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REGULAR ARTICLE

USAGE OF SOME AGRICULTURAL BY-PRODUCTS IN THE REMOVAL OF SOME HEAVY METALS FROM INDUSTRIAL WASTEWATER

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SUMMARY

Adsorption experiments were carried out using different biosorbent to adsorb some heavy metals from wastewater samples (industrial and domestic wastewater). In this work four agricultural residues rice hull, sawdust, sugarcane bagasse and wheat straw were examined as sorbent to remove Zn (II), Cd (II) and Fe (II) from wastewater samples. To modify their sorptive characteristics sorbents were treated with 0.1 M HNO_3. Batch adsorption studies show that the modified rice hull and sawdust show a great ability for extracting metallic ions from wastewater samples as compared with the other sorbents. Sorption capacity of modified rice hull was significantly, in most cases, higher than the modified sawdust. In general, treated sawdust and rice hull sorbed the maximum amount of ions in all wastewater samples. In the column procedure, the removal percentage of Zn (II), Cd (II) and Fe (II) by modified rice hull and sawdust was significantly higher than the removal percentage of these metals by batch procedure. The results showed that the rice hull and sawdust were found to be an attractive low cost alternative for the treatment of wastewater. A good efficiency to remove toxic metal ions was achieved by usage of such by-product.

Key words: Sawdust; Rice hull; Sugarcane bagasse; wheat hull; Wastewater; Biosorption
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1. Introduction

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Today, with the rapidly increasing urban population and water resources becoming more scarce, there is a strong need to reconsider our consumption patterns and the way we use our water resources. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Yu, 2005). The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Manaham, 2000 and Yu, 2005). For example, cadmium causes serious renal damage, anemia, hypertension and itai-itai (Friberg etal., 1974). Children may show signs of toxicity with ingestion of 10-20 mg/kg of elemental iron. Serious toxicity is likely with ingestion of more than 60 mg/kg. Toxic effects of iron may occur at doses of 10-20 mg/kg of elemental iron (Jennifer et al., 2009). Although zinc is an essential nutrient as a trace element for animal, plants and microorganisms, it is toxic to these organisms when present at millimolar concentrations. For example, it is toxic for humans if incorporated at levels of 100 – 500 mg / day (Barceloux, 1999).

Developing countries suffer from water pollution; the high costs of contents and treatments make the major problem in these countries. Egypt is located in hyper- arid regions of the world with average rainfall to be about 200 mm (nearly 7.9 inches) at northern coasts (near Alexandria), decreasing as going to south about to be 50-100 mm in the Nile Delta region. Around Cairo it ranges between 10-30 mm, varying from year to year. The treated wastewater represents 10% of water resource which could be used as alternative for using in agricultural. The average treated wastewater production 6.3 million^3 / day it could be increased to 8.3 milion^3/ day in 2017 (MESA).

Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, refining ores, paint and pigments, tanneries, chloralkali, sludge disposal, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. (Kadirvelu et al., 2001). The conventional methods used to remove toxic metals from aqueous effluents include membrane filtration (Molinari et al, 2004), chemical precipitation (Manaham, 2000), ion exchange (Gode and Pehlivan, 2006), and adsorption (Hu et al., 2003). In the major part of cases the use of these methods in the remediation processes is precluded due to high costs involved (Babel and Kurniawan, 2003). Conventional methods for the removal of heavy metals from wastewaters, however, are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/L (Volesky, 2000). For this reason, low cost adsorbents have been evaluated for the removal of heavy metals from aqueous solutions.

Biosorption is a promising technique for the removal of heavy metals from aqueous environments especially when adsorbents are derived from lignocellulosic materials (Coelho et al., 2007). The search for new technologies to remove toxic metals from wastewaters has directed attention to biosorption, which is based on metal binding to various biological materials. Biosorption is a fast and reversible reaction of the heavy metals with biomass. Laszlo and Dintzis (1994) have shown that lignocellulosics have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. Agricultural by-products vary greatly in their ability to remove metals from solution. The ability of biological materials to adsorb metal ions has received considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment at metal concentrations as low as 1 mg/L (Chong and Volesky, 1995).

In recent years, special attention has been focused on the use of natural sorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view (Babel and Kurniawan, 2003) and (Bailey et al., 1999). Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, when these materials the end of their lifetime, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for natural sorbents.

The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste and coffee (Orhan and Buyukgungor, 1993), hazelnut straw (Cimino et al., 2000), peanut hull (Johnson et al., 2002), sawdusts , pinus bark (Vazquez et al., 1994) and different bark samples (Seki et al.,1997), coconut husk (Babarinde, 2002) , Ponkan mandarin peels (Pavan et al., 2006), modified cellulosic materials (Acemioglu and Alma, 2001), corn cobs (Hawrhorne-Costa et al., 1995) , apple wastes (Maranon and Sastre, 1991), wool fibers (Balkose and Baltacioglu, 1992), tea leaves (Tee and Khan, 1988), banana and orange peels (Annadurai et al., 2002), sugarcane bagasse (Khan et al., 2001), papaya wood (Saeed et al., 2005), maize leaf (Babarinde et al., 2006), leaf powder (Hanafiah et al., 2007), grape stalk wastes (Villaescusa et al., 2004) and different agricultural by-products were used and investigated. (Marshall and Champangne, 1995 and Pehlivan et al.,2006)

Objectives in this work were to i) evaluate the most efficient sorbent of four tested low cost sorbents rice hull, sawdust, sugarcane bagasse and wheat straw, ii) study the modification of sorptive properties rice hull and sawdust in order to increase the power of heavy metal removal from wastewater, iii) find out the effectiveness of less expensive material and the best procedure that could be used as sorbent for the removal of Zn^{+2}, Cd^{+2} and Fe^{+2} ions from wastewater.

2. Material and Methods

2.1. Sorbent materials

Dried samples of sawdust, rice hull, sugarcane bagasse and wheat straw were milled and then passed through 1 mm sieve.

2.2.Wastewater Samples

Adequate samples of three wastewater resources were obtained from El-Asher wastewater treatment station (industrial and domestic wastewater) Sharkia governorate; El-Saff wastewater canal; which comes from sewage treatment station (industrial and domestic wastewater) at Helwan governorate; and Zenin station unit (domestic wastewater), Giza governorate, Egypt. The samples were transferred to laboratory in closed bottles and then filtered by Wattman filter paper to remove any suspended materials.

The filtered wastewater was analyzed for E.C., pH, cations and anions and tested heavy metals showed in Table 1. Adequate amounts of filtered samples were kept in fridge for sorption experiments.

2.3. Experimental work

To achieve the aim of this study, two experiments were conducted.

2.3.1. First experiment

To study the effect of two factors: sorbent type and modification on heavy metals removal of El-Saff wastewater. Four types of biosorbents were used: rice hull, sawdust, sugarcane bagasse and wheat straw, and raw biosrbents and modified biosorbents by acid as the four sorbents were treated with 0.1 M HNO_3 for 4 h at room temperature then washed several times with redistilled water. After washing the sorbents under investigation were dried at 100^oC in an oven to reach a constant weight.

2.3.2. Second experiment

To study the effect of modified rice hull and sawdust to adsorb heavy metals from El-Saff ,Al-Asher and Zenin wastewater by using batch and column procedures.

2.3.2.1 Batch sorption procedure

Batch sorption treatment was carried out with ratio 1 g of raw and treated sorbent materials in 100 ml of wastewater samples. The suspensions in all sorption assays were stirred at room temperature for 1 h and then filtered through Wattman filters to remove any suspended adsorbent. Initial and final concentrations of tested heavy metals were determined by atomic absorption spectroscopy (AAS).

2.3.2.2 Column procedure

The column sorption experiment was done in three wastewater samples. The column internal diameter was 15 cm its length was 15cm. The column filled with regenerated sorbents and wastewater samples passed through the column in ratio of 4 gm/100 ml.

The functional groups contributed in raw and modified sawdust and rice hull were determined by Fouier Transform Infrared (FTIR) spectrophotometer.

2.4. Statistical analysis

The experiment was laid out in randomized complete block design with 4 replications. Pooled data subjected to analyses by M-STAT C, (Russell, 1991). The differences among the means were performed by least significant difference (LSD) at 5% level.

3. Results and Discussion

3.1. First experiment

Effect of sorbent type and modification on heavy metals removal of El-Saff wastewater. Data in Table 1 showed that the concentration of Cd and Fe in El-Saff wastewater is higher than the permissible levels of heavy metals whereas the Zn within the standard range according to the Egyptian manual as guidelines for treated wastewater reuse in agriculture (2005).

Table 1. Physical and chemical characters in the tested wastewater samples.

Sites	pH.	E.C.	Cations				Anions				Zn^{+2} (ppm)	Cd^{+2} (ppm)	Fe^{+2} (ppm)
			Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	CO_3^{-2}	HCO_3^{-}	SO_4^{-2}	Cl^{-}			
El-Saff	7.52	1800	93.38	39.12	180	38.12	59	190	120	330	1.50	0.16	26.31
Al-Asher	6.91	1610	79.15	18.11	270	30.12	-	490.2	138	269.09	1.14	0.10	3.10
Zenine	7.62	873	135	30.5	148	29.21	61	90	-	275	1.45	0.13	2.53

N.B. **I)** The standard range according to the Egyptian manual as guidelines for treated wastewater reuse in agriculture were, Zn 5, Cd 0.01, Fe 5 ppm

II) Wastewater quality guidelines for agricultural use according to FAO were, Zn 2, Cd 0.01, Fe 5 ppm

3.1.1. Sorbent types effect

Data in Table 2 show the effect of sorbent types (sawdust, rice hull, sugarcane bagasse & wheat straw) on the adsorption amount (A.A.) and the removal percentage (R%) of Zn, Cd and Fe in El-Saff. The obtained data indicated that the highest significant A.A. and R% were found in rice hull as compared with other tested sorbents.

There was a severe reduction in the final concentrations of Zn, Cd and Fe after application of different sorbents as compared with the initial contents, such reduction varied from sorbent type to another. For example, the removal percentage of Zn were 91.01, 87, 80.32 &73.17 % of rice hull, sawdust, sugarcane bagasse and wheat straw, respectively.

Table 2. Effect of biosorbent type on sorption amount (A.A.) and removal percentage (R %) of Zn, Cd and Fe from El-Saff wastewater.

Biosorbent types	Zn		Cd		Fe	
	A.A.	R%	A.A.	R%	A.A.	R%
Rice Hull	1.3367	91.017	0.137	84.848	25.403	94.667
Sawdust	1.305	87	0.131	82.717	25.023	93.255
Sugar cane	1.207	80.327	0.119	74.072	23.792	88.673
Wheat Hull	1.098	73.172	0.106	66.74	23.003	85.745
L.S.D. 0.05	0.01258	2.016	0.0126	5.749	0.2516	0.9472

In comparison with sorbents (sawdust, rice hull, sugarcane bagasse and wheat straw) the highest sorption capacity of the three tested heavy metals was achieved using rice hull followed by sawdust, sugarcane bagasse and wheat straw in descending order. Difference in sorption of heavy metals by sorbent materials depends probably on the affinity of metal ions for active groups on the substrate.

Crystian et al., (2009) demonstrated that The rice straw is an attractive adsorbent for divalent Cu(II), Zn(II), Cd(II) and Hg(II) removal from aqueous solutions in a very rapid adsorption process. The rice straw demonstrates a great ability for extracting metallic ions from simulated industrial effluent contaminated individually with Cu(II), Zn(II), Cd(II) or Hg(II) solutions. Use of biosorbent in columns for the removal of metallic ions demonstrated high efficiency for industrial effluents contaminated with Cu, Zn, Cd and Hg. the biosorbent displays high removal efficiency towards Cu, Zn, Cd and Hg.

The rice straw is constituted basically by cellulose, hemicellulose, lignin, extractives, water and mineral ash which is in large amount SiO_2. The lignin is promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion (Rafatullah et al., 2009).

While, Sawdust mainly consists of lignin, cellulose, hemicellulose and many hydroxyl groups such as tannins. All those components are active ion exchange compounds. Lignin, the third major component of the wood cell wall is built up from the phenylpropane nucleus; an aromatic ring with a three carbon side chain is promptly available to interact with cationic metal ions (Fatemeh et al., 2008).

3.1.2. Effect of modification sorbent

In order to increase the adsorption capacities of adsorbents, the four tested adsorbents were modified with 0.1 M HNO_3. Table 3 shows that the removal percentage and amount of adsorption of treated sorbents were significantly higher than the untreated materials. For example, the removal percentage of Zn, Cd and Fe in raw material reached 77.34, 69.78 & 86.36 %, respectively, whereas in regenerated material they reached 88.41, 84.30 & 94.81 %, respectively. This could be attributed to impurities of tested adsorbents, which could be removed by regeneration and more exchangeable surface area becoming available.

Table 3. Effect of modification of biosorbent on sorption amount (A.A.) and removal percentage (R %) of Zn, Cd and Fe from El-Saff wastewater.

Treatments	Zn		Cd		Fe	
	AA	R%	AA	R%	AA	R %
Raw (without)	1.161	77.34	0.111	69.78	23.174	86.364
Modified	1.327	88.414	0.136	84.30	25.437	94.811
L.S.D. 0.05	1.0175	2.702	0.0176	8.508	0.9541	3.540

Sciban and Klasnja, (2004) reported that modification processes of agricultural by-product increase adsorption capacity. Active carbon made of rice hull with high specific surface area and sorption capability of amorph SiO_2 is a biological filter in water and wastewater purification. Active carbon of rice hull able to remove of heavy metals as Cd(II) and Pb(II) (Belalaei et al., 1999). Surplus, low value agricultural by-products can be made into granular activated carbons (GACs) which are used in environmental remediation. Oxidized GACs made from soft lignocellulosics such as soybean hull, sugarcane bagasse, peanut shell, and rice straw adsorbed from a mixture higher amounts of Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} than any commercial GACs. Commercial GACs adsorbed only Pb^{2+} $Cu^{2+}$and Cd^{2+}.

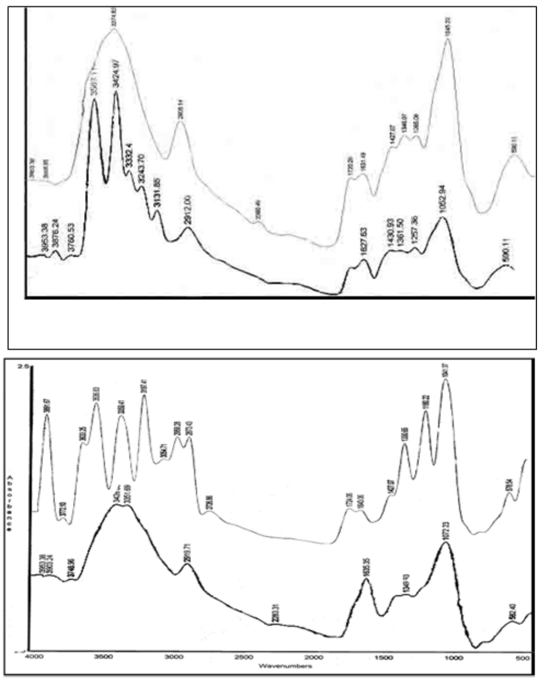

Fig. 1. FTIR spectrum of treated sorbents (rice hull and sawdust) before and after treatment.

N.B. The existence of main shifts through spectra after modification may be reason of sorption.

Results of FTIR showed that, in raw rice hull there is alcoholic group C−OH (3351.69 cm^{-1}) converted into amide group $CONH_2$ (3536.83 cm^{-1}) in modified samples also a new C = O was appeared at 1724.06 cm^{-1} in which it may be aldehyde or ketone or ether group (Figure 1). Whereas, in raw sawdust there was a several picks of amine groups ranged from 3131.70 to 3583.11 cm^{-1} converted to only one broad band at 3374.84 cm^{-1} in modified sawdust (Figure 2). These results explained the superior of rice hull than sawdust due to consequently functional group expose to sorption mechanisms and sorption increased. Although, sites or quantity sorption of heavy metals by such as spectrums is not a realistic indicator but the appearances of new groups and many structural specific changes in sorbents may increase the sorption of heavy metals after acid treatment. These explanations were in agreement with those of (Laszlo and Dintzis, 1994). Gaballah et al., (1993) showed that the main difference was between FTIR spectrums before and after sorption of Cu (II) on tree barks. Some of the bands shifted after Cu (II) sorption.

3.1.3. Interaction effect

The data in Table 4 illustrate the interaction effect of sorbent type and the modification on the adsorbed amount percentage and removal of Zn, Cd and Fe in El-Saff wastewater. The modified rice hull shows the most efficiency in uptake of Zn, Cd and Fe from wastewater as compared with other tested modified sorbents. For example, the removal % of Fe were 98.15, 96.90, 93.00 and 91.19%, of rice hull, sawdust, sugarcane bagasse and wheat straw modified treatment; respectively. These data were in agreement with those of Fatemeh et al., (2008).

Table 4. Interaction effect between types of biosorbents and modification treatment on Zn, Cd and Fe from El-Saff wastewater.

Treatment	Sorbents	Zn		Cd		Fe	
		A.A.	R%	A.A.	R%	A.A.	R%
Raw	Rice Hull	1.297	86.34	0.128	79.053	24.477	91.207
	Sawdust	1.22	81.34	0.123	77.837	24.047	89.607
	Sugar cane	1.147	76.34	0.101	63.783	22.63	84.343
	Wheat Hull	0.98	65.34	0.092	58.447	21.55	80.3
Modified	Rice Hull	1.437	95.69	0.14	79.643	26.33	98.147
	Sawdust	1.39	92.66	0.14	87.197	26 .0	96.903
	Sugar cane	1.267	84.31	0.137	84.36	24 .96	93.003
	Wheat Hull	1.217	81.0	0.120	75.033	24.46	91.19
L.S.D. 0.05		0.01779	2.851	0.0178	8.13	0.3558	1.34

The comparison between four different sorbents indicated that the highest sorption capacity of most heavy metals was observed for the rice hull followed by sawdust (Table 4). The higher sorption capacity of rice hull than the other sorbents for removal of heavy metals is probably due to the presence of silanol (SiOH) groups in structure of rice hull, high Si% and more surface area of rice hull (Fatemeh et al.,2008).

Acid wash inorganic materials such as carbonate and Si from the cell walls of rice hull increases the penetration of N_2 gas to the sorbent surfaces and increases the measured surface area by BET method. Also, the effect in rice hull was more pronounced than sawdust. This may be due to the higher content of organic carbon in sawdust. Because organic materials do not dissolve in acid and their structure is relatively stable with these treatments (Fatemeh et al., 2008).

From the results of the first experiment, it could be concluded that the modified rice hull and sawdust show the great efficiency to remove the three tested heavy metals from El-Saff wastewater.

Naiyaa et al., (2009) in this study rice husk ash used as absorbent for removal of Pb (II) in wastewater from effluent sample from a battery manufacturing unit at Shyamnagar, near Kolkata, India. The batch adsorption study was carried under optimum conditions of pH 5, contact time 1 h and adsorbent dosage level of 5 g/L. Adsorption of Pb (II) on rice husk ash was found to 96.83%.

3.2. Second experiment

Effect of modified rice hull and sawdust were examined to remove heavy metals from three sources of wastewater (El-Saff, Zenin and Al-Asher) by using both column and batch procedure.

The concentration of heavy metals of the tested wastewater except Fe in El-Saff and Cd in the three tested effluent, is within the standard range of FAO (2000) and Egyptian manual as guidelines for treated wastewater reuse in agriculture (2005). However, decreasing of heavy metals concentration can improve the quality of wastewater hogwash.

3.2.1. Effect of sorbent types

The effect of modified sawdust and rice hull on the adsorption amount and removal percentage of Zn, Cd and Fe ions in the three tested wastewater is shown in Table 5. From the tabulated data it could be noticed that the adsorption amount and removal percentage in treated rice hull are significantly higher than those of the modified sawdust in most cases due to higher content of organic carbon in sawdust (Fatemeh et al., 2008).

Both of biosorbent used in this experiment showed high removal efficiency towards the three tested heavy metals. The modified rice hull and sawdust sorbed the maximum ion metals. For example, the uptakes of Zn (II), Cd (II) and Fe (II) by modified rice hull in Zenin were 96.90, 92.90 and 94.17 %, respectively. Meanwhile, the uptakes of Zn (II), Cd (II) and Fe (II) by modified sawdust were 93.97, 88.27 and 92.93 %, respectively.

Table 5. Effect of rice hull and sawdust on sorption amount (A.A.) and removal Percentage (R %) of Zn, Cd and Fe from El-Saff , Al-Asher and Zenin wastewater.

	Zn		Cd		Fe	
Biosorbent types	R%	AA	R%	AA	R%	AA
			El-Saff			
Rice Hull	97.35	1.45	94.07	0.15	99.80	26.37
Sawdust	95.98	1.44	88.60	0.14	97.00	26.03
L.S.D. 0.05	0.29	0.02	2.26	0.02	0.71	0.04
			Al-Asher			
Rice Hull	94.52	1.08	87.75	0.09	92.27	2.86
Sawdust	90.84	1.04	83.00	0.08	88.76	2.75
L.S.D. 0.05	1.86	0.02	0.62	0.02	1.41	0.11
			Zenin			
Rice Hull	96.90	1.41	92.90	0.12	94.17	2.38
Sawdust	93.97	1.36	88.27	0.12	92.39	2.34
L.S.D. 0.05	1.17	0.02	2.65	0.02	1.92	0.08

Concentrations of Zn (II) and Fe (II) was very high in the tested wastewater, therefore the highest uptake was occurred. Whereas the concentration of Cd is less in polluted water so its uptake is less. For example, the removal percentages of Zn (II), and Fe (II) by modified rice hull in Al-Asher were 94.52 and 92.27 %, respectively. Meanwhile, the removal percentage of Cd (II) was 87.75 %.

In this concern, Rafatullah et al., (2009) stated that the initial metal ion concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the solution and solid phases. Therefore, the amount of metal ions adsorbed was expected to be higher with a higher initial concentration of metal ions

3. 2.2. *Effect of procedure types*

The data in Table 6 revealed that, the removal % of sorbents by using column procedure is significantly higher than batch procedure, this observation held true in the three tested wastewater. For example, in column procedure the uptake of modified sorbents in El- Saff wastewater were 98.15, 93.75 and 97.78 % Zn, Cd and Fe, respectively. In comparison with batch method the amount of Zn, Cd and Fe uptake by treated sorbents were 94.17, 88.92 and 96.03, respectively. These results are in agreement with those (Fatmeh et al., 2008) who concluded that amount of uptake of column is higher than the batch method with the application of rice hull and sawdust to adsorb the Zn from synthetic solution.

Table 6. Effect of procedure type on sorption amount (A.A.) and removal percentage of Zn, Cd and Fe from El-Saff , Al-Asher and Zenin wastewater.

Procedure types	Zn		Cd		Fe	
	AA	R%	AA	R%	AA	R%
			El-Saff			
Batch	1.41	94.17	0.14	88.92	26.17	96.03
Column	1.47	98.15	0.15	93.75	26.24	97.78
L.S.D. 0.05	0.02	1.20	0.02	3.02	0.05	0.23
			Al-Asher			
Batch	1.03	89.97	0.09	84.50	2.72	87.80
Column	1.09	95.40	0.10	86.25	2.89	93.22
L.S.D. 0.05	0.02	1.73	0.02	1.81	0.07	2.23
			Zenin			
Batch	1.03	89.97	0.13	89.20	2.72	87.80
Column	1.09	95.40	0.12	90.97	2.89	93.22
L.S.D. 0.05	0.02	1.73	0.02	4.74	0.07	2.23

De Matos et al., (2003) used columns of organic filter for removal of Cu(II) and Zn (II) from wastewater. Each filtering material was placed in a 100 mm diameter, 600 mm long, and PVC column to a height of 500 mm under 12500 Nm^{-2} of compression. Chemical and physical analyses were determined on effluent samples collected for each 1.5 L up to a total of 1.5L. The organic materials reduced the concentration of sediment solids (> 90%), total solids (up to 33%) and Cu (II) (up to 43.6%) of the influent but had little or no effect on Zn(II) concentration.

3.8. *Interaction effect*

Data of the interaction effect of sorbents type and the type of procedure on the removal percentage of Zn, Cd and Fe from El-Saff, Zenin and Al-Asher are shown in Table 7.

Table7. Interaction effect between biosorbent types and procedure types on removal percentage (R %) of Zn, Cd and Fe in El-Saff, Zenin and Al-Asher wastewater.

Biosorbent types	Procedure types	El-Saff			Zenin			El-Asher		
		Zn	Cd	Fe	Zn	Cd	Fe	Zn	Cd	Fe
Rice hull	Batch	95.9	90.64	95.15	95.19	93.09	93.49	90.80	87	90.95
	Column	97	97.5	98.45	98.61	91.70	94.85	98.25	88.5	93.58
Sawdust	Batch	90.66	87.20	91.90	92.06	87.3	91.10	89.13	88	84.65
	Column	91.3	90	92.10	95.9	89.24	93.69	92.55	84	90.86
L.S.D. 0.05		1.70	1.26	1.98	1.14	0.70	0.98	1.45	0.96	0.15

Concentration of Zn (II) and Fe (II) were very high in the three wastewater samples; therefore the highest removal was occurring. The same results were reported by Fatemeh et al., (2008).

In comparison between modified rice hull and sawdust, treated rice hull showed higher significant removal percentage. Also, in comparison with batch method the removal % of Zn, Cd and Fe by treated rice hull and sawdust was significantly higher in column method. This observation held true in the three sources of wastewater.

The obtained data revealed that, the highest removal percentage was recorded in modified rice hull by using column method. The mode of action to explain this finding was reported by Verma et al., (1989) to be the high content of the lignocellulose (lignin, hemicellulose and cellulose together) in rice hull (74.1%); which undoubtedly contributes substantially to metal ion adsorption. Also, Marshall and Champagne, (1995) found that functional groups within the skeletal structure and surface of the cell wall coordinate and complex the metal ions. Moreover, Laszlo and Dintzis, (1994) and Lalvani et al., (1997) showed that lignocellulose has ion exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure.

In the same context, Lee and Rowell (2004) showed that all of the fibers containing lignin remove heavy metal ions therefore lignin does play a role in metal ion sorption. Cell wall chemistry and architecture may also be important factors in the sorption of heavy metals from aqueous solutions using lignocellulosic fiber. (Basso et al,. 2002) found a direct correlation between heavy metal sorption and lignin content of lignocellulosic materials. Also they noted that the cell wall structures and compositions were different for the different lignocellulosics selected, which may have also influenced heavy metal sorption. Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components.

Acemioglu and Alma (2001) postulated that metal ions compete with hydrogen ions for the active sorption sites on the lignin molecules. They also conclude that metal sorption onto lignin is dependent on both sorption time and metal concentration. Metal ions connect to functional groups of sawdust such as COOH and OH and release H^+ ions. Main mechanisms of ion connection to cellulosic sorbents are chelation, ion-exchange, complexing with functional groups and making hydrogenic bounds (Shukla and Roshan, 2005). Researchers have shown that heavy metals such as Cu (II) in reaction with cellulosic materials as sawdust accumulate in secondary septum of wood. This septum is poor from lignin and affluent on cellulose (Costodes et al., 2003).

4. Conclusions

Agricultural by-product materials appear as effective and cheap sorbents for removal of heavy metals from wastewater. The removal of metal ions from effluents is important to many countries of the world both environmentally and for water re-use. The sorption capacity of rice hull was more than sawdust.

In this study, rice hull, sawdust, sugarcane bagasse and wheat straw have been evaluated as possible adsorbents for removal of Zn, Cd and Fe from domestic and industrial wastewater. This study showed that the rice hull and sawdust has higher adsorption efficiency than the other sorbents from tested polluted effluent. As a modification process, of sorbents showed the highest efficiency. These sorbents can be used for several cycles of sorption in column systems. These sorbents can use in large scale for several cycles of sorption and recovery in column systems. Low cost biosorbents are valuable alternatives for commercial sorbents. The optimum exploitation of the agricultural by-product materials is using it in biological treatment of wastewater.

It can be concluded that the modified rice hull and sawdust is a suitable adsorbent for the removal of Zn, Cd and Fe ions from wastewater effluent in terms of low cost, natural and valuable alternatives for commercial sorbents

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