Asian Journal of Chemistry Vol. 22, No. 10 (2010), 7453-7459

Removal of Zn, Pb and Cr in Textile Wastewater Using Rice Husk as a Biosorbent

MAJID MUNEER, IJAZ A. BHATTI and SHAHID ADEEL*
Department of Chemistry, University of Agriculture, Faisalabad-38040, Pakistan
E-mail: saidmittaha@yahoo.com, majidchemist8@yahoo.com; shahid_agrichemist@hotmail.com

Biosorption technique has been employed for the treatment of textile processing industrial wastewater using rice husk as biosorbant for the metal binding. The samples were collected from textile-processing units located in the premises of Faisalabad city. The concentration of heavy metals Zn, Pb and Cr were examined using atomic absorption spectrometry. The concentration of these metals were detected in the range of 1.05-5.36, 0.50-2.2 and 0.45-8.33 (ppm), which were higher than the permissible limits recommended by environmental protection agency (EPA), Pakistan. The wastewater samples were treated using rice husk as biosorbant in a continuous flow system using glass column and adsorption capacity was calculated in order to study the adsorption of metals on the biomass. There was a remarkable decrease in the concentration of Zn, Pb and Cr after adsorption, furthermore the other quality parameters such as pH, turbidity, electrical conductivity (EC), total hardness (TH), total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD) and dissolved oxygen (DO) were also investigated before and after adsorption. It was found that the concentrations of Zn, Pb and Cr were decreased up to 57, 59 and 58 %, respectively. The metal binding capacity of rice husk for the removal of heavy metals from the wastewater was as Zn < Cr < Pb.

Key Words: Wastewater, Textile industry, Heavy metals, Binding capacity and biosorption.

INTRODUCTION

With its multifarious uses, water is one of the most precious gifts of nature, without which no life could survive on earth. Any human activity that impairs the use of water as a resource may be called water pollution. Textile industries are the major contributors to water pollution. A large number of pollutants get mixed in the water, the processing wastewater contains many hazardous materials as well as heavy metals above the permissible limits.

Textile wastewater contains substantial load of pollutants in terms of chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), total dissolved solids (TDS), heavy metals *etc*. Removal of heavy metals has been a severe problem for the environmentalists[1]. Many industries, such as dyestuffs, textile, paper and plastics use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored and polluted wastewater[2,3]. The need for effective treatment method also increase with the increase of literacy and WTO implication in all the industrial sectors particularly textile industry which is major contributor of Pakistan export. The industrial sector of Pakistan has definitely to comply with international standard organization (ISO) 14000[4].

The textile effluents contain Cr and Pb which are dominant toxic metals while Co, Cd, Zn, Ni, Mn and Fe also have their common origin in the textile effluents. The elevated concentration of these metals emerging from the textile industrial effluents ultimately leading to contaminate the soil and groundwater in their proximity. Earlier research evidences showed that boosting up the industrial production also gave rise to saturation levels of toxic heavy metals in the environment close to industrial estates. Specific studies on evaluating the toxicity caused by textile effluents rich in the toxic metals have also been carried out. The environmental contamination situation demands a treatment programs for the effluents coming out from textile industry and safe disposal of the effluents[5].

An array of suitable methods exists for the removal of metal pollutants from wastewater that include precipitation, evaporation, electroplating, ion exchange, membrane separation *etc*. However, these methods also have several disadvantages, such as incomplete metal removal, excessive use of reagents, energy requirements and generation of toxic sludge or other waste products that require proper disposal and further treatments. Most of these methods become ineffective as well as uneconomical when the concentration of heavy metal are raised 10-100 times than the permissible limits which is mostly less than[6] 1 mg/L. The development of procedures and protocols, which can remove toxic metals from wastewater, has remained a focus for the last several decades. Biosorption is relatively suitable technique, which can be used to reduce the load of heavy metals in the wastewater since various biological materials have metal binding capacities. The major advantages of biosorption over conventional treatments include low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, and regeneration of biosorbent and possibility of metal recovery[7].

The focuses on the potential of a wide variety of low cost sorbents for the removal of heavy metals, requires less prior processing, abundantly available in nature, a by-product or waste material of another industry. The binding sites capable to take up metals suggest the use of rice husk as a possible low cost natural adsorbent for metals. Rice husk is a bye-product of milling process of rice crop, comprises of 23 % of rice grain, considered a significant waste disposal problem. It is widely cultivated in Asian countries. It is also used as fodder for animals or discarded as agricultural waste, as it is abundantly available. Maximum cost of commercially available rice husk is *ca.* 40 kg/2US $. The main components of rice husk, which may be responsible for sorption, are carbon and silica. Silica is composed of $SiO_4 \cdot 4H_2O$ in which each oxygen atom is shared between two adjacent tetrahedrons. The Si-O bond is about 50 % ionic owing to the large difference in the electronegativity of oxygen and silicon[8].

Heavy metals such as chromium, copper, lead, cadmium, *etc.* in wastewater are hazardous to the environment, because of their toxicity and their pollution affect the ecosystem that poses human health risk[9]. Lead pollution is a major concern as it has been used as industrial raw materials in printing, pigments, fuels, photographic materials, explosive manufacturing, *etc.* Lead compounds are highly toxic to human; its presence in drinking water even at low concentration may cause severe diseases *e.g.* anemia, encephalopathy, hepatitis and nephritic syndrome *etc.*[10,11,12]. Chromium has been used widely in a variety of industries *e.g.* textile manufacturing, wood preserving, chrome tanning and metal finishing plants *etc.* In wastewater and some natural water chromium exists in two oxidation states, hexavalent chromium Cr(VI) and trivalent chromium Cr(III). The toxicity of Cr(VI) is believed to be much higher than Cr(III), it is necessary to treat the Cr(VI) containing wastewater before discharged into the environment[13]. Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters[14].

Conventional methods for removing heavy metals from industrial wastewater include reduction, reduction followed by chemical precipitation, adsorption on the activated carbon, solvent extraction, cementation, freeze separation, reverse osmosis, ion-exchange and electrolytic methods which are often inadequate for the effective treatment. Adsorption is an effective and versatile method for removing heavy metals[15-21].

Faisalabad is the 3rd biggest city of Pakistan. It is known as the home of textile industries since it comprises of small, medium and big textile units working in different fields related to textile processing and dyeing. The environmental condition of Faisalabad city and its premises becoming worst with time due to the outfall of pollutants of different nature. The use of natural adsorbents for removal of heavy metals is related to the treatment of industrial effluents. In the present study rice husk has been used for the removal of zinc, lead and chromium from the effluents obtained from textile industries.

In this study textile effluents have been selected since they contain metals like Zn, Pb, Cr, *etc.* that have alarming pollution impact on the environment. The wastewater samples were treated using glass column in a continuous flow process. The concentrations of heavy metals were analyzed before and after treatment along with other water quality parameter.

EXPERIMENTAL

Collection of samples: The wastewater samples were collected at the end of unit operation which contains the wastewater of all process such as weaving, sizing, desizing, mercerizing, dyeing, printing, bleaching, finishing *etc.* in polyethylene tetraphtalate PET bottles. Aliquots of the volumes collected and then composite samples were stored at 4 °C until analysis[22].

Biosorption material: Fresh rice husk was obtained from a local rice mill and was passed through different sieve sizes and particle between 425 and 600 mm (geometric mean size: 505 mm) was selected. Rice husk was washed thoroughly with distilled water and dried at 60 °C. The sorbent thus obtained was designated raw rice husk (RRH)[23].

Column treatment: The wastewater samples were percolated through the 100 cm long glass column which has internal diameter of 5 cm in which glass wool was placed that serves as a bed and then 10 g rice husk having particle size 505 mm was filled which acts as adsorbent. The wastewater samples were passed through this column at a flow rate of 4 mL/min.

Analysis of samples: The effluent samples which contain several metals and organic compounds were analyzed to measure their pH, electrical conductivity (EC), Turbidity and dissolved oxygen (DO) by pH, EC, Turbidity and DO meters while total hardness (TH), total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD), using standard methods[24].

Heavy metal determination: Perkin-Elmer a analyst 300 atomic absorption spectrometer equipped with an air-acetylene flame was used and controlled by Intel personal computer to examine the concentrations of metals in water samples before and after treatment. The hollow cathode lamps for Zn, Pb and Cr were operated at particular wavelength and slit was 0.2 nm for the metal ions[25].

Statistical analysis: The T-paired tests were applied to compare values of all the parameters before and after treatment by using statistical software Minitab 15 to evaluate the significance of treatment.

RESULTS AND DISCUSSION

The results obtained show the distribution of metals in the textile wastewater samples which are reported in tables as a descriptive parameter. Table-1 shows the values of pH, EC, DO and COD values before and after treatment. Before treatment pH of the samples were found in the range from 8.1-12.2 and after treatment the pH decreased up to 3.70 % and the results were significant. The EC values of water samples before treatment were in the range from 5.10-9.60 µS/cm, which were very high, but after treatment the values decreased and values decreased up to 50 %. The values of dissolved oxygen and chemical oxygen demand were in the range of 0.45-2.60 and 355-710 mg/L, respectively before treatment and after treatment there was a significant decrease found in DO and COD values. It was also noted that COD values of treated samples become in the safe limit for agriculture runoff as prescribed by environmental protection agency (EPA) Pakistan[26].

Table-2 shows the values of turbidity, hardness, total dissolved solids and total suspended solids before and after treatments. The turbidity values were ranged from 62-90 mg/L in the samples and after treatment the values were reduced to a level 32-51 mg/L, which show a significant decrease in all the samples but the maximum decrease was up to 58.75 % for sample 1. Similarly hardness, TSS and TDS values of treated wastewater samples reduced up-to 64, 40 and 70 %, respectively.

TABLE-1
pH, ELECTRICAL CONDUCTIVITY, DISSOLVED OXYGEN AND CHEMICAL OXYGEN DEMAND BEFORE AND AFTER TREATMENT

Sam. No.	pH		EC		DO		COD (mg/L)	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
1	9.40±0.376	9.10±0.36	7.60±0.30	3.92±0.15	0.65±0.029	0.80±0.036	640±27.52	550±14.95
2	10.20±0.408	9.00±0.36	5.10±0.20	2.43±0.12	1.00±0.045	1.10±0.051	570±26.22	530±24.38
3	7.80±0.310	7.55±0.30	5.80±0.25	3.10±0.13	0.85±0.039	0.90±0.041	632±27.17	530±29.00
4	8.13±0.320	8.05±0.32	8.20±0.36	4.80±0.21	1.20±0.056	1.24±0.058	445±20.40	355±19.35
5	8.10±0.280	7.80±0.31	6.30±0.28	3.21±0.12	0.90±0.041	0.92±0.041	569±25.60	510±23.40
6	9.85±0.394	9.70±0.38	9.60±0.38	5.57±0.25	2.60±0.110	2.64±0.120	485±21.82	428±24.66
7	9.65±0.380	9.50±0.38	8.27±0.33	4.30±0.20	0.45±0.200	0.48±0.023	720±30.95	560±20.24
8	10.40±0.410	10.20±0.40	9.00±0.36	5.54±0.25	1.60±0.070	1.63±0.074	563±25.89	505±25.07
9	8.40±0.330	8.30±0.33	7.50±0.30	3.89±0.17	0.70±0.032	0.71±0.032	672±30.24	602±28.57
10	12.20±0.480	12.00±0.48	5.60±0.22	3.02±0.13	1.10±0.050	1.10±0.050	781±35.93	710±33.30

Values (mean ± SD) are average of samples in triplicate ($p < 0.02$) analyzed by T-paired test.

TABLE-2
TURBIDITY, TOTAL HARDNESS, TOTAL DISSOLVED SOLIDS AND TOTAL SUSPENDED SOLIDS BEFORE AND AFTER TREATMENT

Sam. No.	Turbidity		Hardness.		TDS		TSS	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
1	80±3.20	33±1.48	689±31.00	328±13.15	1100±49.00	335±15.00	1795±89.75	1075±48.37
2	70±3.15	32±1.47	480±22.08	225±9.45	1200±60.00	722±32.50	1050±47.02	632±28.44
3	71±3.20	33±1.46	880±40.50	368±15.80	1350±60.00	800±36.00	600±30.00	375±32.62
4	62±2.79	41±1.64	650±30.55	342±14.70	2600±117.00	1550±69.00	1200±54.00	725±32.60
5	67±3.35	42±1.65	500±21.50	269±12.10	2500±112.00	1507±67.80	1500±67.00	922±44.25
6	68±2.72	38±1.71	400±18.00	215±9.67	1820±81.90	1100±49.50	1000±45.00	614±26.40
7	90±3.6	51±2.30	935±42.0	328±14.76	2372±106.74	1425±64.00	963±43.33	580±26.00
8	77±3.45	42±1.63	1240±57.00	622±26.76	3220±128.00	1950±87.75	995±44.77	600±28.20
9	65±2.90	35±1.48	887±37.25	614±27.63	2729±122.00	1635±73.50	1325±59.65	798±36.70
10	69±3.10	32±1.45	592±27.23	294±12.34	2665±119.00	1600±72.00	550±25.30	342±14.70

Values (mean ± SD) are average of samples in triplicate ($p < 0.02$) analyzed by T-paired test.

The concentrations of Zn, Pb and Cr in the wastewater samples before and after treatment are shown in Table-3. The concentrations of Zn in untreated samples were found in the range 1.05-5.36 mg/L and after treatment it was 0.45-3.75 mg/L, which is below than the standard value given by environmental protection agency Pakistan. Sample 1 shows the maximum decrease of concentration of Zn that is 57.1 %. Similarly the concentration of Pb and Cr also reduced significantly by the biosorption treatment. Sample no. 7 shows the reduction in concentration of Pb upto 59 % and sample no. 4 also shows the decrease in the concentration of Cr to a level of 58.75 %. It was also indicated from the results that some samples even after treatment shows higher concentration than permissible limits recommended for Pb < 0.5 and Cr < 1 ppm[26].

Table-4 shows the efficiency of treatment in term of adsorption capacity of rice husk for the metal binding. The adsorption capacity was calculated by using mass balance equation[27].

TABLE-3
CONCENTRATION OF Zn, Pb AND Cr BEFORE AND AFTER TREATMENT

Sample No.	Concentration of Zn		Concentration of Pb		Concentration of Cr	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
1	1.05±0.0470	0.45±0.020	1.44±0.0648	0.90±0.040	0.90±0.040	8.33±0.374
2	2.05±0.0940	1.55±0.060	2.20±0.0990	1.24±0.055	1.24±0.055	0.85±0.039
3	1.90±0.0870	1.42±0.065	0.5±0.0230	0.30±0.013	0.30±0.013	0.45±0.020
4	1.42±0.0639	1.12±0.051	1.92±0.0880	1.15±0.051	1.15±0.051	3.20±0.150
5	1.12±0.0500	0.79±0.035	0.61±0.0280	0.36±0.016	0.36±0.016	5.92±0.278
6	1.06±0.0470	0.68±0.029	2.76±0.1290	1.57±0.065	1.57±0.065	0.83±0.035
7	2.90±0.1300	1.45±0.062	1.06±0.0490	0.43±0.019	0.43±0.019	1.40±0.063
8	4.88±0.2200	3.47±0.159	0.99±0.0420	0.57±0.025	0.57±0.025	0.92±0.042
9	5.36±0.2100	3.75±0.175	1.08±0.0510	0.53±0.014	0.53±0.014	1.45±0.066
10	1.20±0.0540	0.98±0.045	1.15±0.0490	0.55±0.025	0.55±0.025	2.31±0.103

Values (mean ± SD) are average of samples in triplicate ($p < 0.02$) analyzed by T-paired test.

TABLE-4
ADSORPTION CAPACITIES OF RICE HUSK FOR THE REMOVAL OF Zn, Pb AND Cr

S. No.	Adsorption capacity for Zn mg/g	Adsorption capacity for Pb mg/g	Adsorption capacity for Cr mg/g
1	6.00	5.40	40.0
2	5.00	9.60	3.30
3	4.80	2.00	1.70
4	3.00	7.70	18.80
5	3.30	2.50	25.20
6	3.80	11.90	3.40
7	14.50	6.30	7.20
8	14.10	4.20	4.20
9	16.10	5.50	4.70
10	2.20	6.00	9.30

$$q = \frac{V(Ci - Cf)}{M}$$

where q is amount of heavy metal adsorbed, V is volume of effluents used, Ci is concentration of metal before adsorption, Cf is concentration of metal after adsorption and M is amount of adsorbent used (rice husk).

From these results it is manifested that heavy metals Zn, Pb and Cr are the chief pollutants coming from the textile effluents along with other toxic species that deteriorate the quality of water may be reduced significantly using biosorption method. The use of rice husk provide a low cost sorbent as compared to the activated carbon or synthetic ion-exchanger. In the agricultural countries such as Pakistan it is easily available at low price which has a potential to serve as an alternative of other costly treatments. Rice husk also contains lots of silica which is also reported to be a good sorbent for the number of metal cations and dyes[28,29].

Conclusion

Rice husk *Oryza sativa* was used as biosorbant for the removal of heavy metals Zn, Pb and Cr as well as for the improvement of water quality parameters. The metal removal phenomenon depends upon the physical adsorption on surface. Treatment is significant for the improvement in pH, EC, DO, COD, Turbidity, Total hardness, TDS and TSS. Decrease in the concentration of metals. Some samples show high affinity of adsorption as compared to the others. The efficiency of the biosorption phenomenon can be enhanced by increasing the length of column as well as by repeating the treatment in order to get the concentration of metals in the permissible limits. The biosorption process is safe and cheaper method for the industrial wastewater treatment especially the countries like Pakistan.

REFERENCES

1. V. Tiwari, B. Ghoparde and P.S. Vankar, *Colourage*, **47**, 18 (2000).
2. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol.*, **77**, 247 (2001).
3. I.M. Banat, P. Nigam, D. Singh and R. Marchant, *Bioresour. Technol.*, **58**, 217 (1996).
4. http//www.cpp.org.pk.
5. S. Manzoor, M.H. Shah, N. Shaheen, A. Khalique and M. Jaffar, *J. Hazard. Mater.*, **A137**, 31 (2006).
6. Z.R. Holan and B. Volesky, *Biotechnol. Bioeng.*, **43**, 1001 (1994).
7. D. Kratochvil and B. Volesky, *Water Res.*, **34**, 3186 (2000).
8. M. Akhtar, M.I. Bhanger, S. Iqbal and S.M. Hasany, *J. Hazard. Mater.*, **B128**, 44 (2006).
9. M. Nourbakhsh, Y. Sag, D. Ozar, Z. Aksu, T. Kutsal and A. Caglar, *Proc. Biochem.*, **29**, 1 (1994).
10. W. Lo, H. Chua, K. H. Lam and S.P. Bi, *Chemosphere*, **39**, 2723 (1999).
11. R. Jalali, H. Ghafourian, Y. Asef, S. J. Davarpanah and S. Sepehr, *J. Hazard. Mater.*, **92**, 253 (2002).
12. M.M.D. Zulkali, A.L. Ahmad and N.H. Norulakmal, *Biores. Technol.*, **97**, 21 (2006).
13. Y. Chen and G. Gu, *Biores. Technol.*, **96**, 1722 (2005).
14. G. Donmez and Z. Aksu, *Proc. Biochem.*, **38**, 751 (2002).
15. S.D. Kim, K.S. Park and M.B.Gu, *J. Hazard. Mater.*, **93**, 155 (2002).
16. A. Ozer, H.S. Altundogan, M. Erdem and F. Tumen, *Environ. Pollut.*, **97**, 107 (1997).
17. L. Monserand and N. Adhoum, *Separa. Puri. Tech.*, **26**, 137 (2002).
18. A.P. Padilla and E.L. Tavani, *Desalination*, **126**, 219 (1999).
19. S. Rengaraj, C.K. Joo, Y. Kim and J. Yi, *J. Hazard. Mater.*, **102**, 257 (2003).
20. C. Namasivayam and R.T. Yamuna, *Chemosphere*, **30**, 561 (1995).
21. G.S. Agarwal, H.K. Bhuptawat and S. Chaudhari, *Biores. Technol.*, **97**, 949 (2006).
22. L.C. Alves, H.M. Henrique, A.M.F. Xavier and M.C. Cammarota, *Biores. Technol.*, **96**, 1650 (2005).
23. U. Kumar and M. Bandyopadhyay, *Biores. Technol.*, **97**, 104 (2006).
24. American Public Health Association Standard Methods for Examination of Water and Wastewater, Washington, D.C., edn. 21 (2005).
25. C.R.T. Tarley and M.A.Z. Arruda, *Chemosphere*, **54**, 987 (2004).
26. WWW.Environment.Gov.Pk/.
27. B. Volesky and Z.R. Holan, *Biotechnol. Progr.*, **11**, 235 (1995).
28. K.S. Low and C.K. Lee, *Biores. Technol.*, **61**, 121 (1997).
29. U. Kumar and M. Bandyopadhya, *J. Hazard. Mater.*, **B129**, 253 (2006).

(*Received*: 29 July 2009; *Accepted*: 5 July 2010) AJC-8859