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Biosorbents as Healthy Challenge for the Environment

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ABSTRACT
Contamination of water by heavy metals through the discharge of industrial waste water is a worldwide environmental problem. Different methods for water pollution control are being used, however, adsorption has been found to be superior to other techniques in flexibility and simplicity of design, inexpensiveness, ease of operation and insensitivity to toxic pollutants. Several adsorbents can be used to treat polluted waters, but the success of an adsorption process starts with the choice of an adsorbent. In present article we used waste products and natural low cost products (olive waste, maize cobs, bentonitic clay, wheat bran, coal ash and coffee waste) as adsorbents for removal of iron, cadmium and manganese ions. All untreated adsorbents used showed very good results toward removing of Fe^{2+}, Mn^{2+} and Cd^{2+} ions, however coal ash was most effective by removing of all ions from 97.5 - 99.6%.

KEYWORDS
olive waste, maize cobs, bentonitic clay, wheat bran, coal ash, coffee waste, adsorption,

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Introduction

At one time, clean fresh water supplies were considered inexhaustible. Only recently have we begun to understand that we will probably exhaust our usable water supplies and this can be directly attributed to human abuse in the form of pollution. Now days there are many possible sources of water pollution. It is clear that water pollution should be a concern of every citizen. Progressive increase of industrial and technological development causes various types of pollutants to the environment and human life. Heavy metal pollution is one of these problems. Some of the heavy metals are among the most harmful pollutants.

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Contamination of water by heavy metals through the discharge of industrial waste water is a worldwide environmental problem. Industrial activity alters the natural flow of materials and introduces novel chemical into the environment which effluents contain toxic substances especially heavy metals, dyes, phenols, etc., (Igwe, J.C., *et al.*, 2006). The increase of urbanization affects the rate at which effluents are discharged into the environment, especially water bodies. Most of these effluents contain toxic substances. The presence of these toxic substances in the environment is of major concern because of their toxicity and bioaccumulating tendency (Choudhari, D., et al., 2013). Availability of clean water for different activities is becoming the most challenging assignment for researchers worldwide. For decontamination of polluted waters different methods (adsorption, electrolytic or liquid extraction, electro dialysis, chemical precipitation, membrane filtration) have been developed (Qdais, H.A., & Moussa, H., 2004; Gode, F. & Pehlivan, E. 2005; Low, K.S., *et al.*, 1999; Lacour, S. 2001; Yu, L.J., 2003).

From all methods used for purification of water, adsorption has been found to be superior to other techniques, in flexibility and simplicity of design, ease of operation, inherent low cost, robustness and insensitivity to toxic pollutants (Gupta, V.K., & Ali, I., 2006, 2013; Amit, B., & Minocha, A.K., 2006; Alinnor, I .J., 2007; Jiuhui, Q.U., 2008).

Several adsorbents can be used to treat polluted waters, but the success of an adsorption process starts with the choice of an adsorbent.

Activated carbon has been a popular choice as an adsorbent for long time (Kula, I., et al., 2008; Jamil, A., 2009) but its high cost poses an economical problem. Different authors tried different low cost adsorbents like agricultural materials (Bestani, B., 2008; Girods, P., 2009), clays (Cadena, F., et al., 1990), microbial and plant derived biomass (Sarabjeet, S.A., & Dinesh, G., 2007; Kubilay, Ş., et al., 2007), chitin and zeolites (Moattar, F., & Hayeripour, S., 2004), sawdust (Bryant, P.S., *et al.*, 1992), rice husk (Ajmal, M., *et al.*, 2003), soybean hulls (Marshall, W.E., *et al.*, 1999), sugarcane bagasse (Ayub, S., *et al.*, 2001), perlite (Torab-Mostaedi, M., et al., 2010), etc.

In present study we've analyzed some low cost materials, olive waste, maize cobs, bentonitic clay, wheat bran, coal ash and coffee waste as potential adsorbents for removing of Fe^{2+}, Mn^{2+} and Cd^{2+} ions from standard solutions.

Materials and methods

Adsorbents

The starting materials, maize cobs, wheat bran, and coffee waste were obtained commercially from Kosovo, coal ash was obtained from Thermo Power Plants in Kosovo, bentonitic clay from Vitia, Kosovo while olive waste were obtained from olive oil industry in Ulqin, Montenegro. All the adsorbent used where sieved and dried at 105ºC to a constant weight.

General procedure for adsorption studies

The sorption of Fe^{2+}, Mn^{2+} and Cd^{2+} ions on used adsorbents (olive waste, maize cobs, bentonitic clay, wheat bran, coal ash and coffee waste) was studied using a batch technique. The general method used for this study is described as follows. The stock solution of $FeCl_2$, $MnCl_2$ and $CdCl_2$ at a concentration of 10 mg/L was used in all experimental runs. A known weight of adsorbent (1g and 5g) was equilibrated with Fe^{2+}, Mn^{2+} and Cd^{2+} + solutions of known concentrations in a stopped pyrex glass flask at a fixed temperature in a thermostatic shaker bath (300 rpm) for a known period of time (30 min and 60 min). After equilibration, the suspension was filtered and analyzed with AAS.

Results and Discussion

Treatment of heavy metals, as natural components of the Earth's crust, is of special concern, due to their recalcitrance and persistence in the environment. Considering they cannot be degraded or destroyed a diversity of adsorbents as raw materials is being studied, since these materials are renewable, usually available in large amounts and less expensive than other materials too. Recently there has been increasing interest in studying also natural waste materials that arise from different industries. Double-fold advantage, with respect to environmental pollution, is to use such wastes and to convert them in inexpensive adsorbent for water pollution control. This way a part of waste material could be reduced, and the developed low-cost adsorbents can treat industrial wastewaters at a reasonable cost.

In the last decade, olive oil production has increased and this implies a proportional increase in huge quantities of liquid and solid wastes. Some authors used these solid waste materials as adsorbents for removing of heavy metals (Aziz A, *et al.*, 2009; Babakhouya, N., *et al.*, 2010). Solid residues from corn production such as corn cobs can also be used as raw materials in the production of adsorbents (Arunkumar, C., *et al.*, 2014; Tsai W T, *et al.*, 2001; Haghdoost, G., & Aghaie, H., 2015). Wheat bran, another agricultural waste was studied for its adsorbent properties (Bulut, Y., & Baysal, Z. 2006; Farajzadeh, M.A., & Monji, A.B., 2004). Also natural waste materials that arise from food industry have been used as bioadsorbents, e.g. coffee waste (Kyzas, G.Z., 2012; Djati Utomo, H. & Hunter, K.A. 2006), those that come through various industrial processes, like coal ash (Alinnor, I .J., 2007; Kirk, D.W., *et al.*, 2003) and other natural low cost materials, like bentonitic clays (Kubilay, Ş., *et al.*, 2007; Vega, J.L. *et al.*, 2005).

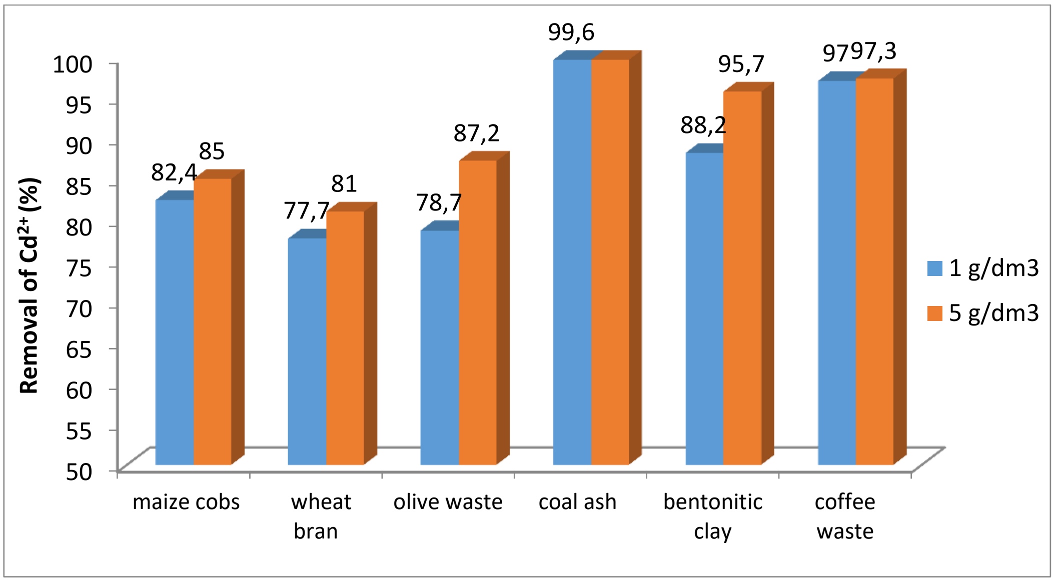
Batch experiments were carried out for the samples with known initial concentration. Table 1 and 2 shows the results of analysis of aqueous solutions of Cd^{2+}, Mn^{2+} and Fe^{2+} before and after treatment with used untreated adsorbents (olive waste, maize cobs, bentonitic clay, wheat bran, coal ash and coffee waste).

Table 1. Concentrations of Cd^{2+}, Mn^{2+} and Fe^{2+} (mg/dm^3) before and after treatment with maize cobs, wheat bran and olive waste.

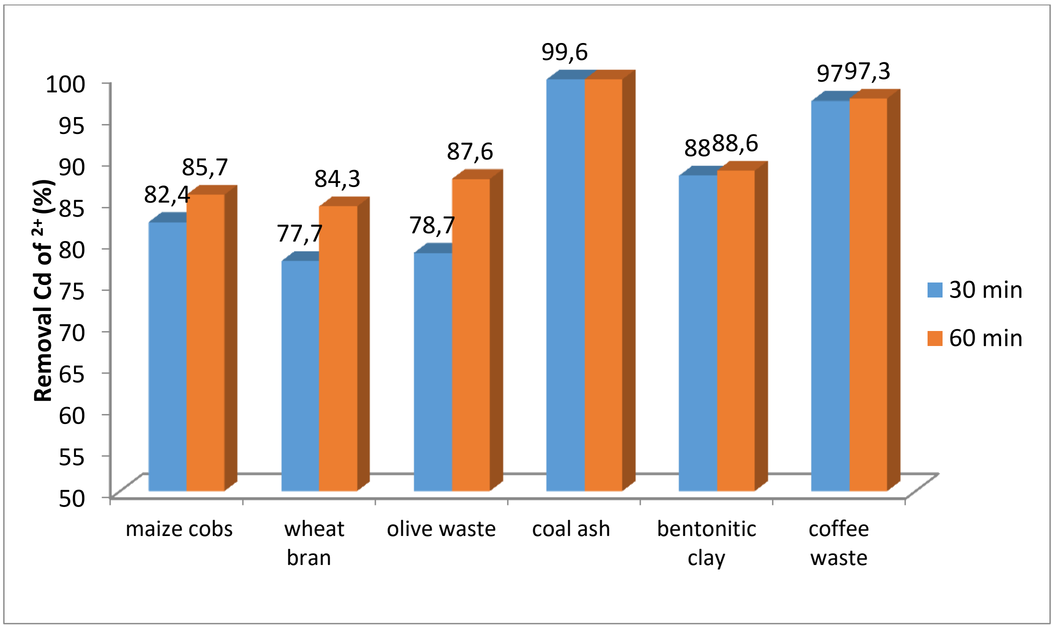
	maize cobs				wheat bran				olive waste			
Time (min)	30	30	60	60	30	30	60	60	30	30	60	60
Adsorbent dosage (g/dm^3)	1	5	1	5	1	5	1	5	1	5	1	5
Conc. of Cd^{2+} before treatment 5.17 (mg/dm^3)												
Conc. of Cd^{2+} after treatment (mg/dm^3)	0.91	0.78	0.74	0.71	1.15	0.98	0.81	0.43	1.10	0.66	0.64	0.52
Removal of Cd^{2+} (%)	82.4	84.9	85.7	86.3	77.7	81.0	84.3	91.7	78.7	87.2	87.6	89.9
pH	5.8	5.5	6.1	6.0	6.2	6.1	6.0	5.8	6.3	6.0	6.0	6.2
EC (μS/cm)	0.00	0.07	0.00	0.07	0.00	0.07	0.02	0.09	0.02	0.12	0.02	0.12
Conc. of Mn^{2+} before treatment 3.07 (mg/dm^3)												
Conc. of Mn^{2+} after treatment (mg/dm^3)	0.91	0.82	0.60	0.31	1.11	1.07	1.04	1.00	1.21	1.04	0.89	0.31
Removal of Mn^{2+} (%)	70.4	73.3	80.5	89.9	63.8	65.2	66.1	67.4	60.5	66.1	71.0	89.9
pH	6.2	5.9	5.8	5.8	5.2	5.2	5.0	5.4	5.9	6.1	5.5	5.4
EC (mS/cm)	0.01	0.07	0.01	0.07	0.00	0.07	0.01	0.07	0.02	0.04	0.02	0.12
Conc. of Fe^{2+} before treatment 3.96 (mg/dm^3)												
Conc. of Fe^{2+} after treatment	1.68	1.52	1.39	1.25	1.49	1.19	0.92	0.77	0.99	0.69	0.5	0.4
Removal of Fe^{2+} (%)	57.6	61.6	64.9	68.4	62.4	69.9	76.7	80.6	75.0	82.6	87.4	89.9
pH	5.7	5.5	5.7	5.7	5.7	5.5	5.7	5.0	5.7	5.5	5.7	5.0
EC (mS/cm)	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01

Table 2. Concentrations of Cd^{2+}, Mn^{2+} and Fe^{2+} (mg/dm^3) before and after treatment with coal ash, bentonitic clay and coffee waste.

	coal ash				bentonitic clay				coffee waste			
Time (min)	30	30	60	60	30	30	60	60	30	30	60	60
Adsorbent dosage (g/dm^3)	1	5	1	5	1	5	1	5	1	5	1	5
Conc. of Cd^{2+} before treatment 5.17 (mg/dm^3)												
Conc. of Cd^{2+} after treatment (mg/dm^3)	0.02	0.02	0.02	0.02	0.61	0.22	0.59	0.20	0.15	0.14	0.14	0.13
Removal of Cd^{2+} (%)	99.6	99.6	99.6	99.6	88.2	95.7	88.6	96.1	97.1	97.3	97.3	97.5
pH	10.5	11.4	9.6	11.6	5.97	6.18	6.30	6.40	6.32	6.50	6.18	6.11
EC (mS/cm)	0.12	1.12	0.23	1.26	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.08
Conc. of Mn^{2+} before treatment 3.07 (mg/dm^3)												
Conc. of Mn^{2+} after treatment (mg/dm^3)	0.16	0.09	0.13	0.06	0.75	0.45	0.38	0.20	0.45	0.31	0.42	0.31
Removal of Mn^{2+} (%)	94.8	97.1	95.8	98.1	75.6	85.3	87.6	93.5	85.3	89.9	86.3	89.9
pH	7.80	8.90	7.40	8.20	4.44	4.33	4.90	4.36	5.05	5.48	5.39	5.58
EC (μS/cm)	0.31	0.61	0.29	0.61	0.04	0.04	0.03	0.03	0.04	0.09	0.04	0.09
Conc. of Fe^{2+} before treatment 3.96 (mg/dm^3)												
Conc. of Fe^{2+} after treatment	0.25	0.13	0.21	0.10	1.19	0.89	0.83	0.79	1.58	1.19	1.19	1.09
Removal of Fe^{2+} (%)	93.7	96.7	94.7	97.5	69.9	77.5	79.0	80.1	60.1	69.9	69.9	72.5
pH	10.1	11.3	8.78	11.3	6.12	6.73	6.10	4.41	5.73	5.21	5.64	5.10
EC (mS/cm)	0.21	1.03	0.18	1.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00



(a)



(b)

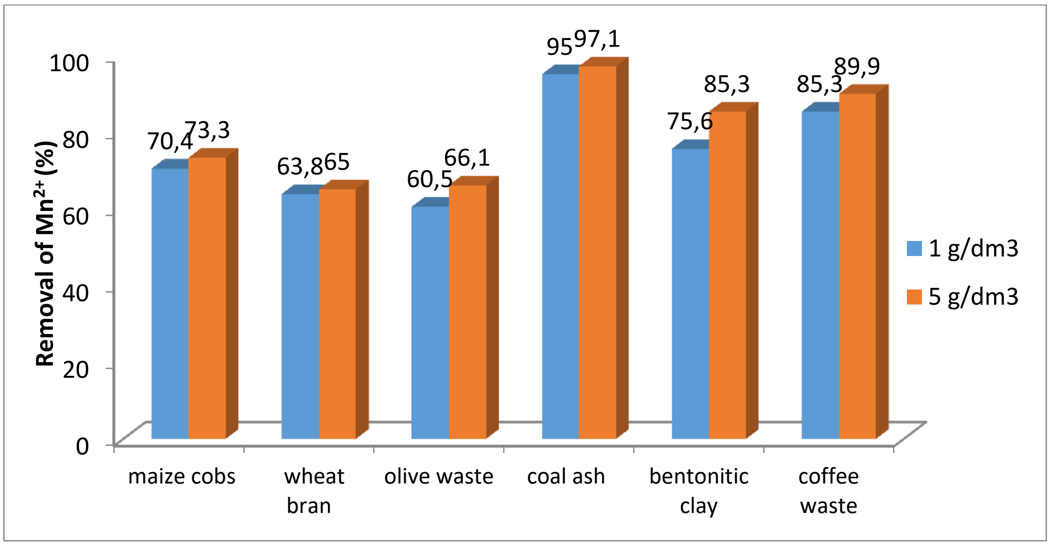
Figure 1. Percentage removal of Cd(II) in dependence from (a) adsorbent dosage, 1g and 5g; and (b) from time, 30 min and 60 min.

Table 1, 2 and Figure 1a presents the effect of adsorbent (olive waste, maize cobs, bentonitic clay, wheat bran, coal ash and coffee waste) dose on the adsorption of Cd2+. Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate. This figure shows percentage of removal of Cd^{2+} ions in dependence of 1g and 5g, respectively, of different untreated adsorbents. As can be seen, all adsorbents showed very good adsorption capacities toward Cd^{2+} ions, starting with wheat bran with lowest adsorption of 81% and coal ash with highest adsorption from 99.6%.

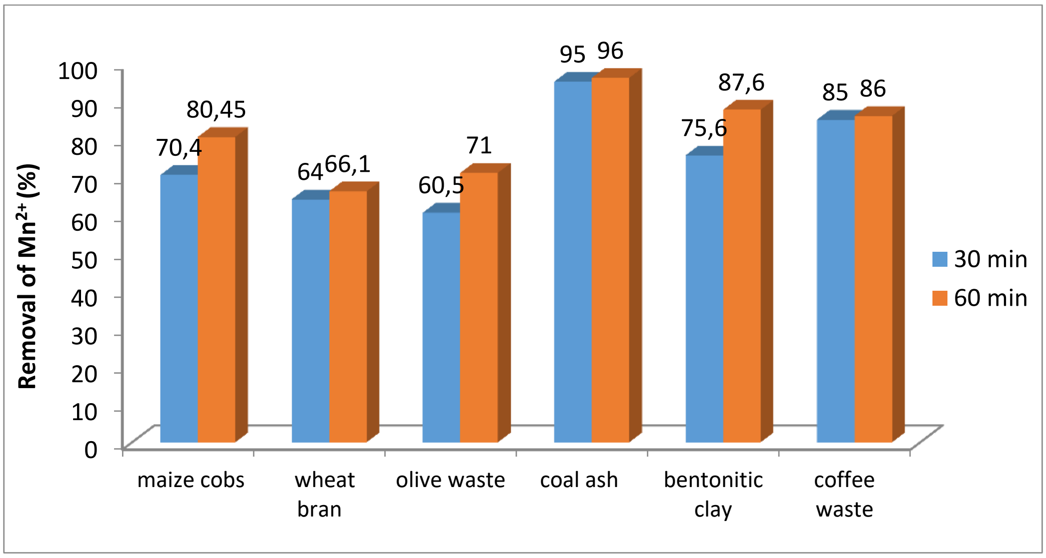
From this figure it can be noted that there is no significant impact in percentage removal of cadmium ions with the increase in adsorbent dosage from 1g to 5g. Slightly greater removal of cadmium is noticed with olive waste 8.5% and bentonitic clay with 7.5% increase, while with other adsorbents the impact was very small. Coal ash and coffee waste demonstrated no effect when adsorbent dosage was increased.

Figure 1b shows the effect of contact time on percentage removal of Cd^{2+}. It was observed that percentage removal slightly increases with contact time. Highest increase in percentage removal in dependence of contact time was observed with olive waste 8.9% and wheat bran 6.6%, while with other adsorbents the effect was very small. Coal ash and coffee waste did not show any effect with increase of contact time.

From these results it can be concluded that the impact of the adsorbent dosage (1 and 5 g/dm3) and contact time (30 min and 60 min) had more effect on olive wastes and wheat bran; had little effect on maize cob and bentonitic clay and had no effect on coal ash and coffee waste.



(a)

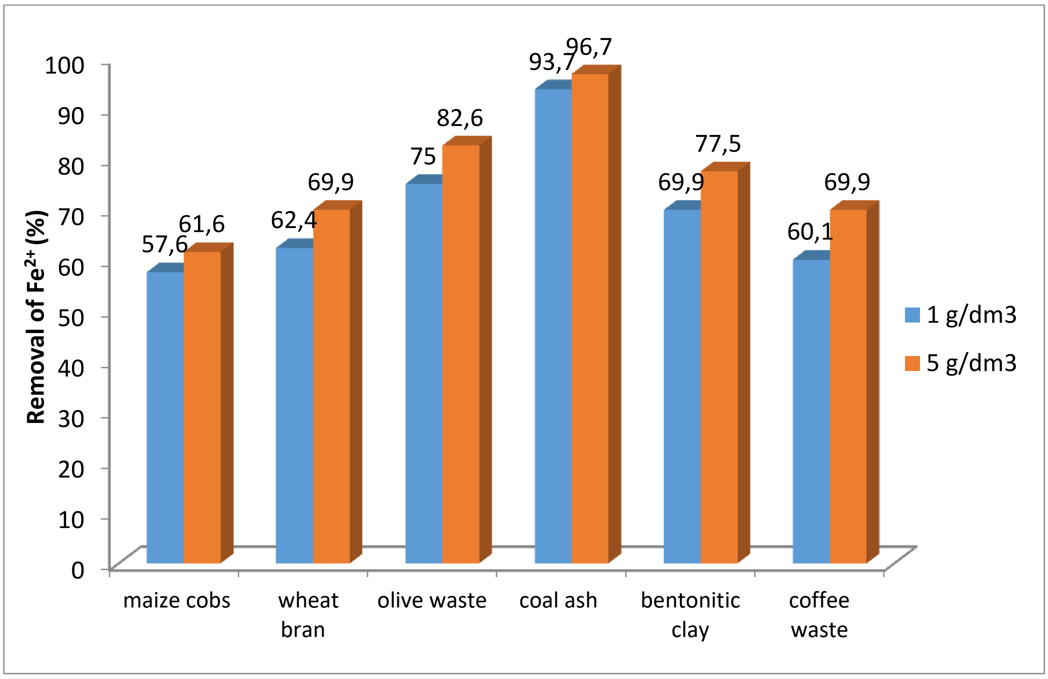


(b)

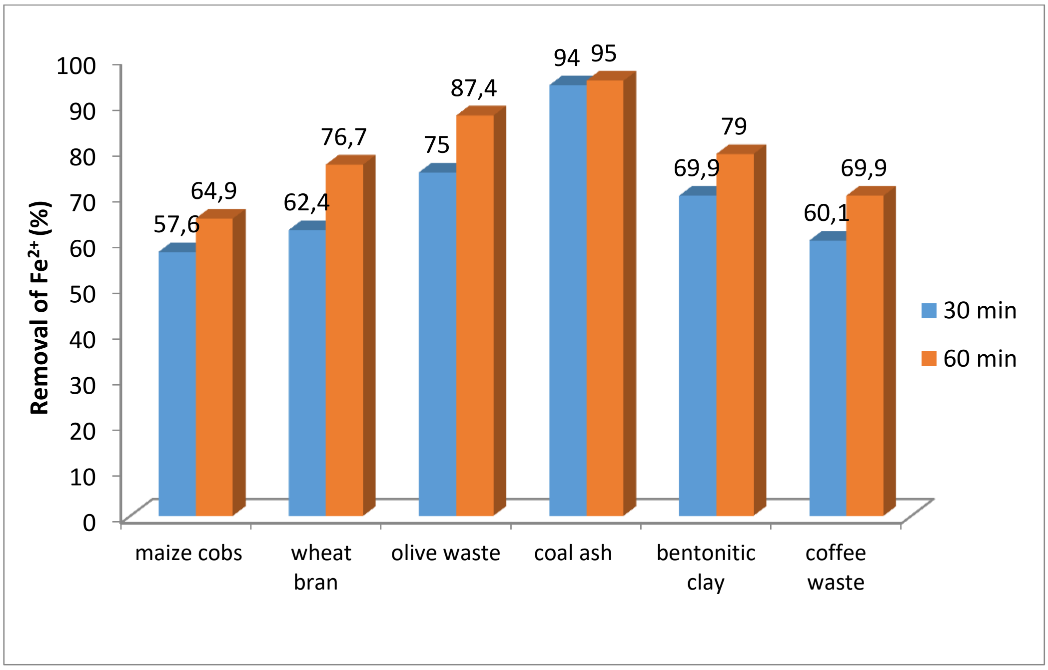
Figure 2. Percentage removal of Mn (II) in dependence from (a) adsorbent dosage, 1g and 5g; and (b) from time, 30 min and 60 min.

Table 1, 2 and Figure 2(a) shows the effect of adsorbent dose (1 and 5 g/dm3 for 30 min) on the adsorption of Mn^{2+} ions. From these results it can be noted that coal ash was best adsorbent for removal of Mn^{2+} ions with 97.1% of removal while lowest removal was with olive waste, 60.5%. Increasing adsorbent dose from 1g to 5g didn't have big effect on removing of Mn^{2+} ions. Adsorption on bentonitic clay was increased for 9.6%, on olive waste for 5.6% while with wheat bran increasing in percentage removal was 4.6%. Other adsorbents showed small increase for fivefold increase in adsorbent dosage, while wheat bran showed smallest effect in percentage removal of Mn^{2+} ions with 1.4% increase.

The effect of contact time on percentage removal of Mn^{2+} is shown in Figure 2(b). It was observed that increasing contact time from 30 min to 60 min had more effect on percentage removal of Mn^{2+} than it did with Cd^{2+}. Highest increase in percentage removal was observed with bentonitic clay, with total increase from 12%, with olive waste 10.5% and maize cob with 10.1%. Wheat bran and coffee waste had very small effect in percentage removal of Mn^{2+} ions in dependence of contact time, while coal ash almost had no effect at all.



(a)



(b)

Figure 3. Percentage removal of Fe (II) in dependence from (a) adsorbent dosage, 1g and 5g; and (b) from time, 30 min and 60 min.

Table 1, 2 and Figure 3(a) and 3(b) shows percentage removal of Fe^{2+} ions from all used adsorbents. Figure 3(a) shows results of percentage removal of Fe^{2+} after treatment with all adsorbents with dosage of 1g and 5g for 30 min of contact time. From achieved results it can be seen that removal of Fe^{2+} ions was most effective with coal ash with total removal of 96.7%.

Increasing adsorbent dosage, from 1g to 5g, had most effect in coffee waste, increasing percentage removal for 9.8%, while it had same effect on bentonitic clay and olive waste with total increase of 7.6%. Smaller impact was noted with other used adsorbents.

Percentage removal of Fe^{2+} ions, in dependence from increasing contact time from 30 min to 60 min, Figure 3(b), was higher than for other metals. Increasing contact time had most effect on wheat bran with total increase of 14.3%, than on coffee waste with 9.8%, while on other adsorbents had smaller effect. Coal ash showed smallest effect in percentage removal in dependence of contact time with total increase from 1%.

Form these figures (3a and 3b) we can conclude that adsorbent dosage and contact time had more effect on removing of Fe^{2+} ions than it did for Cd^{2+} and Mn^{2+} ions.

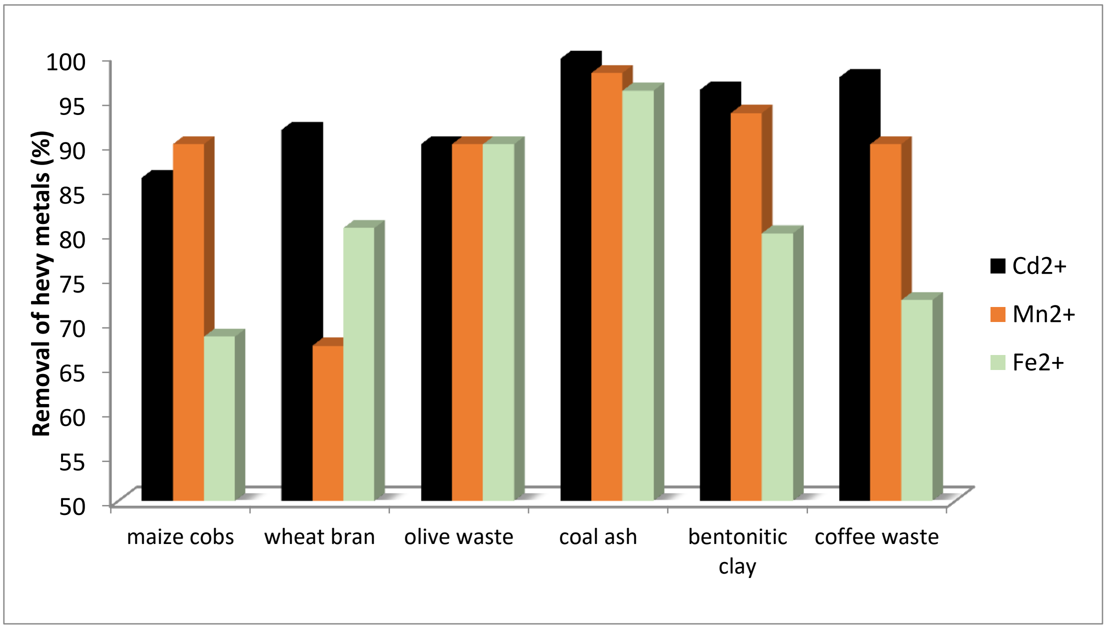


Figure 4. Percentage removal of Cd^{2+}, Mn^{2+} and Fe^{2+} ions by all used adsorbents.

Results on percentage removal of Cd^{2+}, Mn^{2+} and Fe^{2+} ions by all used adsorbents (olive waste, maize cobs, bentonitic clay, wheat bran, coal ash and coffee waste) are given in Figure 4. It can be noted that different adsorbents have different adsorption capacities toward heavy metal ions. Maize cob most adsorbed Mn^{2+} ions with 89.9% of total removal than Cd^{2+} ions with 86.3% of removal and last Fe^{2+} ions with 68.4% of total removal. Wheat bran was more effective on removal of Cd^{2+} ions with 91.7% removal, than Fe^{2+} ions with 80.6% removal and was least effective on removal of Mn^{2+} ions with 67.4% of total removal. Coal ash was more effective on removing Cd^{2+} ions, 99.6%, than Mn^{2+} ions, 98.1% and least effective on removing Fe^{2+} ions with 97.5% of total removal. Same aligning was noted with coffee waste and bentonitic clay, while olive waste showed same percentage removal for all three metal ions, from 90% of total removal.

Conclusion

The present study shows that all adsorbents used were an effectual biosorbents for removal of Cd^{2+}, Mn^{2+} and Fe^{2+} ions from aqueous solution. Maize cob most adsorbed Mn^{2+} ions with 89.9% of total removal than Cd^{2+} ions with 86.3% of removal and last Fe^{2+} ions with 68.4% of total removal. Wheat bran was more effective on removal of Cd^{2+} ions with 91.7% removal, than Fe^{2+} ions with 80.6% removal and was least effective on removal of Mn^{2+} ions with 67.4% of total removal. Coal ash was more effective on removing Cd^{2+} ions, 99.6%, than Mn^{2+} ions, 98.1% and least effective on removing Fe^{2+} ions with 97.5% of total removal. Same aligning was noted with coffee waste and bentonitic clay. Olive waste showed same percentage removal for all three metal ions, from 90% of total removal. For all adsorbent used, adsorbent dosage and contact time did not have significant impact in their adsorption capacities. Using low cost adsorbents are with double-fold advantage, with respect to environmental pollution, is to use such wastes and to convert them in inexpensive adsorbent for water pollution control.

Disclosure statement

The authors declare that there are no competing interests regarding the publication of this paper.

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