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Removal of Common Heavy Metals from Aqueous Solutions by Waste *Salvadora persica* L. Branches (Miswak)

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ABSTRACT: The adsorption ability of miswak (Salvadora persica L.) waste was investigated for the removal of common heavy metals; Pb(II), Cu(II), Ni(II) and Cd(II), from aqueous systems. The miswak mainly consists of saponins, tannins, silica and resin, which are accounted for the removal of heavy metal ions from aqueous systems. The effects of various parameters, such as solution pH, contact time, initial concentration of the heavy metal ions and adsorbent dosage were examined. The linear correlation coefficients of Langmuir and Freundlich isotherms were obtained and the results revealed that the Freundlich isotherm fitted the experiment results better than Langmuir isotherm (r2=0.974–0.993). The maximum adsorption capacities of Pb(II), Cd(II), Cu(II) and Ni(II) for per g miswak waste were calculated as 6.84±0.23, 5.91±0.20, 4.56±0.17 and 3.73±0.15 mg, respectively. Five cycles of adsorption-desorption were carried out revealing the strong reuse potential of this low-cost adsorbent. The results indicate that the miswak waste, which has a very low economical value, could be used to effectively adsorb common heavy metals from aqueous systems for environmental cleaning purposes.

Key words: *Salvadora persica* L., Miswak, Adsorption, Low-cost materials, Heavy metals

INTRODUCTION

Water pollution caused by toxic metal ions from various industrial effluents is a global problem that has received worldwide attention. The effluent water of many industries, such as mining, refining ores, tanneries, and producers of fertilizer, batteries, paper, plastics, pigments, and so on, contains toxic heavy metal ions (Gupta *et al.*, 2009; Han *et al.*, 2006). The heavy metals most commonly found in contaminated waters are Pb(II), Cr(II), As(II), Zn(II), Cd(II), Cu(II) and Hg(II) (Zhang *et al.*, 2006). So, their removal from contaminated waters has become a major topic of research in recent years, due to the toxicological problems caused by the metal ions to the environment and to human health (Kyzas, 2012). Several methods have been applied during many years for the elimination of these metal ions present in industrial wastewaters. The commonly traditional methods used for removal of heavy metal ions from aqueous solution include precipitation, filtration, ion exchange, evaporation, reverse osmosis, solvent extraction, electrochemical treatment and membrane technologies. However, these traditional methods are either inefficient or expensive when heavy metals exist in lower concentrations (Tsekova *et al.*, 2010). Consequently, it is essential to find new methods for effective removal of heavy metals from water and wastewater. Compared with other traditional methods, adsorption is quite popular due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents (Orhan *et al.*, 1993; Babel and Kurniawan, 2003). Activated carbon is the best useful adsorbent of heavy metals, dyes, pesticides, phenols, etc. from waste water. However, the cost of activated carbon is high; its regeneration also requires additional expense. So, researchers in science and engineering have interest in finding low-cost adsorbents such as agricultural wastes or industrial by-product.

In recent years, various adsorbents as an alternative adsorbent have been used for the removal of heavy metal ions from aqueous solution. However, new adsorbents which are locally available, having

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higher removal capacity and economical still needed. Several authors have reported studies on various adsorbents. A number of adsorbent materials such as, tea factory waste (Cay *et al*., 2004), pigeon peas hulls (Ramana *et al*., 2012), rice husk (Kamsonlian *et al*., 2012), tamarind and neem leaves (Sivakumar *et al*., 2012), coffee grains (Garrido-Rodriguez *et al*., 2013) , nut shell (Kumar *et al*., 2012), honeycomb biomass (Reddy *et al*., 2012), hazelnut shell (Cimino *et al*., 2000), olive tree pruning waste (Uzunosmanoglu *et al*., 2011), coconut shell (Singha and Das, 2013), sunflower seed (Liou, 2010), sugarcane bagasse (Shah *et al*., 2013), banana peel (Ashraf *et al*., 2012), orange peel (Gupta and Nayak, 2012), mussel shell (Cerino-Cordova *et al*., 2013) and corncob (Levya-Ramos *et al*., 2005) have been used in heavy metal removal from wastewaters. The obvious advantage of removal method is the lower costs involved. Hence, there is a need to search for more economical and effective adsorbents (Moradi *et al*., 2012). Miswak is used as chewing stick obtained from the roots, twigs or stems of *Salvadora persica* L. and widely used in Middle Eastern and Eastern African cultures. The World Health Organization has recommended and encouraged the use of chewing sticks as an effective tool for oral hygiene in areas where such use is customary (Al-Bayaty *et al*., 2010). It possessed various biological properties including significant antibacterial and anti-fungal effects. The anti-microbial and cleaning effects of miswak have been attributed to various chemicals detectable in its extracts. (Mohamed *et al*., 2012). The parts of the miswak trees that inconvenient for the use as chewing sticks called miswak waste. The miswak waste contains a number of functional groups for binding metal ions and it is available in abundance and low cost particularly in rural area of Middle Eastern and Eastern African. In this study, the adsorption ability of miswak waste was investigated for the removal of Pb(II), Cu(II), Ni(II) and Cd(II) from aqueous solutions. The effect of pH, contact time, adsorbent dosage and initial metal concentrations were investigated. The FTIR spectra and SEM results were also evaluated.

MATERIALS & METHODS

A Unicam 929 atomic absorption spectrometer (AAS) operating with an air-acetylene flame and equipped with a Unicam Cu-Hollow cathode lamp at 4mA and Cathodeon Cd, Pb, Ni-Hollow cathode lamps 6mA, 8mA and 12mA current settings (respectively) were employed. The surface properties of the miswak waste were analyzed by using scanning electron microscopy (SEM, Hitachi S-3000N). The pH measurements were performed by employing a Jenway Model 3010 pH meter combined with a glass electrode. Containers were shaken during the adsorption experiments by a water bath shaker (Clifton, England) set to 200-cpm. Mse-Mistral Model centrifuge at 2500-rpm rate was used to separate miswak waste from the solutions after complete adsorption. Five standard solutions for each metal ion (1-10 ppm) were prepared in 100 mL flasks. Calibration graphs for each batch of experiments were re-constructed by using the standard solutions. Metal salts ($CuCl_2.2H_2O$, $CdCl_2.4H_2O$, $Pb(NO_3)_2$ and $NiSO_4.6H_2O$) were supplied by Merck (Germany) and used without further purification. All experiments were repeated 4 times and the experimental points display the average of the data found. This was realized in order to diminish the experimental faults.

The miswak waste was obtained from commercial sales in Samsun, Turkey. Prior to the experiments, soluble and coloured components were removed from the crushed miswak waste by washing with hot water (105°C), ethanol and hexane for 1-hour periods until a colourless solution of miswak waste is spectrometrically observed at room temperature. The properties of untreated miswak waste are shown in Table 1. Then, it was treated with 2% formaldehyde solution in order to reduce organic leaching and avoid mould formation during batch adsorption. The miswak waste cleaned with hot water was dried in oven at 105°C and 60–170 mesh particles were used in the adsorption experiments without any further modification. All solutions were prepared in glass-distilled water and the results presented in this paper were the average of at least three measurements. The uptake of Pb(II), Cu(II), Ni(II) and Cd(II) ions by miswak waste from aqueous solutions (ranging 5-100 ppm) were studied by a batch technique at room temperature (25±0.3°C). A known quantity of processed and dried miswak waste (0.05g) was added in to 50 mL aqueous solutions and stirred continuously. One-hour period was accepted for the optimum contact time. Using filter paper in any step to separate adsorbent materials from the final solutions causes remarkable systematic errors (constant type error) on the final concentration of the analysed solutions (Engin *et al*., 2012). So, the aqueous phase was separated from miswak waste by centrifugation and the remained concentrations of metal ions in the solutions (diluted if necessary) were determined by AAS. The uptake of the metal ions from aqueous systems was calculated by the difference between their initial and final concentrations. Effect of pH (1-8), contact time (0-150 minutes), initial concentration of heavy metal ions (0-30 ppm) and quantity of the miswak waste (0-2.5 g L^{-1}) to heavy metal ions uptake were also studied and optimum values were used in the experiments. The pH values (1 to 8) were adjusted by using 0.10 M NaOH and 0.10 M HCl solutions. For the recovery calculations, 0.1 g miswak waste was added into 50 mL of each heavy metal

Table 1. Properties of the miswak waste

Chemical properties	Content (%)
Moisture	7.92
Volatile matter (150 °C)	0.65
Ash (700 °C)	1.70
Total loss of ignition	89.8
Elemental analysis	C(38.84), H(5.80), S(1.72), N(0.54)
Physical properties	**Measurement unit**
Surface area (BET)	0.5 m^2 g^{-1}
Bulk density	0.534 g cm^{-3}

solutions (25 ppm of Pb(II), Cu(II), Ni(II) and Cd(II)) and optimum conditions were applied. Following adsorption, the aqueous phase was separated and the remained concentrations of metal ions in the solutions were determined. The adsorbed amount of heavy metal ions was deduced from the differences of the initial and final concentrations. The separated solid phase was dried in the oven and the adsorbed heavy metal ions were stripped from the solid phase by adding 50 mL of 0.1 M HCl. The amount of the metal ions in the acid solutions was determined and recovery (%) for each situation is calculated from the adsorbed and recovered metal ion concentrations.

RESULTS & DISCUSSION

The FTIR spectrums of the miswak wastes which were treated with hot water, ethanol and hexane are shown in Fig. 1. The absorbance near at 3400 /cm is assigned to the O-H stretching vibration of water and the alcoholic groups. Due to the nitrogen content in the elemental analysis result, there is a contribution in the region related to the vibrational stretching of the N–H bond of amide groups (3500–3300 cm^{-1}). The bands observed at 2900 and 2850 /cm are due to -CH2- groups, which are the characteristic peaks for alkyl groups. The evident absorbance of a signal, near 1700/ cm for miswak waste, indicates the presence of a C=O group on the surface. The presence of the alkyl groups is also by their -CH2- bending vibrations at 1375 and 1450 /cm. The intense peak at 1035 /cm is assigned to the C-O stretching vibration of the alcoholic groups. The -CH2- rocking more is seen at near 700 /cm. As expected, the FTIR spectrums exhibited that miswak wastes have rich hydroxyl and carboxyl groups on their surfaces. Consequently, the results obtained revealed that the complexation was a potential adsorption mechanism between the test heavy metals and the miswak waste.

Fig. 2. presents the morphology of miswak waste according to SEM micrographs taken. It is obvious

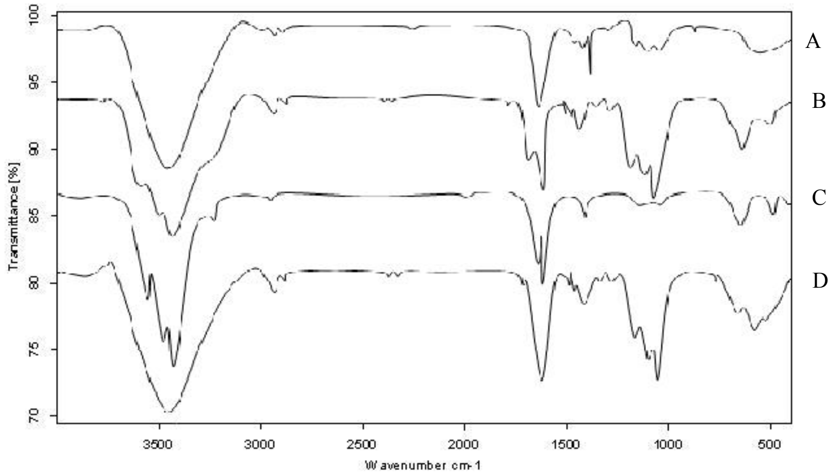

Fig. 1. The FTIR spectrums of the miswak waste. Untreated (A), hot water-treated (B), ethanol-treated (C), hexane-treated (D)

that its surface exhibited a rough structure with an irregular surface (Fig.1a). The hot water, ethanol and hexane treatments have changed the surface morphology of the miswak waste (Fig. 1b, 1c, 1d). The treatments showed that, hot water treated, which the most hydrolysable materials had been cleaned is the best form for using as an adsorbent. On the basis of this fact, it can be concluded that the adsorbent has an adequate morphology for metal ion adsorption. The batch adsorption experiments were conducted at different contact times (0-150 min) for an initial concentration of heavy metal ions. The percentages of Pb(II), Cu(II), Ni(II) and Cd(II) removed from aqueous systems as a function of time are presented in Fig. 3. It can be seen that the adsorbed amount of heavy metal ions increases from 20 to 60 minutes time, after that a maximum removal is reached. Therefore, 60 minutes was selected as a suitable contact time for the systems.

The hydrogen ion concentration in the adsorption process is considered as one of the most important critical parameters that influences the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction (Vimala and Das, 2009). The effect of pH was studied by varying the pH in the range of 1–8 for Pb(II), Cu(II), Ni(II) and Cd(II) (Fig. 4). It can be seen from Fig. 4 that adsorption percentages are very low at strong acidic medium. After pH=3, uptakes increase sharply up to pH=5.5 and thereafter they stay almost constant for greater pHs. No pH values over 8.0 were studied since precipitation of heavy metals occurs. The optimum pH for systems was graphically determined as 6 and used in all experiments (very close to the original pH of the solutions).

The dependence of adsorbent dosage on the adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) ions was studied by varying the amount of adsorbent from 0.1-2.5 g/L, while keeping all other variables (pH, adsorbent concentration, contact time, and temperature) constant. The effects of miswak waste dosage on the removal of Pb(II), Cd(II), Cu(II) and Ni(II) removal are shown in Fig. 5. This is an expected result because as the adsorbent concentration increases, the number of adsorbent particles

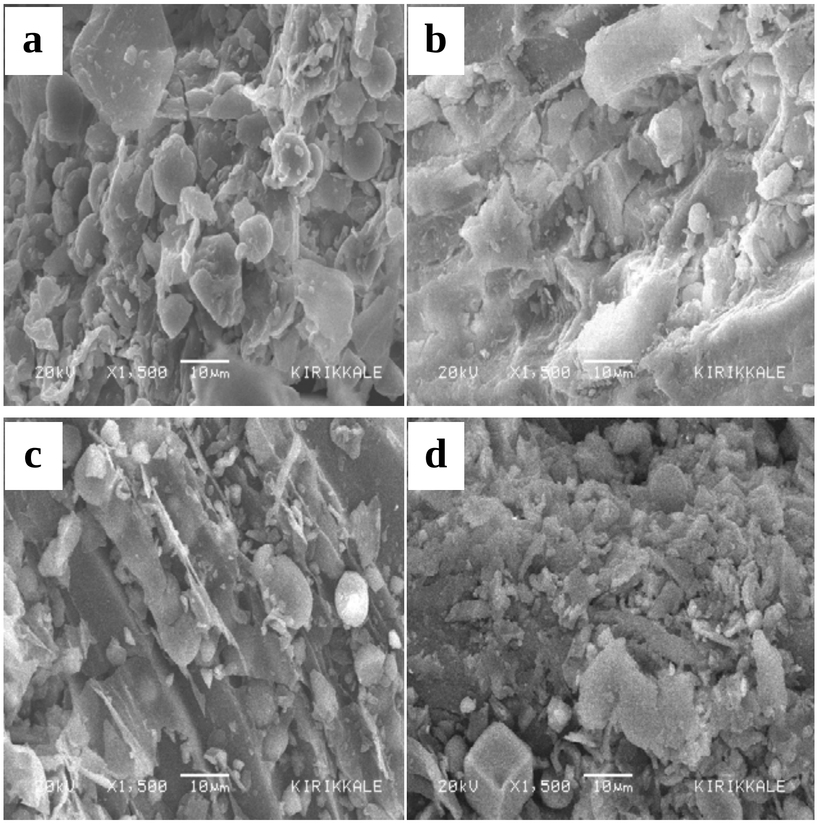

Fig. 2. SEM micrographs of miswak waste. a. Untreated, b. Hot water-treated, c. Ethanol-treated, d. Hexane-treated

surrounding the metal ions or ratio of adsorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces. Adsorption isotherms describe the relationship between the amount of ions adsorbed by adsorbent mass related to the concentration of the solution used, and the determination of equilibrium parameters provides important information for the interpretation of data obtained in adsorption (Vitek-Krowiak *et al*., 2011). The experimental sorption data of Pb(II), Cd(II), Cu(II) and Ni(II) in miswak waste were obtained with the Langmuir and Freundlich isotherm models. Both models fit the experimental data reasonably based on the correlation coefficient (r^2). The results revealed that the Freundlich isotherm fitted the experiment results better than Langmuir isotherm. The fit of data by adsorption models would not reflect any sorption mechanism and can hardly have a meaningful physical interpretation due to the complex nature and varied active sites of miswak waste. However, the Freundlich model was used due to the nature of the adsorbent under study (Velazquez-Jimenez *et al*., 2009).

Freundlich isotherm is given as following equation.

$x/m = K_f.C_e^{1/n}$

The linearised equation is

$\log x/m = \log K_f + 1/n \log C_e$

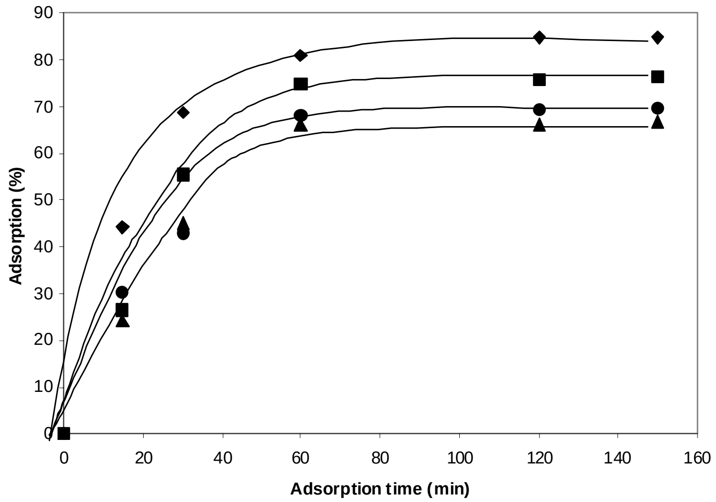

Fig. 3. Effect of contact time on the adsorption (25°C, pH=6, 1g/L adsorbent, 5 ppm initial concentration).

Ni(II) ▲; Cu(II) •; Cd(II) ■; Pb(II) ♦.

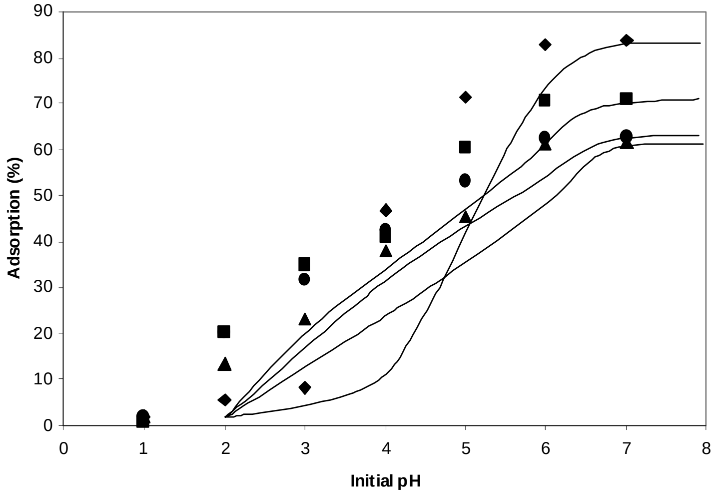

Fig. 4. Effect of pH on the adsorption (25°C, contact time 1h, 1g/L adsorbent, 5 ppm initial concentration).

Ni(II) ▲; Cu(II) •; Cd(II) ■; Pb(II) ♦.

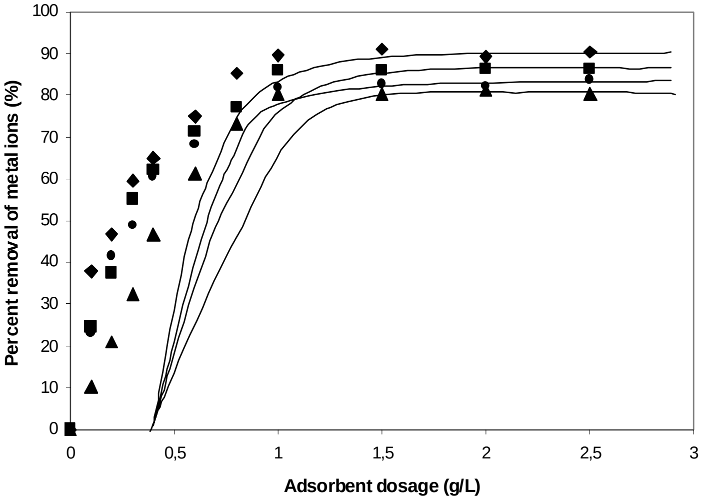

Fig. 5. Effect of the miswak waste dosage on the removal of heavy metals (25ºC, pH=6, contact time 1h, 5 ppm initial concentrations).

Ni(II) ▲; Cu(II) •; Cd(II) ■; Pb(II) ♦.

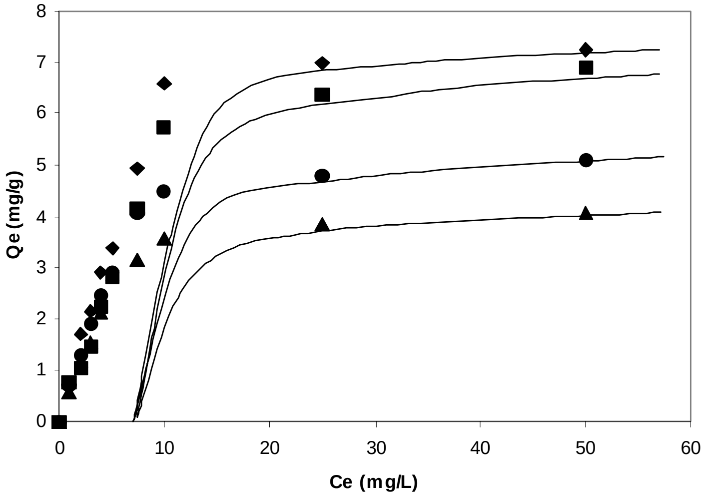

Fig. 6. Adsorption capacities of the miswak waste. (25ºC, contact time 1h, pH=6, 1g/L adsorbent).

Ni(II) ▲; Cu(II) •; Cd(II) ■; Pb(II) ♦.

where x/m represents the amount of metal ions adsorbed at the equilibrium (mg/g), C_e is equilibrium concentration (mg/L), K_f is the measure of adsorption capacity, 1/n is adsorption intensity and including other parameters. A plot of log(x/m) versus logC_e gives a straight line, the slope and intercept of which correspond to 1/n and logK_f respectively. Pb(II), Cd(II), Cu(II), and Ni(II) adsorption isotherms in miswak waste are shown in Fig. 6, where it can be seen that affinity sequence is Pb > Cd > Cu > Ni. The maximum adsorption capacities of Pb(II), Cd(II), Cu (II), and Ni(II) per gram of miswak waste were calculated as 6.84±0.23, 5.91±0.20, 4.56±0.17 and 3.73±0.15 mg, respectively. The Freundlich isotherm data together with Langmuir isotherm data for the investigated heavy metal ions on miswak waste are summarised in Table 2. The linear Langmuir and Freundlich isotherms for adsorption of Pb(II), Cd(II), Cu (II), and Ni(II) on miswak waste are presented in Fig.7 and Fig 8. Application of Freundlich model to the equilibrium data Pb(II), Cd(II), Cu(II) and

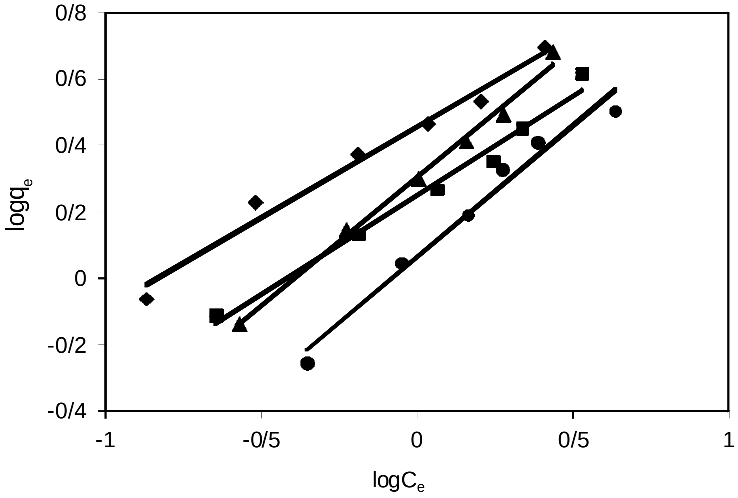

Fig. 7. Linear Freundlich isotherms of the miswak waste. (25ºC, contact time 1h, pH=6, 1g/L adsorbent).

Ni(II) ▲; Cu(II) •; Cd(II) ■; Pb(II) ♦.

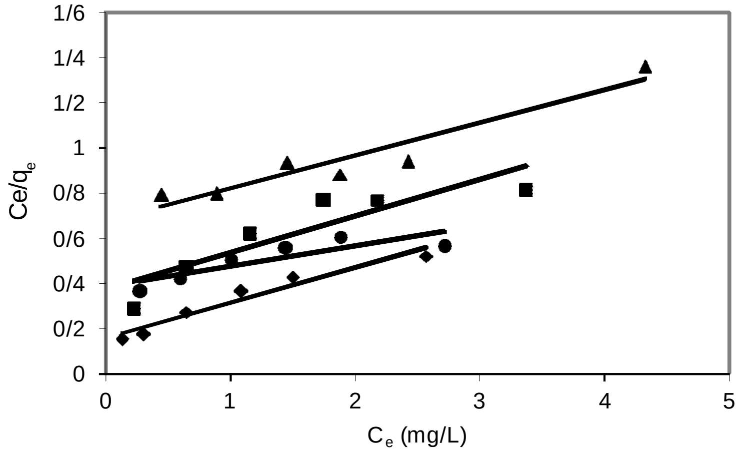

Fig. 8. Linear Langmuir isotherms of the miswak waste. (25ºC, contact time 1h, pH=6, 1g/L adsorbent).

Ni(II) ▲; Cu(II) •; Cd(II) ■; Pb(II) ♦.

Table 2. Freundlich and Langmuir isotherm equations for Pb(II), Cd(II), Cu(II) and Ni(II) systems.

	Freundlich Equation			Langmuir Equation		
System	K_F (mg/g(L/mg)$^{1/n}$)	1/n	r^2	q_m (mg/g)	b (L/mg)	r^2
Pb(II)	2.86	0.548	0.979	6.45	40.31	0.941
Cd(II)	2.02	0.778	0.993	11.36	29.20	0.732
Cu(II)	1.79	0.596	0.983	6.17	16.45	0.791
Ni(II)	1.16	0.788	0.974	6.89	10.17	0.910

Ni(II) indicates the monolayer coverage of miswak waste by the heavy metal ions, but this was to non-distinct or multiple sites of adsorption unlike the Langmuir model which is to distinct localised adsorption sites (Cay *et al.*, 2004). It is well known that the Langmuir isotherm corresponds to a dominant ion exchange mechanism while Freundlich isotherm showing adsorption-complexation reactions taking place in the adsorption process.

However the actual mechanism is not known well, it is thought that ion exchange, complexation and electrostatic interactions plays an important role in the whole adsorption process of miswak waste. Ion exchange mechanism considers the well-known model of metal binding and proton releasing reaction. FTIR, pH measurements and desorption results confirmed that oxygen containing groups (e.g. carboxylic and phenolic) are involved in metal sorption. Therefore, based on the experimental results, a possible adsorption mechanism for miswak waste is proposed:

$$(= \mathrm{R\,COOH})_n + n\mathrm{M}^{z+} <> (=\mathrm{R}^{-}\mathrm{COO})_{n-1}\mathrm{M}^{(z+)-1} + n\mathrm{H}^{+}$$

where M = Pb^{2+}, Cd^{2+}, Cu^{2+} or Ni^{2+}. A similar mechanism is suggested for cyclic groups, as phenolic and pyranose structures (Velazquez-Jimenez *et al.*, 2013). Experimental pH measurements of the original metal solutions, before and after adding miswak waste showed that ion exchange is only a part of the whole adsorption process since the ratio of the theoretical and experimental pH changes deviated considerably from unity.

The plausible explanation for the higher adsorption is also explained as ionic radius also influences adsorption of metal ions by adsorbent where ions with a greater ionic radius are preferentially adsorbed (Kamari and Ngah, 2009; Tarley and Arruda, 2004). The higher adsorption of Pb(II) as compared to Cd(II), Cu(II), and Ni(II) on adsorbents could be due to the greater ionic radius 0.119 nm for Pb(II) relative to 0.097 nm for Cd(II), 0.073 nm for Cu(II) and 0.069 nm for Ni(II), respectively. So, Pb(II) offers a bigger coordination sphere than the other heavy metals since it has a bigger ionic radius. Hence, Pb ions can bind better with two distant functional groups. Besides, the coordination sphere of Pb(II) embraces a higher number of OH and COO" groups, making Pb(II) complexes more stable than Cd(II), Cu(II) or Zn(II)-complexes.

A further goal of any adsorbent used is the reuse potential. Reuse of adsorbent keeps the processing cost down and opens the possibility of recovering the metal(s) extracted from the liquid phase. The percent recoveries of the heavy metal ions for the elution method were calculated the aqueous systems. For this purpose, 0.1 g miswak waste was added in to 50 mL of each heavy metal solutions and optimum conditions were applied. Adsorbed metal ions were stripped from the solid phase by adding 50 mL of 0.1 M HCl. Percent recoveries calculated (n=5) were 94.23±1.40%, 95.45±0.98%, 92.73±1.73% and 92.05±1.36% for Pb(II), Cu(II), Ni(II) and Cd(II), respectively. The results indicate that following the successful adsorption of heavy metals, the miswak waste may be recovered for consecutive uses with advantage. The adsorption capacity of the miswak waste changed by about 4–5 % for all metal ions during each adsorption–desorption cycle. These results show that the miswak waste could be repeatedly used at least five cycles without changing retention capacity remarkably.

CONCLUSION

The present study evaluates Pb(II), Cd(II), Cu(II) and Ni(II) removal by the use of miswak waste. The major components of miswak waste are carboxyl, hydroxyl, sulfur and nitrogen containing groups. Therefore, the nature of the material allows capturing of heavy metal ions efficiently due to the active sites of the carboxylic groups. The adsorption performance was strongly affected by parameters such as initial pH of solution, adsorbent dosage, contact time, and initial metal ion (Pb(II), Cd(II), Cu(II) and Ni(II)) concentration. The results demonstrated that both the ion exchange and complexation were the adsorption mechanisms of adsorbents relative to the heavy metals. It can be also concluded that the miswak waste is new, effective, natural, low cost and alternative adsorbent for the removal of common heavy metal ions from an aqueous solutions in terms of high adsorption capacity. The results of this study indicate the possibilities that exist in the cleanup of the environment with the use of natural resources.

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REFERENCES

Al-Bayaty, F. H., Al-Koubaisi, A.H., Ali, N. A.W. and Abdulla, M. A. (2010). Effect of mouth wash extracted from Salvadora persica (Miswak) on dental plaque, formation: A clinical trail. J. Med. Plants Res., **4 (14)**, 1459–1467.

Ashraf, M.A., Maah, M. J. and Yusoff, I. (2012). Batchwise biosorption of Sn2+ ions by using chemically treated banana peel. Res. J. Biotechnol., **7 (3)**, 81–87.

Babel, S. and Kurniawan, T. A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater., **97 (1-3)**, 219–243.

Cay, S., Uyanik, A. and Ozasik, A. (2004). Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste. Sep. Purif. Technol., **38 (3)**, 273–280.

Cerino-Cordova, F. J., Diaz-Flores, P. E., Garcia-Reyes, R. B., Soto-Regalado, E., Gomez-Gonzalez, R., Garza-Gonzalez, M. T. and Bustamante-Alcantara, E. (2013). Biosorption of Cu(II) and Pb(II) from aqueous solutions by chemically modified spent coffee grains. Int. J. Environ. Sci. Technol., **10 (3)**, 611–622.

Cimino, G., Passerini, A. and Toscano, G. (2000). Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. Water. Res., **34 (11)**, 2955–2962.

Engin, M. S., Uyanik, A., Cay, S. and Icbudak, H. (2010). Effect of the adsorptive character of filter papers on the concentrations determined in studies involving heavy metal ions. Adsorpt. Sci. Technol., **28 (10)**, 837-846.

Garrido-Rodriguez, B., Fernandez-Calvino, D., Novoa-Munoz, J. C., Arias-Estevez, M., Diaz-Ravina, M., Alvarez-Rodriguez, E., Fernandez-Sanjurjo, M.J. and Nunez-Delgado, A. (2013). pH-dependent copper release in acid soils treated with crushed mussel shell. Int. J. Environ. Sci. Technol., **10 (5)**, 983–994.

Gupta, V. K., Carrott, P. J. M., Carrott, M. M. L. R. and Suhas. (2009). Low-cost adsorbents: growing approach to wastewater treatmenta review. Crit. Rev. Env. Sci. Technol., **39 (10)**, 783–842.

Gupta, V. K. and Nayak, A. (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe2O3 nanoparticles. Chem. Eng. J., **180 (2012)**, 81–90.

Han, R., Li, H., Li, Y., Zhang, J., Xiao, H. and Shi, J. (2006). Biosorption of copper and lead ions by waste beer yeast. J. Hazard. Mater., **137 (3)**, 1569–1576.

Kamari, A. and Ngah, W. S. W. (2009). Isotherm, kinetic and thermodynamic studies of lead and copper uptake by H_2SO_4 modified chitosan. Colloid. Surface. B., **73 (2)**, 257–266.

Kamsonlian, S., Suresh, S., Ramanaiah, V., Majumder, C. B., Chand, S. and Kumar, A. (2012) Biosorptive behaviour of mango leaf powder and rice husk for arsenic(III) from aqueous solutions. Int. J. Environ. Sci. Technol., **9 (3)**, 565–578.

Kumar, P. S., Ramalingam, S., Sathyaselvabala, V., Kirupha, S. D., Murugesan, A. and Sivanesan, S. (2012). Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell. Korean J. Chem. Eng., **29 (6)**, 756–758.

Kyzas, G. Z. (2012). Commercial coffee wastes as materials for adsorption of heavy metals from aqueous solutions, Materials, **5(10)**, 1826–1840.

Levya-Ramos, R. L., Bernal-Jacome, L. A. and Acosta-Rodriguez, I. (2005). Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. Sep. Purif. Technol**., 45 (1)**, 41–49.

Liou, T. H. (2010). Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation. Chem. Eng. J., **158 (2)**, 129–142.

Mohamed, S. A., Al-Malki, A. L., Khan, J. A., Sulaiman, M. I. and Kumosani, T. A. (2012). Properties of peroxidase from chewing stick miswak. Afr. J. Pharm. Pharmaco., **6 (9)**, 660–670.

Moradi, O., Mirza, B., Norouzi, M. and Fakhri, A. (2012). Removal of Co(II), Cu(II) and Pb(II) ions by polymer based 2-hydroxyethyl methacrylate: thermodynamics and desorption studies. Iran J. Environ. Health. Sci. Eng., **9 (31)**, 9–31.

Orhan, Y. and Buyukgungor, H. (1993). The removal of heavy metals by using agricultural wastes. Water Sci. Technol., **28 (2)**, 247–255.

Ramana, D. K. V., Reddy, D. H. K., Yu, J. S. and Seshaiah, K. (2012). Pigeon peas hulls waste as potential adsorbent for removal of Pb(II) and Ni(II) from water. Chem. Eng. J., **197**, 24–33.

Reddy, D. H. K., Lee, S. M. and Seshaiah, K. (2012). Biosorption of toxic heavy metal ions from water environment using honeycomb biomass-an industrial waste material. Water Air Soil Poll., **223 (9)**, 5967–5982.

Shah, B., Mistry, C. and Shah, A. (2013). Seizure modeling of Pb(II) and Cd(II) from aqueous solution by chemically modified sugarcane bagasse fly ash: isotherms, kinetics, and column study. Environ. Sci. Pollut. R., **20 (4)**, 2193–2209.

Singha, B. and Das, S. K. (2013). Adsorptive removal of Cu(II) from aqueous solution and industrial effluent using natural/agricultural wastes. Colloid. Surface. B., 107, 97–106.

Sivakumar, K. K., Balamurugan, C., Ramakrishnan, D. and Dheenadayalan, M. S. (2012). Heavy metal removal from aqueous solution by tamarind and neem leaves. Asian. J. Chem., **24 (10)**, 4686–4688.

Tarley, C. R. T. and Arruda, M. A. (2004). Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. Chemosphere, **54 (7)**, 987–995.

Tsekova, K., Todorova, D., Dencheva, V. and Ganeva, S. (2010). Biosorption of copper(II) and cadmium(II) from aqueous solutions by free and immobilized biomass of Aspergillus niger. Bioresour. Technol., **101 (6)**, 1727–1731.

Uzunosmanoglu, O., Uyanik, A. and Engin, M. S. (2011). The removal of cadmium(II), copper(II) and lead(II) from aqueous solutions by olive tree pruning waste. Fresen. Environ. Bull., **20 (12)**, 3135–3140.

Velazquez-Jimenez, L. H., Pavlick, A. and Rangel-Mendez, J. R. (2013). Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water. Ind. Crop. Prod., **43**, 200–206.

Witek-Krowiak, A., Szafran, R. G. and Modelski, S. (2011). Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. Desalination, **265 (1-3)**, 26–134.

Zhang, M. K., Liu, Z. Y. and Wang, H. (2010). Use of single extraction methods to predict bioavailability of heavy metals in polluted soils to rice. Commun. Soil. Sci. Plan., **41 (7)**, 820–831.