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Research Article

Removal of Cr and Mn from wastewater using food wastes as low-cost biosorbents

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This study investigated the ability of three common food wastes (eggshell, potato peel, and tea waste) as low cost and environmentally friendly bio sorbent for Chromium (Cr) and manganese (Mn). The effect of three parameters (wastewater pH biosorbent dose, and contact time on removal of heavy metal (HM) removal efficiency were studied, where heavy metal removal increased as each of these three parameters increased. Of the three wastes studied, tea waste was the most efficient biosorbent, with potato peel waste being less active in adsorption than tea waste, and eggshell having the least ability to adsorb HMs. Irrespective of the waste used Cr was adsorbed in higher amounts than Mn. The adsorption data were fit to both the Langmuir and Freundlich adsorption isotherms the data best fit the Langmuir model when tea waste adsorbed Cr and the results fits more suitable under freundlich when egg shell absorbed Mn.

Key words: Adsorption, biosorption, heavy metal, water treatment

INTRODUCTION

Globally Heavy Metal (HM) pollution of water ways by various industries including metal processing, battery manufacturers, hospitals, pharmaceuticals, and mining is a major issue King et al. (2006). HMs are a major concern because they are non-biodegradable and can accumulate in organisms causing diseases and detrimental effects such as anemia, high blood pressure, toxicity and coma Orodu et al. (2014). Thus efficient removal of HMs from contaminated water is of high priority and a variety of remediation approaches have been successfully used to achieve this goal. Some of the most common techniques have included adsorption on ion-exchange resins and activated carbons, precipitation Bailey et al. (1999); Saka et al. (2012), reverse osmosis, Rengaraj et al. (2001) electrodialysis, (Gadd, 1993). Solvent extraction, phytoextraction, ultrafiltration Kizilkaya et al. (2010), and coagulation/flocculation (Lai and Lin, 2003). All of these methods, while generally successful under the right conditions do have some limitations. The two major concerns which have restricted the widespread uptake of such traditional technologies is that they are relatively expensive and often involve the use of environmentally harmful chemicals. The use of biosorption is a cheap and environmentally friendly alternative to such traditional techniques, where environmental biosorption is specifically defined as adsorption which uses plant and animal remains (i.e. agricultural waste) as the main adsorptive components (Chang and Chen, 2005; Prasad and Saxena, 2004). For example, adsorbents derived from cellulosic lignin material generally have good removal efficiencies for many HMs Coelho et al. (2007). A wide range of common waste biosorbents have been used for HM adsoption. Suyama et al. (1994) used eggshell membrane to accumulate three metals, Au, Pt, and Pd, from dilute aqueous solution with efficiencies of 55, 25, and 22, respectively Suyama et al. (1994). Arunlertaree et al. (2007) also found eggshells had some capacity to remove lead from battery manufacturing wastewater where the contact time, initial pH, eggshell dose, affected removal efficiency Arunlertaree et al. (2007). Likewise, Tabatabaee et al. (2016) used a variety of waste products including almond skin, walnut shell, sawdust, rice bran, and eggshell to adsorb four HMs (Cd

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(II), Cr (II), Ni (II), and Pb (II) from aqueous solution and compared the removal efficiency with two traditional materials, activated carbon and an ion exchange resin. They found that the best removal was achieved with waste eggshell which was very close to the efficiency observed for activated carbon Tabatabaee et al. (2016). Low-cost adsorbents are not solely useful for removing HMs and they can also be applied for the removal of other common wastewater pollutant For example, Mohammed-Ridha and Abdul-Ahad (2014) used barley husks and eggshells to remove Levofloxacin from synthetic wastewater. Levofloxacin is an antibacterial agent which becomes a high environmental risk when contaminates aquatic environments (Mohammed-Ridha and Abdul-Ahad, 2014). Kanyal and Bhatt (2015) also found that large scale removal of HMs could be achieved using inexpensive household wastes (Kanyal and Bhatt, 2015). They showed that chicken eggshells, banana peels, and pumpkins could all be used as good biosorbents for Cu and Pb. This study also investigated the effects of various parameters (pH, agitation speed, and contact time) and found the optimal removal was achieved within 90 min at pH 7 and 100 rpm. Cheraghi et al. (2015) used waste tea leaves to remove Pb from aqueous solution with a maximum removal efficiency of 97.9%, where the initial metal concentration, amount of adsorbent, temperature, contact time, and pH all affected Pb (II) adsorption, which generally decreased as the initial metal concentration increased Cheraghi et al. (2015). The capability of eggshell derived adsorbents to adsorb Cu(II) and Cd(II) ions from aqueous solution was also effected by temperature, agitation speed, initial metal concentration, adsorbent dose, initial solution pH, and contact time Abd Ali et al. (2016). Eggshells were successfully used by Koçyiğit and Şahin, (2017) as a low–cost adsorbent to remove many different HMs from aqueous solution, where the removal effectiveness was attributed to the high concentrations of both carbon and calcium and the high porosity and availability of functional groups on the eggshell surface, where pH, egg concentrations and contact time all affected removal efficiency (Koçyiğit and Şahin, 2017). Jayan and Anitha, (2015) also found that in addition to the use of egg shell as a biosorbent for HM adsorption, eggshell could also be used as an alternative to traditional sand filter media. Instead of sand, Jayan and Anitha egg shell powder mixed with Chitosan could be used instead of a sand filter with high removal efficiencies for Pb (97.8%) and Cu (94.11%). (Jayan and Anitha, 2015). Abdulsalam et al. (2014) used two novel agricultural by-products, oil-free Moringa oleifera cake and sweet potato peel, to remove Cr (VI) ions from tannery wastewater; where the biosorbent was applied in both a modified and an unmodified form (Abdulsalam, 2014). Bisorbent modification involved treating oil-free Moringa oleifera powder separately with 6 N HCl (acid treatment) and 1 N NaOH (alkaline treatment) for one hour prior to filtration and, washing thoroughly with distilled water to obtain a clear (turbidity free) mixture. . In each case the water layer was removed and the treated oil-free Moringa oleifera powder dehydrated in an oven at 50˚C for 24 h until a constant weight was obtained. Such modifications improved Cr (VI) removal, with removal efficiencies of 59% and 74% of unmodified and modified samples, respectively, which was attributed to enhanced surface metal-binding capacity of the biosorbent upon modification. Abdul-Raheim et al. (2015) used potato peel to prepare nanoparticles modified with acrylic acid Abdul-Raheim et al. (2015). The modified potato starch-magnetic nanoparticles (MPS-MNPS) were then used to remove Cu^{2+},Pb^{2+} and Ni^{2+}ions from wastewater with removal efficiencies influenced by pH, contact time, and temperature. In these studies, the monomer and initiator concentrations also effected the grafting process and hence removal efficiency. Şen et al. (2015) used tree bark as a green alternative to activated carbon for HM removal, and showed that removal with unmodified tree bark was relatively good and thus acceptable as a low cost biosorbent Şen et al. (2015).Banana (Musa sapientum) and potato (Solanum tuberosum) peel were both successfully used by Pooja et al. (2016) as biosorbents for Cu removal from wastewater. They found that potato peel adsorbed more Cu than banana peel. At the highest experimental solution concentration used (50 mg/L) banana peel removed 57.7% of the Cu. However, at the lowest experimental solution concentration (2 mg/L), banana peel removed 91.5% of the Cu. Adsorption rate expressed mathematically by Langmuir and Freundlich models (Pooja, 2016). Aslan et al. (2016) studied the variation in the adsorption ability of tea waste for Ni (II) and Cu (II) with different temperature and pH. They found that pH affected removal efficiencies' more than temperature. The highest removal efficiencies of Cu (II) (59%) and Ni (II) (43%) were observed at 50˚C, but removal efficiencies of Cu (II) and Ni (II) were increased from about 25% to 60% and from 35% to 43% respectively by simply increasing pH from 2.0 to 5.0 Aslan et al. (2016). Low-cost organic wastes can also be used to adsorb HMs from soil. For example, tea waste and potato peels were successfully used to reduce mercury (Hg) toxicity in a soil, where both waste sorbents decreased the uptake of HMs by the Phaseolus Vulgaris plant when grown under greenhouse condition in a Hg contaminated soil Askari et al. (2017).Tea waste was also successfully used as a low-cost adsorbent to remove Cd from aqueous solution; where adsorbent dose, contact time, pH, an initial Cd concentration all affected removal efficiencies The maximum efficiency of Cd adsorption was 99.50% obtained at pH of 5, a contact time of 90 minutes and 10 g/L of adsorbent, Isotherm data for both the Langmuir and Freundlich isotherm models acceptably fir the data where kinetic analysis indicated that adsorption kinetics followed a second-degree kinetic adsorption model Ghasemi et al. (2017). Bharti et al. (2017) found that the Cu removal efficiency by potato peel varied with contact time, pH, initial Cu concentration, and adsorbent dose. At ambient temperature an optimum Cu removal efficiency of 76.5% was obtained at pH 6 with an adsorbent dose of 5 g and an initial Cu centration of 10 ppm Bharti et al. (2017). Sun et al. (2017) also used potato peel to remove As (III), Pb^{2+} and Hg^{2+} from water and found that pH was the most important parameter affecting biosorption Sun et al. (2017). In addition to food waste agricultural materials, other materials such as expanded perlite have also been used to remove HMs like Cu (II) from industrial leachate with removal that followed pseudo-second-order kinetics Ardali et al. (2014) and where fitting of the data to the Elovich and intraparticle diffusion kinetic models showed that expanded perlite had excellent ability to adsorb Cu (II) from industrial leachate Ardali et al. (2014). Mendoza et al. (2014) used denim fiber scraps as cheap, ecofriendly sorbent to remove four common HM pollutants (Pb^{2+}, Cd^{2+}, Zn^{2+} and As) from aqueous solution. They found that denim fiber scraps were able to adsorb these HM ions more effectively than other more commonly used synthetic and natural sorbents such as activated carbons and zeolites. They also found that denim fiber scraps were also able to adsorb As (V) from aqueous solution with sorption capacities >1.5 mg/g Mendoza-Castillo et al. (2014) . Previous studies have shown that HM removal occurs in two stages, initially HMs adhere to the active surface sites of biosorbent followed by slower diffusion of metal ions into the adsorbent pores by intraparticle diffusion Kumar et al. (2008). In such a mechanism the physiochemical characteristics of both the heavy metal to be adsorbed and those of the biosorbent are likely to be important. In this study the ability of three common inedible food wastes (tea, potato peel and egg shell) where evaluated for their ability to adsorb chromium (Cr) and manganese (Mn) Selected physiochemical properties of the three biosorbent used (e.g. pore volume, carbon content, hardness and porosity) were also determined to understand how these parameters influenced HM removal efficiency Finally in practical terms operating pearamteres that could also influence removal such as contact time, solution pH, and biosorbent dose were also studied and the practical removal efficiency compared with previous studies.

MATERIALS AND METHODS

Bio sorbent Preparation: Egg shell, potato peel and tea waste were collected from household food waste, washed with distilled water and air dried in the sun, prior to being crushed and sieved <0.5 mm. Waste Water Preparation: A simulated wastewater was prepared by adding Mn and Cr to distilled water (100 mL) in a plastic container to give final concentrations of 10 ppm for each heavy metal. Heavy Metal Measurement: The total concentrations of both Mn and Cr were determined by Atomic Absorption Spectroscopy (Shimadzu spectrophotometer).

Adsorption Experiments: A known mass of dried and sieved biosorbent was initially added to (100 mL) water pH 7 and vigorously shaken at 200 rpm for 1 min. pH of water was adjusted to desired value by adding HCL or NaOH as required. The wastewater-sorbent mixture was then left for a predefined periods (48, 72, 100, 120, 150, 180 min) before being filtered, and the residual HM content in the supernatant measured. The percentage of HM removal was then calculated using the following equation expressed as:

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \text{ .... (1)}$$

Where C: Was the initial concentration of HM before adsorption (mg/L)

C_e: Was the equilibruim concentration of HM in solution after adsorption (mg/L)

All experiments were repeated using the three different biosorbents (chicken eggshells, potato peel and tea leaf waste), at three different initial pHs (3, 5 and 7), and three biosorbent doses (0.16 g, 0.2 g, 0.3 g).

Adsorption experiments

The target biosorbent (0.16 g – 0.3 g) was added to an aliquot of pH 7 wastewater (100 mL), and the mixture shaken at 200 rpm for 1 min prior to being left to stand for 100 min (the equilibrium time), before being filtered and the concentration of metal ions in the solution at equilibrium (mg/L) Ce measured. The amount of metal adsorbed onto the biosorbent (qe) was then calculated using equation 2 Repo et al. (2011)

$$qe = \frac{c_i - c_e}{W} V \text{ ....(2)}$$

Where C_i: was the initial concentration of HM before adsorption (mg/L),

C_e: Is the equilibrium concentration of HM in solution after adsorption (mg/L), V was the volume of the solution (L) and W was the weight of biosorbent added (g).The adsorption data where then fitted to the Langmuir or Freundlich isotherm models

Adsorption isotherm

A-Langmuir isotherm: The Langmuir equation assumes homogeneous adsorption where the sorption activation energy is equal for each molecule on the surface. The linear form of Langmuir isotherm is represented by equation 3 (Langmuir 1916).

$$\frac{1}{q_e} = \frac{1}{q_m k_l C_e} + \frac{1}{q_m} \text{ .... (3)}$$

Where qe (mg/g) is the amount of adsorbate per unit weight of adsorbent, Ce (mg/L) is the concentration of heavy metals in solution at equilibrium, KL (L/g) is the Langmuir equilibrium constant and qm (mg/g) is the maximum capacity of adsorbed onto the adsorbent as a monolayer.

B-Freundlich isotherm: The freundlich adsorption isotherm assumes adsorption to heterogeneous surfaces where the linear form of this isotherm is expressed as (Freundlich 1906):

$$Log q_e = \log k_f + \frac{1}{n} \log C_e$$

Where KF (L/g) is the Freundlich constant, n (g/L) is the Freundlich exponent.

RESULTS AND DISCUSSION

Effect of contact time on HM adsorption

The adsorption of both Cr and Mn increased with contact time (Figure 1). For all three wastes, the greatest HM removal was obtained at 100 min .and there after the percentage HM removal remained constant at after 100 min (Figure 1). This was attributed to equilibrium being reached and 100 mins was thus sufficient time to allow full interaction of all biosorbent adsorption sites, with metal ions Kumar et al. (2008). Thus the available sites became saturated and no further adsorption was possible. This result agreed with many previous studies. For example, Ardali et al. (2014) showed that the removal of Cu from industrial waste leachate using expanded Perlite increased with contact time Ardali et al. (2014). Likewise, Orodu et al. (2014) also found that the adsorption of both Cd and Fe *via* snail shell powder increased with contact time Orodu et al. (2014). Koçyiğit and Şahin (2017) found that the adsorption of Pb also increased with contact time. (Koçyiğit and Şahin, 2017) and the same result was observed by Arunlertaree et al. (2007) during removal of Pb from battery manufacturing wastewater by eggshell Arunlertaree et al. (2007). Abdul-Raheim et al. (2015) found that the removal of Pb, Cu, and Ni *via* a modified starch iron oxide nanocomposites increased as the contact time increased until equilibrium was reached at 60 min Abdul-Raheim et al. (2015). Ahirwar et al. (2017) found that the removal of Cu *via* potato peel increased with contact time Ahirwar et al. (2017). Kanyal and Bhatt (2015) found that the uptake of Cu and Pb *via* chicken eggshells, Banana peels, and Pumpkins increased with contact time (Kanyal and Bhatt, 2015).

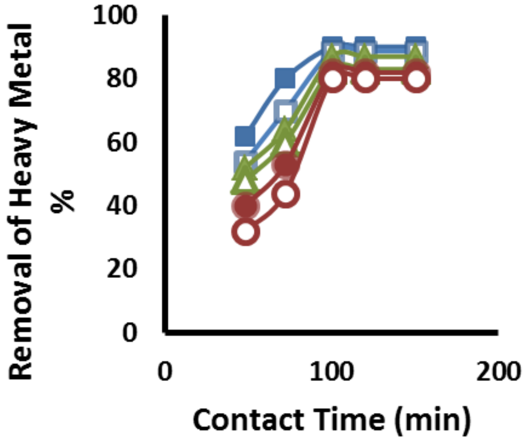

Figure 1. Variation in Cr and Mn removal efficiency (%) with contact time using eggshell, potato peel and tea waste biosorbents at an initial dose of 0.3 g and a solution PH=7. **Note:** (—■—) tea waste , Cr, (—□—) tea waste, Mn, (—▲—) potato peel , Cr, (—△—) potato peel, Mr, (—●—) egg shell, Cr, (—○—) egg shell, Cr.

Effect of solution pH on HM adsorption

Metal speciation can also control adsorbent efficiency by effecting the association between active functional sites on the adsorbent and the metal ion Azouaou et al. (2010). Likewise pH can also affect adsorption because [H+] increases at lower pH and can thus compete with HM cations for the active sites of the biosorbent, leading to reduced removal of HMs (i.e. increased HM release) under excessive acidic conditions (Nuhoglu and Oguz, 2003). Similar increases in HM adsorption with pH have been observed in previous studies. Ardali et al. (2014) found that the removal of Cu from industrial waste leachate using expanded Perlite increased as pH increased Ardali et al. (2014). Likewise, Aslan et al. (2016) found that the adsorption of Ni (II) and Cu (II) using tea leaf waste increased with pH Aslan et al. (2016). Ghasemi et al. (2016), found that Cd adsorption using tea leaf waste increased with pH Ghasemi et al. (2016). Orodu et al. (2014) found that the adsorption of Cd and Fe by snail shell powder increased with pH Orodu et al. (2014). When using eggshell, Koçyiğit and Şahin (2017) found that the adsorption of Pb^{2+} increased with pH (Koçyiğit and Şahin, 2017). In agreement with this current study Arunlertaree et al. (2007) also observed that the removal of Pb from battery manufacturing wastewater by eggshell increased with pH. Rohaizar et al. (2013) also observed increases removal of Cu from wastewater using chicken eggshell as pH increased Rohaizar et al. (2013). Abdul-Raheim et al. (2015) used a modified starch iron oxide nanocomposites and found that the removal of Pb, Cu, Ni increased with pH Abdul-Raheim et al. (2015). In agreement with the current study, Anuja (2015) found that the uptake of Cu and Pb when using chicken eggshells, Banana peels, and Pumpkins all increased with pH (Kanyal and Bhatt, 2015).

The effect of biosorbent dose on HM adsorption

Heavy metal adsorption increased with biosorbent dose (Figure 2). The greatest HM removal was observed at a dose of 0.3 g of tea waste (Table 1). The increase in HM removal with increasing biosorbent dose was attributed to increases in adsorbent surface area and the greater availability of more active binding sites (Lewinsky 2007; Das and Mondal 2011). This result was not unexpected and was in agreement with many previous studies. Ardali et al. found that Cu removal from industrial waste leachate increased with the dose of the expanded Perlite biosorbent Ardali et al. (2014). Ghasemi found that Cd adsorption increased with the dose of biosorbent tea waste Ghasemi et al. (2016). Koçyiğit and Şahin (2017) found that Pb adsorption increased with dose when using eggshell as a biosorbent (Koçyiğit and Şahin, 2017). The same result was also observed for the removal of Pb from battery manufacturing wastewater using eggshell Arunlertaree et al. (2007). Bharti et al. (2017) found that the removal of Cu using potato peel also increased with biosorbent dose Bharti et al. (2017). Abdulsalam (2014) found that the uptake of Cr from tannery waste increased with biosorbent dose when using two novel agricultural products (Abdulsalam, 2014).

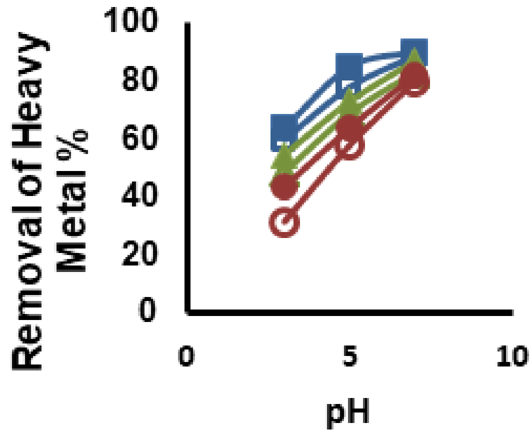

Figure 2. Variation in Cr and Mn removal efficiency (%) with pH using egg shell, potato peel and tea waste) at an initial dose of 0.3 g and a contact time of 100 min. **Note:** (—■—) tea waste , Cr, (—□—) tea waste, Mn, (—▲—) potato peel , Cr, (—△—) potato peel, Mr, (—●—) egg shell, Cr, (—○—) egg shell, Cr.

Table 1. Properties of biosorbent.

Biosorbent	Carbon percentage		Mean pore volume (cm^3/g)
Tea waste	Carbon hydrate %	1.3 (Al-Malik and Al-Masoudi)	0.004 (Jirawan and Doungkamon)
Potato peel	Carbon hydrate %	68.7 (Arapoglou,2010)	0.002 Osman et al.
Egg shell	Caco3 %	96.48 Arunlertaree et al.	0.015 Bansal et al.

Of the three biosorbents considered here, the best biosorbent was consistently tea waste, followed by potato peel and finally eggshell. This variation in removal efficacy was attributed to the variation in the properties of biosorbent which as discussed below had a significant effect on the ability of the materials to adsorb HMs.

One important parameter of the biosorbent is the pore volume since previous studies had shown that ability of a biosorbent to adsorb HMs increased with increasing mean pore volume Mangun et al. (1998). This was also supported by the results obtained here, were as the mean pore volume (cm^3/g) decreased from tea waste to potato peel to eggshell (Table 2) the observed HM removal increased. Likewise the carbonate content of the biosorbents also seemed to be an important parameter since previous studies have shown that as the carbon content increased the hardness of the metal increased Wang et al.(2019) and as the hardness increased the porosity decreased (Jang and Matsubara, 2005) leading indirectly to decreased ability of the biosorbent to adsorb HMs. Thus in agreement with this trend as carbonate content increased from tea waste to potatoes peel to eggshell (Table 2), the observed HM removal decreased. Irrespective of the biosorbent used Cr was consistently adsorbed more than Mn (Figures 1-3). This was attributed to the most positive metal/surface area will interact more strongly to the biosorbents because of biosorbent charge is negative, and Cr would be +3 charged compared to Mn being only +2 . Also Cr (III) is most reactive in the activation of C–H and O–H bonds, because Cr–O relativity long due to the strongly binding of chromium bonds Jaeheung et al. (2011) .The superoxo ligands are bound in a side-on fashion to the chromium centers and are capable of reacting with weak O−H bonds.(Marie-Louise Wind, 2019)M. Unlike most of the other transition metal-oxygen adducts with chromium can be handled at room temperature even under air-free (Susannah Lesley Scot, 1991). So Cr can make chemical bonds with oxygen function group better than MN.

Tea waste biosorbent absorbed Cr more suitable under Langmuir isotherm because the langmuir model predicts the formation of an adsorbed solute monolayer, with no side interactions between the adsorbed ions. It also assumes that the interactions take place by adsorption of one ion per binding site and that the sorbent surface is homogeneous and contains only one type of binding site (Fourest and Volesky, 1996; Wallace et al. (2003). Egg shell absorbed Mn fits more suitable under freundlich isotherm because The Freundlich model does not predict surface saturation. It considers the existence of a multilayered structure (Fourest and Volesky, 1996; Wallace et al. (2003).

Table 2. Best fit parameters for adsorption of Cr and Mn to the Langmuir and Freundlich isotherms for three bio sorbents.

Adsorbent	**Egg shell**		**Potato peel**		**Tea waste**	
Heavy metal	Mn	Cr	Mn	Cr	Mn	Cr
Langmuir Isotherm						
Qmax (mg/g)	21.22	28.25	20.01	30.08	17.28	33.26
K_L	0.0716	0.0599	0.0940	0.0822	0.1820	0.1016
R^2	0.994	0.999	0.992	0.998	0.991	0.977
Freundlich Isotherm						
1/n	0.7432	0.7846	0.7195	0.7423	0.6360	0.6679
K_F	1.581	1.739	1.870	2.484	2.725	3.397
R^2	0.998	0.998	0.996	0.974	0.999	0.865

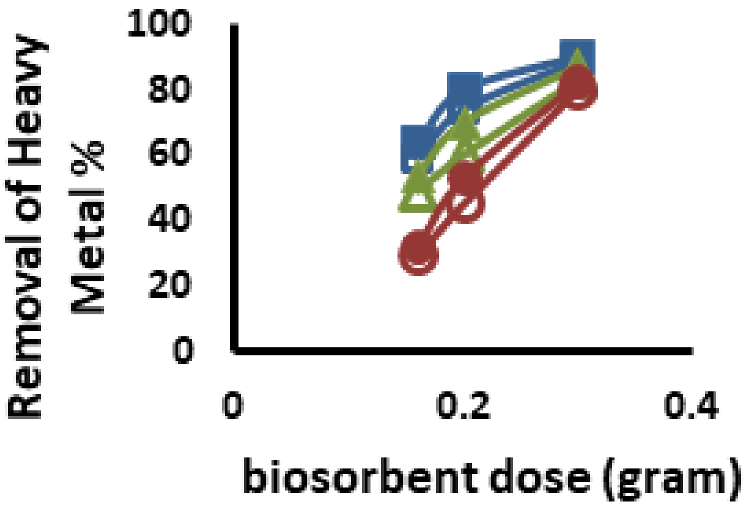

Figure 3. Variation in Cr and Mn removal efficiency (%) with biosorbent dose using egg shell, potato peel and tea waste at pH=7 and contact time of 100 min. **Note:** ( ) tea waste , Cr, ( ) tea waste, Mn, ( ) potato peel , Cr, ( ) potato peel, Mr, ( ) egg shell, Cr, ( ) egg shell, Cr.

CONCLUSION

This study indicated that waste foods like eggshell, potato peels, and tea waste could all be used as inexpensive, eco-friendly biosorbents for the removal of HMs from wastewater. The three main factors that affected the adsorption of such HMs were wastewater pH, the adsorbent dose, and the contact time. Removal was favored by an increased adsorbent dose, a long contact time (>100 min) and a more alkaline pH. Tea waste, was generally the best biosorbent for Cr, being better then both potato peel or eggshell. The less efficient HM removal by eggshell was due to the wastes innate physiochemical properties such as carbon content induced porosity changes and pore volume. As carbon content increased, hardness increased, leading to decreased porosity which in turn led to less efficient adsorption. On the other hand as pore volume increased the ability of the biosorbent to adsorb HMs also increased. Overall, irrespective of the biosorbent used Cr was adsorbed more than Mn because chromium charge more positive than manganese that lead to strongly interact to the biosorbents which have negative charge also because Cr makes chemical bonds with oxygen strongly than Mn. The result fits with lungmuir and freundlich isotherm and it is more suitable with lungmuir when tea waste adsorbed Cr and the results fits more suitable under freundlich when egg shell absorbed Mn.

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