Pol. J. Environ. Stud. Vol. 28, No. 1 (2019), 337-341
DOI: *10.15244/pjoes/81268* ONLINE PUBLICATION DATE: 2018-08-01

Original Research

Reverse Osmosis Removal of Heavy Metals from Wastewater Effluents Using Biowaste Materials Pretreatment

Bashkim S. Thaçi[1], Salih T. Gashi[2]*

[1]University of Prishtina, Department of Chemistry, Republic of Kosova
[2]Academy of Sciences and Arts of Kosova, Republic of Kosova

Received: 28 September 2017
Accepted: 17 December 2017

Abstract

The objective of this paper was to investigate the applicability of using biowaste materials prior to reverse osmosis treatment of water and wastewater effluents. The physico chemical properties of wheat bran, maize cob, and olive waste, and adsorption parameters such as metal concentration, adsorbent dose, contact time, and temperature of Cd(II) onto wheat bran are presented. The optimal parameters achieved in these experiment were used for sorptive removal of metal ions (Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}) from synthetic aqueous solution as well as from wastewater effluents of the mining flotation process. At short pretreatment time, retentate of sufficient concentration was achieved with above biosorbents for further treatment. It is used as feed for reverse osmosis tests. The high removal efficiency of metal ions from synthetic as well as wastewater samples was obtained with low-pressure heterogeneous asymmetric reverse osmosis membranes almost completely by this process.

Keywords: adsorption, biosorbents, heavy metals, pretreatment, reverse osmosis

Introduction

The rapid increase in industrial activities during the last decades has caused severe changes in the environment. This development has led to contamination of water resources with toxic contaminants such as heavy metals nutrient ions and dyes. Mining, mineral processing, and metallurgical operations (electroplating units, alloy manufacturing, etc.) generate a considerable amount of polluted water containing toxic heavy metals, which are almost persistent and non-degradable in nature, and which in turn cause adverse effects in the environment. Therefore, the treatment of these wastewaters becomes necessary before being discharged into the environment and river water streams, respectively. Several conventional methods (e.g., chemical precipitation, coagulation, sedimentation, adsorption, reduction, oxidation, solvent extraction, electrolytic extraction, evaporation, ion exchange, dialysis/electrodialysis, membrane processes, etc.) have been used to achieve effective and rapid removal of these environmental contaminants – particularly metal ions because of their toxic nature and high production cost, and limited or decreasing availability of metal deposits [1-2].

However, some of these techniques have constrains on their application, such as the high operating cost, energy-intensive use hazardous chemicals, and

*e-mail: salihtg@yahoo.com

generating disposal of residual metal sludge, which can be a source of secondary contamination. On the contrary, sorption using biosorbents and biochars has seen significant advancement and is a promising technology for recovering heavy metals from water and wastewaters with subsequent recovery from them. A wide variety of biomaterials has been identified and examined extensively to generate low-cost sorbents for the treatment of water and wastewater such as peels of various fruits and vegetables, and bio-wastes from agricultural and industrial by-products like the production of cereals, rice husks, waste coffee, waste tea, sugar beet pulp, fungi, algae, etc.

Wheat bran was used as an adsorbent for removal of Pb(II) from wastewater [3], while waste olive cake, maize cob, and corn cob have been used for adsorption of Zn(II), Ni(II), Mn(II), and Cd(II) from aqueous solutions, respectively [4-8]. They were established as a potent adsorbent for heavy metal removal due to their good performance and large available quantities and excellent resources for environmental production purposes [9-11]. The performance of an aromatic polyamide (ES20) ultra-low-pressure reverse osmosis membrane for separating divalent (Cu^{2+}), (Ni^{2+}) and hexavalent (Cr^{6+}) heavy metals from bulk solution was investigated. The rejection of heavy metals was found to be greater than 95% for tested membranes [12].

Synthetic wastewater samples containing Cu^{2+} and Cd^{2+} ions at various concentrations subjected to treatment by RO and NF in a laboratory showed high removal efficiency of the heavy metals. Thus by RO process we achieved (98% and 99% for Cu^{2+} and Cd^{2+}, respectively). However, NF was capable of removing Cu^{2+} more than 90% of the time. The effectiveness of RO and NF membranes in treating wastewater containing more than one heavy metal was also investigated [13].

There is data about removing particular heavy metal ions by separate methods, but not much data about their combination exists. This paper aimed to represent the applicability of biowaste materials in natural form and their use in the pretreatment process before reverse osmosis treatment of water and wastewaters containing heavy metals.

Material and Methods

The materials wheat bran, maize cob, and olive waste were washed with distilled water and dried (80°C) for 20 hours. The dried samples were saved (0.1 mesh), and fractions of >0.2 mm were used for experiments. The adsorbents used for examination of mineral content were prepared as follows: 1 g of dry adsorbents were burnt in a porcelain flask and the remaining ash was treated with aqua regia to dissolve the heavy metals (Tables 1-2). The stock solution of reagent grade $PbCl_2$, $CdCl_2xH_2O$, $NiSO_4x7H_2O$, $ZnCl_2$, $MnSO_4xH_2O$, and $Co(NO_3)_2x6H_2O$ at a 30 mg/dm^3 concentration was used in all experimental runs. The 5 g of above adsorbents

Table 1. Mass of adsorbents before and after ignition.

Adsorbents	Mass (mg)	Mass of ash after ignition (mg)
Wheat bran dm	1000	78.14
Olive waste “	1000	69.76
Maize cob “	1000	84.80

Dm = dry matter

Table 2. Metal content derived from adsorbent ash material.

Elements	Olive waste (mg/g)	Wheat bran (mg/g)	Maize cob (mg/g)
K am	3.577	18.34	23.49
Mg “	2.856	8.241	3.630
Ca “	2.747	2.684	1.121
Na “	1.234	2.744	2.219
Zn “	1.065	1.516	0.946
Pb “	0.673	0.767	0.731
Mn “	0.088	0.101	0.452
Ni “	<0.5ppb	<0.5ppb	0.976
Cd “	<0.1ppb	<0.1ppb	<0.1ppb
Co “	<0.2 ppb	<0.2 ppb	<0.2 ppb

am = ash material

was equilibrated with the above solution of known concentrations in a stopped Pyrex glass flask at 25°C in a thermostat with a mixer stirring for a 30 min. A rather fast uptake occurs during the first 30 min of the adsorption process, followed by a slower stage as the adsorbed amount of elements reaches its equilibrium value. After that, the suspension was filtered and retentate was used as feed for reverse osmosis experiments. The concentration of metals in feed, after adsorption by sorbents and after reverse osmosis experiments, was analyzed by inductive coupled plasma optical emission spectroscopy (ICP-OS 2100DV). The procedure with an industrial sample from Trepça Mine flotation plants was the same as with synthetic samples.

The amount of adsorbed Cd(II) ions per gram wheat bran at equilibrium, qe (mg/g), and the removal percentage, (% A), were calculated using the following equations:

$$\%A = C_0 - C_e / C_0 \times 100 \quad (1)$$

$$q_e = (C_0 - C_e)V/m \quad (2)$$

…where C_0 and C_e are the initial and equilibrium concentrations of Cd(II), respectively (mg/dm^3); V is the volume of Cd(II) solution (dm^3); and m is the weight of wheat bran used (g). The composition of adsorbents was

Table 3. Metal content in synthetic samples pretreated with biosorbents and treated by heterogeneous reverse osmosis membranes (batch 317) at pressure (1.76 MPa).

	Standard solution (mg/dm^3)	Pretreated with olive waste (mg/dm^3)	Treated with memb. (mg/dm^3)	Pretreated with wheat bran (mg/dm^3)	Treated with memb. (mg/dm^3)	Pretreated with maize cobs (mg/dm^3)	Treated with memb. (mg/dm^3)
Pb	30.41	2.943	0.040	2.778	0.043	3.539	0.032
Cd	30.42	11.70	0.125	18.76	0.114	18.99	0.191
Ni	29.51	11.00	0.195	17.54	0.209	17.36	0.234
Zn	28.93	9.506	0.356	16.33	0.305	17.01	0.416
Mn	30.69	18.68	0.179	21.62	0.138	20.44	0.182
Co	29.23	13.92	0.207	16.91	0.216	17.54	0.273
pH	5.75	5.20	6.10	5.30	6.10	5.20	6.00

examined by an FTIR spectrophotometer (Shimadzu, FTIR 8400 S with KBr disc).

The retentate of biosorbent pretreatment was subjected to heterogeneous (cellulose acetate-coal) asymmetric reverse osmosis membranes (batch 317). The reverse osmosis film details and experimental reverse osmosis procedure is described elsewhere [14].

Results and Discussion

The wheat bran, maize cob, and olive waste were used as adsorbents in this study. Their characteristics and optimization factors influenced efficiency of heavy metal removal from water and wastewater as well as their use in the pretreatment step before reverse osmosis treatments are discussed.

Characterizing Biosorbents

The properties of materials used in the adsorption test are given in Tables 1-2. The presented results give different adsorbent contents of ash material and their mineral content in it. Mineral content – namely K, Na, and Mg – is higher in wheat bran and maize cob, while Ca is lowest in maize cobs and the contents of heavy metals Pb, Zn, Mn, and Ni, are higher in wheat bran and maize cob.

The spectra of adsorbents (wheat bran, maize cob, and olive waste) used in this paper recorded by FTIR spectroscopy are shown in Fig. 1. From the FTIR spectra it could be seen that there is a large number of functional groups characteristic for biosorbent used. Some major functional groups that predominate on the surface of resulting adsorbents are hydroxyl, carbonyl, aromatic ring, and amine.

Effect of the Initial Sorbate Concentration and Contact Time

Many adsorbents and many factors contribute to the efficiency of removing heavy metals. A lot of data exists about different adsorbents and methods for rejection of heavy metals from water and wastewater [15-16]. In the present work we examined the effect of initial (Cd^{2+}), concentrations at time intervals, constant adsorbent dose, temperature, and pH.

The experiments were performed at two different initial cadmium concentrations (15.0 and 30mg/dm^3) at time intervals, 25ºC, and pH 5.30 for wheat bran. A rather fast uptake occurs during the first 30 min of the adsorption process, followed by slower stage as the adsorbed amount of elements reaches its equilibrium value and there does not seem to be much benefit from a stirring time longer than 30 min. The equilibrium was independent of initial adsorbate concentration. Therefore, an equilibrium time of 30 min and adsorbate concentration of 30mg/dm^3 was selected for all further experiments.

Pretreatment and Reverse Osmosis Tests

The effects of removal of heavy metals from synthetic sample by biosorbents and heterogeneous asymmetric reverse osmosis membranes (batch 317) are given in Table 3.

It could be seen that synthetic samples containing heavy metals pretreated by biosorbents showed different removal efficiencies for resulting adsorbents and elements at near the same constant initial concentration,

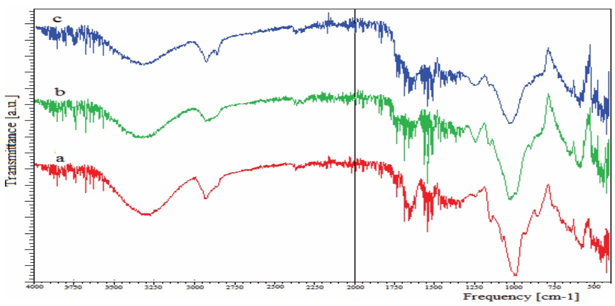

Fig. 1. FTIR spectra of: a) wheat bran, b) maize cobs, c) olive waste.

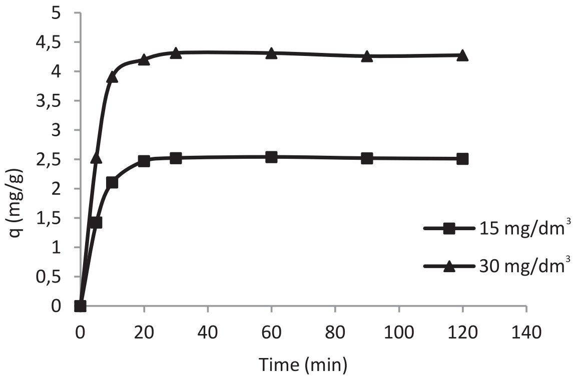

Fig. 2. Adsorption of Cd^{2+} of concentrations of 15.0 mg/dm^3 and 30 mg/dm^3on wheat bran at time intervals constant adsorbent dose, 25ºC, and pH 5.30.

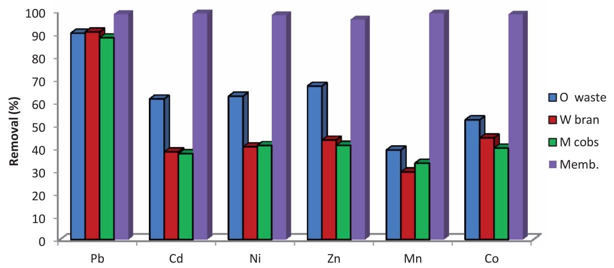

Fig. 3. Removal efficiencies (%) of heavy metal from synthetic sample, pretreated by biosorbents and treated by heterogeneous reverse osmosis membranes (batch 317).

adsorbent dose and contact time, temperature, and pH. The best removal efficiency of ions was achieved by olive waste (in comparison with wheat bran and maize cob) due to different surface areas, adsorption capacities, active sites of pores of adsorbent, nature of the ions, etc. The rejection order of elements was: Pb^{2+} >Zn^{2+} >Ni^{2+} >Cd^{2+} >Co^{2+} >Mn^{2+}. These natural biosorbents contain a large number of functional groups (Fig. 1) that bind target metal ions from aqueous solutions through various processes such as passive electrostatic attraction or ion exchange, adsorption on the surface of adsorbent, surface precipitation/co-precipitation, or surface complexation, respectively [17]. The retentate of synthetic samples was used as feed for reverse osmosis experiments. These data are presented in Fig. 3.

The rejection of heavy metals is found to be 40-90% with biosorbents used in pretreatment step and near completely with low pressure (1.76MPa) heterogeneous asymmetric reverse osmosis membranes (batch 317).

The experimental results of wastewater samples of mine flotation plants (Trepça) conducted under the same conditions as synthetic sample are given in Table 4. The removal of heavy metals from mine flotation plants wastewater effluents (Trepça) for most elements is very high by the used bio-waste materials, which confirms the prediction that the adsorption is a preferable process for low-concentration heavy metals wastewaters [18-19]. The data (Table 4) also show that the rejection of heavy metals from industrial wastewater effluents by reverse osmosis membranes pretreated with resulting adsorbents under experimental conditions used in this study is almost complete (99.8 %).

Conclusions

Biowaste materials (wheat bran, maize cob, and olive waste) are a good source for the adsorption of heavy metals from wastewaters. Their performance data showed that short contact time, pH, and temperature are very convenient for further treatment of industrial wastewaters by reverse osmosis without any agent addition. We also found that the biosorbents used in this study improve the applicability of heterogeneous asymmetric reverse osmosis membranes. They could be feasible and sustainable materials for pretreating wastewater prior to reverse osmosis treatment. The combination of these methods could be of potential use and look promising for complete recovery of heavy metals from water and wastewater, water reclamation, and reuse.

Table 4. Metal content in Trepça Mine flotation plant wastewater effluent samples pretreated with biosorbents and treated by heterogeneous reverse osmosis membranes (batch 317) at pressure (1.76 MPa).

	Feed (mg/dm^3)	Pretreated with olive waste (mg/dm^3)	Treated with memb. (mg/dm^3)	Pretreated with wheat bran (mg/dm^3)	Treated with memb. (mg/dm^3)	Pretreated with maize cobs (mg/dm^3)	Treated with memb. (mg/dm^3)
Pb	0.034	<1ppb	<1ppb	<1ppb	<1ppb	0.009	<1ppb
Cd	0.025	<0.1ppb	<0.1ppb	0.007	<0.1ppb	0.002	<1ppb
Ni	0.004	<0.5ppb	<0.5ppb	<0.5ppb	<0.5ppb	<0.5ppb	<0.5ppb
Zn	0.153	0.024	0.002	0.069	0.002	0.062	0.004
Mn	1.146	1.028	0.006	1.051	0.022	0.871	0.003
Co	0.018	<0.2ppb	<0.2ppb	0.015	0.003	<0.2ppb	<0.2ppb
pH	7.50	6.35	6.12	6.80	5.72	6.94	5.95

Conflict of Interest

The authors declare no conflict of interest.

References

1. DAS N. Recovery of precious metals through biosorption-A rewiev. Hydrometallurgy. **103** (180), **2010**.
2. DODSON J. R., PARKER H., MUNOZGARCIA A., HICKEN A., ASEMAVE K., FARMER TH., HE H., CLARK H. J., HUNT J. A. Bio-derived materials as a green route for precious critical metal recovery and reuse. Green Chemistry. **19** (51), **2015.**
3. YASEMIN B., ZÜBEYDE B. Removal of Pb(II) from wastewater using wheat bran. J of Envir. Man. **78** (2), **2006**.
4. FERNANDO A., MONTEIRO S., PINTO F., MENDES B. Production of biosorbents from waste olive cake and its adsorption characteristics for Zn^{2+} ion. Sustainability. **1** (2) **2009**.
5. MUTHUSAMY P., MURUGAN S., SMITHA M. Removal of nickel ion from industrial waste water using maize Cobs. ISCA J. of Biological Sci. **1** (2), **2012**.
6. HAGHDOOST G., AGHAIE H. Application of corn cob as a natural adsorbent for the removal of Mn(II) ion from aqueous solutions and thermodynamics. Ind. J. of Fund. and Appl. Life Sci. **5** (3), **2015**.
7. MAHMOUD M. A. Thermodynamics and kinetics Studies of Mn(II) Removal from Aqueous solution onto Poweder Corn Cobs. J. Chromatogr. Sep. Tech. **6** (7), **2015**.
8. SINGH K. K., SINGH A. K., HASAN SH. Low cost biosorbent wheat bran for the removal of cadmium from wastewater: Kinetic and equilibrium studies. Biores. Techn. **994** (97), **2006**.
9. WANG J., CHEN C. Biosorbents for heavy metals removal and their future. Biotechn. Advanc. **195** (27), **2009**.
10. RANGBHASHIYAM S., ANU N., SELVARAJU N. Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbent. J of Environ. Chem. Eng. **1** (4), **2013.**
11. FU F., WANG Q. Removal of heavy metal ions from wastewaters; review. J of Environ. Menag. **92** (3), **2011**.
12. OZAKI H., SHARMA K., SAKTAYWIN W. Performance of an ultra low pressure Reverse osmosis membranes for separating heavy metal: effects of interference parameters. Desalination. **144** (1-3), **2002**.
13. QDAIS H. A., MOUSSA H. Removal of heavy metals from waste water by membrane process: A comparative study. Desalination. **162** (2), **2004**.
14. GASHI S. T., DACI N. M., PODVORICA F., SELIMI T., THAÇI B. Effect of the modification time of coal with aryldiazonium salts on performance of cellulose acetate-coal heterogeneous reverse osmosis membranes. Desalination. **240** (1), **2009**.
15. TRIPATHI A., RAJAM M. R. Heavy Metal Removal from Wastewater Using Low cost Adsorbents. J. of Biorem & Biodegrad. **6** (6), **2015**.
16. DEMIRBAS A. Heavy metal adsorption agrobased waste materials, a review. J. Hazard. Mat.**157** (220), **2008**.
17. TAN X., LIU Y., ZENG G., WANG X., HU X., GU Y., YANG Z. Application of biochars for removal of pollutants from aqueous solutions. Chemosphere. **125** (70), **2015**.
18. RAOUF A. M. S., RAHEIM A. R. M., Removal of Heavy metals from Industrial waste water by Biomass-Based, Materials: A Review. J. of Poll. effects & Contra **5** (1), 2017.
19. PARK D., YUN S. J. The past present and future trends of biosorption. Biotechn an Bioprocess Engin. **15** (86), **2010**.