTA

Figure 3 shows highest DE for EDTA followed by HNO_3 while dil. H_2O showed least desorption for Pb^{2+}sorbed-WPP. The DE by EDTA as the highest observed was below 50%, and also the Qed of desorbed Pb^{2+} per unit mass WPP is <10mg/g of adsorbed-WPP , the two values were less than 50% of adsorbed for Pb^{2+} <50% of adsorbed (AE = 98.34 and Qe = 24.65 mg/g). Higher desorption by eluents have been observed in many other biosorbent materials [25, 32, 33]. Perhaps the molarity of 0.1M EDTA used at present is weak or need for its improvement for efficient recovery of Pb^{2+} and regeneration of WPP.

Isotherm models

Freundlich adsorption isotherm model was used to fit adsorption process for uptake of Cu, Ni, Cd and Pb II ions in aqueous solution by WPP. Figure 4 shows the linear curve for log Qe versus log Ce at 25°C under equilibrium condition of pH6 at 60 min for the metals. The Freundlich constant kf ranged between -4.2 to $1.3x10^3$ indicating high adsorption capacity of WPP for the metals that decrease with increasing degree of site occupation. The value of n obtained for the metals are higher than unity, which also indicate favourable adsorption with adsorption sites distributed exponentially with heat of adsorption. Therefore, there is favourable adsorption mechanism with formation of strong binding force between the adsorbate and adsorbent. The coefficient of correlation (R^2) of >0.90 obtained for all metals was a good fit for Freundlich isotherm model and is similar to reports of many similar studies[33].

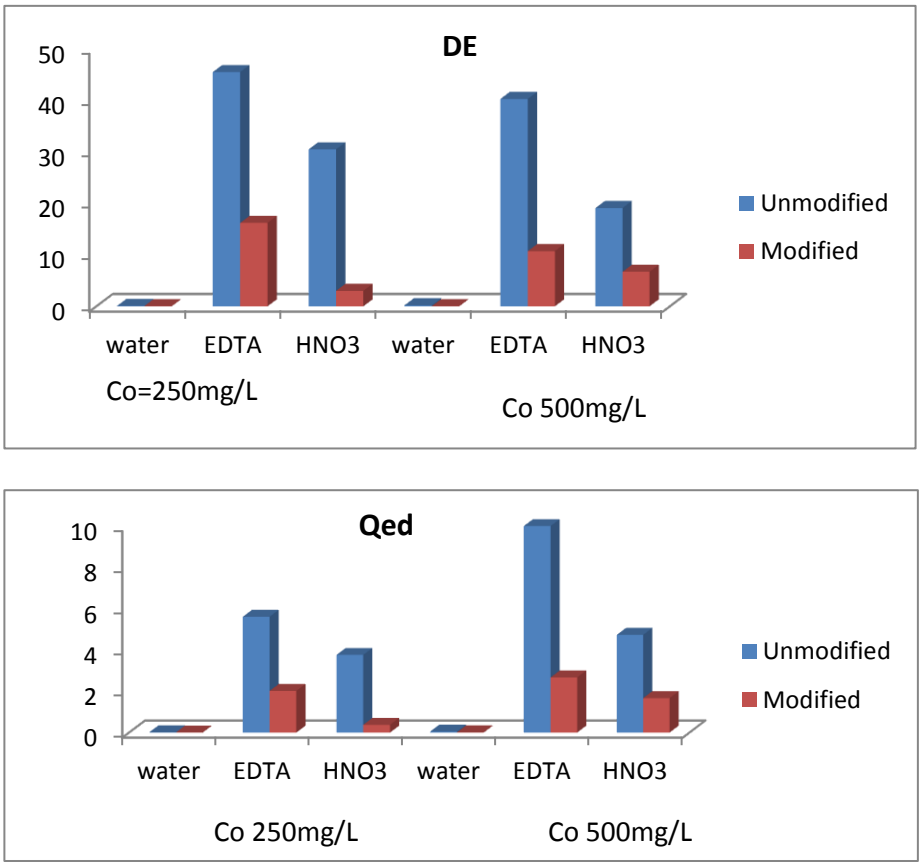

Fig.3: Desorption capacity of three solvents for possible recovery of lead (II) ion from sorbed-WPP DE, desorption efficacy, Q_{ed}, amount of Pb^{2+} desorbed by unit mass of WPP

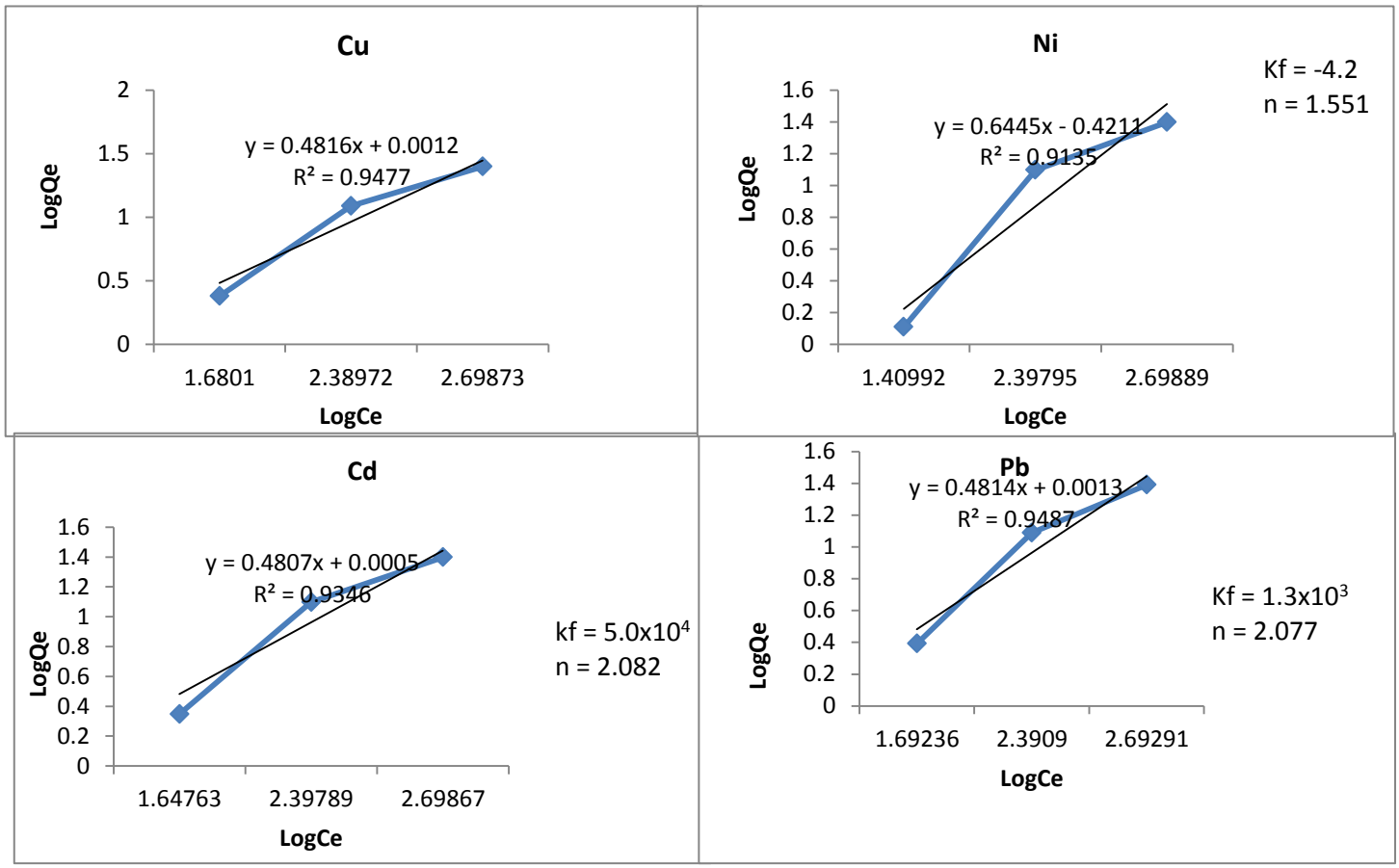

Fig. 4: Freundlich isotherm model fit for Cu^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} by PPW at equlibrium

CONCLUSION

WPP has good potential as biosorbent for heavy metals uptake from aqueous solution for it attained AE >95.0% for the assessed metals, which may be an indication of its non-requirement of modification for an improved adsorption, and moreover, H_2O_2 caused a significant reduced Cd II and Ni II uptake. Therefore, the observed results necessitate FITR of chemical modified and unmodified WPP, for possible functional group distortion. Less than fifty per cent of adsorbed Pb^{2+} by WPP was recovered by 0.1M EDTA, indicating the recovery efficacy of WPP might be unimpressive for economic and environmental concern and requires further investigation.

REFERENCES

1. Marques, P., Rosa, M.F., and Pinhetro, H.M., Biopress Eng., 23 (2000) 135.
2. Hanif, M.A., Nadeem, R., Bhatti, H.N., Ahmad, N.R and Ansari, T.M., Journal of Hazardous Materials, 139 (2007) 345.
3. Chuan, R. I., and Gupta, D. A., Arbor science public MI (2005) 59.
4. Yupeng, G., Jurui, Q., Shaofeng, Y., Kaifeng, Y., Zichenm, W. and Hongding, X., Journal Material Chemical and Physical, 78 (2002) 132.
5. World Health Organisation, in Carolyn, V., ed., WHO chemical safety, P. 17, WHO publication 2011.www.who.int/features/10chemicals_en.pdf

6. Kobya, M. E., Demirbas, E., Senturk, E. and Ince, M.. Bioresource Technology, 96 (2005) 1512.

7. Francesca, P., Sara, M., and Luigi, T V., water research, 42 (2008) 2953

8. Guangyu, Y. and Chari, V. T., Water Resource, 37 (2003) 4486.

9. Caesar, R.T. and Marco, A., Chemosphere, 54 (2004) 987.

10. Chen, G.Q., Zeng, G.M., and Tang, L., Bioresource Technology, 99 (2008) 7034.

11. Dursun, A.Y., Biochem Eng. J., 28 (2006) 187.

12. Satapathy, D. and Natarajan, G.S., Adsorption, 12 (2006) 147.

13. Vijayaraghavan, K., Palanivelu, K., and Velan, M., Bioresource Technology, **97** (2007) 1411.

14. Wang, X., Xia, S., Chen, L., Zhao, J., Chovelon, J. and Nicote, J. Journal of Environmental Science, 18 (2006) 840.

15. Preetha, B. and Viruthagiri ,T. Separation and Purification Technology, 57 (2007) 126.
16. Vieira, R.H and Volesky, B., International, 3 (2000) 17.

17. Rao, M. and Parwate, A.V. journal of Environmental Pollution Control, 5 (2002) 12.

18. Sudha Bai R and E. Abraham,. Bioresources Technology, 87 (2003) 17.

19. Hashem, A., Akasha, R.A., Ghith, A. and Hussein, D.A., Energy Education Science and Technology, 19 2007) 69.

20. Ahalya N., Ramachandra, T. V., and kanamadi, R. D., J Chem and Envir. 7(4) (2003) 7179

21. Deng, L., Zhu, X., Wang, X., Su, Y. & Su, H., Biodegradation, 18 (2007a) 393.

22. Ahmaruzzaman, M., Gupta, V. K., Industrial and Engineering Chemistry Research, 50 (2011) 13589.

23. Buasri, A. N., Tapang, C. K., Panphrom, S. J. S., Civil and Environmental Research, 2 (2012) 17.

24. Roh, H., Kim, S., and Jung, J., Korean J. Chem. Eng., 31 (2014) 31.

25. Zhang, H., Universitat Autonomia De Barcelona, PhD Dissertation, 2014 Pp275.

26. Suryan, S. and Ahluwalia, S.S., Int J Environ Sci., 2 (2012).1331

27. Rao, P. R. and Bhargavi, Ch. International journal of Chemistry and Chemical Engineering, 3 (2013) 171.

28. Wan, N. W. S. and Hanafiah, M. A. K., Bioresources Biotechnology, 99 (2008) 3935.

29. Loaëc M., Olier, R., and Guezennec, J., Water Res., 31 (1997) 1171**.**

30. Yan G. and Viraraghavan, T., Water SA., 26 (2000) 119.

31. Davis, T. A., Volesky, B., Vieira, R. H., Water Res., 34 (2000) 4270.

32. Deng, L., Su, Y., Su, H., Wang, X., and Zhu, X., Journal of hazardous materials, 143 (2007b) 220.

33. Sekimoto, Y., Okiharu, Y., Nakajima, H., Fujii, T., Shirai, K., Moriwaki, H., Sci. Pollut., (2013) 1.