Short Communication

Evaluation of chromium (III) biosorption efficiency of rice husk and leftover tea waste

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Abstract: Chromium has now become a threat for environment and health due to its extensive use in leather tanning in Bangladesh. Considering easy availability and cost effectiveness, rice husk and leftover tea waste biomass were used as biosorbent for chromium (III) absorption. Through batch experiment, absorption efficiencies at different parameters (pH, chromium concentration, absorbent dosage, exposer time) were determined and measured by FAAS. The results showed that efficiencies of left over tea waste and rice husk were 87.14% and 85.71% respectively. Our study revealed that 7.5 gm/L biosorbent works best to absorb 0.5 mM chromium(III) solution under 45-60 minute exposer in room temperature at pH 4.0- 5.0. At natural condition, 72% and 78.4% chromium were absorbed from the raw tannery effluent by rice husk and tea waste respectively. FT-IR studies indicated the functional groups (O-H, C-H, C=C, C=O, C≡C and C≡N) might be involved in the sorption of Cr (III) onto leftover tea waste and rice husk biomass. The findings indicate that these biosorbents could be employed in the removal of Cr (III) from aqueous solutions and industrial effluents.

1. Introduction

Chromium is an industrially valuable heavy metal which is used in the tanning of leather, the catalytic hydrocarbon processing and in the production of painting materials, stainless steel and other alloys etc. (Netzahuatl-Muñoz *et al.*, 2015). Due to the widespread use and inappropriate management of chromium compounds, environmental chromium (Cr) contamination has raised environmental and public health concerns (Belay, 2010).Though, Cr(III) is non-toxic but it is rapidly oxidized into toxic Cr(VI) when released into the environment. In Bangladesh, most of the effluents from tannery industries that contain high concentration of Cr(III) ions are directly released into different water bodies. Specially, the pollution of the river Buriganga by the effluents of tanneries situated at Hazaribagh area is remarkably alarming (Arias-Barreiro *et al.,* 2010; Bhuiyan *et al.,* 2011; Shams *et al.,* 2009). It has been reported that Cr(VI) has detrimental effects on broad spectrum of organisms in the aquatic ecosystem. Besides, high levels of chromium are observed in the liver, skin and bones of poultry chicken due to the use of solid tannery wastes in the production of poultry feed (Mazumder *et al*., 2013). As a result, undesirably high level of chromium is getting incorporated into our food chain. So, it is high time we took some scientific measures along with awareness building initiatives to compensate and limit environmental chromium pollution.

To date, various methods have been worked out to adsorb heavy metal from aqueous solution in an efficient and cost-effective way. Biosorption of cadmium (Cd), nickel (Ni), lead (Pb) and zinc (Zn) are found quite efficient using microalgae (Wilke *et al.*, 2006; Kumar *et al.*, 2009). In Nigeria, leaf biomass of *Calotropis procera* (BomBom) was thoroughly studied for Cr(III) biosorption (Overah, 2011). A group of scientists showed that mango leaf powder and rice husk are very efficient in biosorption of arsenic(III) (Kamsonlian *et al.*, 2012).

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Similar research was done with mango leaf for removal of copper(II) from aqueous solution (Ong *et al.*, 2013). Rice husk has also been found to be very promising in biosorption of different heavy metals (Khalid *et al.*,1989; Krishnani *et al.*, 2008; Munaf *et al.*, 1997). According to Ahluwalia *et al.*, 2005 and Amarasinghe *et al.*, 2007 waste tea leaf is also a promising low-cost adsorbent for the removal of copper, lead, iron, zinc and nickel from wastewater. In Bangladesh, controlling heavy metal pollution through biosorption methodology is still a new concept and exploration in this field is inadequate. In our study, we aimed to determine the Cr(III) biosorption efficiency of rice husk and tea waste (leftover biomass after tea preparation). These materials are selected for study considering their easy availability and cost effectiveness.

2. Materials and Methods

Rice husk and tea waste samples that are used in this work were collected, respectively, from Narsingdi district, Bangladesh and different roadside tea-stalls within Dhaka city. Collected samples were washed thoroughly with deionized water to remove dust, soil particles and other things. Samples were, then, dried at room temperature for six days. Dried samples were crushed throughusing a Glen Creston mill and the fraction with particle size 0.42 to 0.50 mm was used in the Cr(III) removal experiments. The crushed biomaterials were stored in an airtight zipper bag. Cr(III) stock solution (20mM) was prepared using appropriate amount of $Cr(NO_3)_3.9H_2O$ in a standard volumetric flask and then preserved in 4°C. The stock solution was then diluted to 0.5 mM, 1.0 mM and 1.5 mM solutions to carry out further study.

Initially, the effectiveness of these two biomaterials was checked by mixing 0.14 gram of waste rice husk and tea biomass separately in 20 mL 1 mM (pH 3.0) Cr(III) solution. Samples were placed in orbital shaker (150 rpm) for 1 hour at 37°C. Then, the solutions were filtered to remove tea waste/rice husk particles and the filtrate were collected for determination of residual Cr(III) ions. The Cr(III) concentration within a solution was determined through Flame Atomic Absorption Spectrometry (FAAS) (Overah,2011) and all measurements were done using air/acetylene flame. It was found that about 87.14% and 85.17% Cr(III) ions were adsorbed by tea waste and rice husk, respectively. Determination of the optimum pH, salt concentration and biosorbent dosages were carried out through triplicate batch experiments and the means were computed for each set of values. In all cases, one set of negative controls (without biosorbent) were prepared and the mixture were agitated in orbital shaker at 150 rpm at 37°C. The functional groups on the walls of the biosorbent which are responsible for the biosorption process were also carried out by FT-IR analysis of the samples (Overah, 2011).

3. Results and Discussion

The triplicate batch experiments to determine the effect of pH on biosorption of Cr(III) were carried out at pH 2.0, 3.0, 4.0, 5.0 and 6.0. After agitation in orbital shaker at 150 rpm in 37°C for 60 minutes, the solutions were filtered out through Whatman filter paper and filtrates were analyzed to determine the concentration of residualCr(III) ions. For rice husk, maximum adsorption of Cr(III) was observed at pH 4.0 (88.18%) and for tea waste at pH 5.0 (88.10%). In both cases, the adsorption declined at higher pH (Table 1). Next batch experiments were performed to determine the optimum biosorbent doses for adsorption. Biosorbent doses ranging from 2.5 g/L to 10 g/L were added to 20 mL 0.5 mM Cr(III) solution at optimum pH (4.0 and 5.0 respectively for rice husk and tea waste), mixtures were agitated, filtrated and analyzed by FAAS as before. In both cases, 7.5 g/L biosorbent showed maximum adsorption of 85.71% and 87.14% for rick husk and tea waste respectively. At 10 g/L biosorbent dosage adsorption decreased heavily (Table 1). It is probably due to the fact that at high biosorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on biosorbent and also the interference between the binding sites. Another, possibility is the aggregation of biosorbents when they are at high concentration (Karthikeyan *et al.*, 2007).

To evaluate the effect of contact period, 7.5 g/L biosorbent (rice husk/tea waste) was added with 20 mL 0.5mM Cr(III) solution at pH 4.0 and 5.0 respectively for rice husk and tea waste for varied time of incubation: 20 min, 30min, 45 min and 60 min. The optimum contact period for biosorption were about 45 minutes for rice husk and 60 minutes for waste tea biomass at 37°C(Table 1).When experiments were carried out by mixing 20 mL of 0.5 mM/ 1.0 mM/ 1.5 mM Cr(III) solution with 7.5 g/L biosorbents (rice husk/ tea waste) at optimum pH and contact period (pH 4.0, 45 min and pH 5.0, 60 min respectively for rice husk and tea waste), result shown that adsorption reduced with the increasing salt concentration. At 0.5 mMCr(III) concentration, rice husk and tea waste adsorbed maximum Cr(III) ion (85.34% and 85.45% respectively) (Table 1).

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Table 1. Effect of pH, biosorbent dosages, contact period and salt concentration on Cr(III) biosorption.

	Effect of pH		
Serial no.	pH	Percent of adsorption (Rice husk)	Percent of adsorption (Tea waste)
1	2	87.1	87.01
2	3	75	87.04
3	4	88.18	87.14
4	5	77.75	88.10
5	6	54.19	80.17
	Effect of biosorbent dosages		
Serial no.	Biosorbent (gm/L)	Percent of adsorption (Rice husk)	Percent of adsorption (Tea waste)
1	2.5	70.4	71.02
2	5	67.35	79.1
3	7.5	85.71	87.14
4	10	33.58	68.58
	Effect of contact period		
Serial no.	Contact Time (min)	Percent of adsorption (Rice husk)	Percent of adsorption (Tea waste)
1	20	32.9	63.93
2	30	53.8	70.5
3	45	89.4	70.7
4	60	85.71	87.14
	Effect of salt concentration		
Serial no.	Salt conc. (mM)	Percent of adsorption (Rice Husk)	Percent of adsorption (Tea Waste)
1	0.5	85.34	85.45
2	1.0	71.47	73.28
3	1.5	57.96	48.63

Raw tannery effluent samples were collected from Hazaribagh, Dhaka and filtered through Whatman filter paper and preserved in reagent bottles at 4°C. The biosorption efficiency of rice husk and tea waste were determined by using its intrinsic pH (pH 4.0) and the optimum conditions derived from the previous batch experiments. At these conditions, 72% and 78.4% chromium were absorbed from the raw tannery effluent by rice husk and tea waste respectively. In comparison to standard solution, the percentage of chromium adsorption for tannery sample is low due to the presence of other materials like proteins, lipids and other chemicals. Other metals like sodium, calcium etc. present in the effluent might also compete with chromium which reduced its efficiency remarkably.

The functional groups on the walls of the biosorbent which are responsible for the biosorption process were found out by FT-IR analysis of unloaded and metal-loaded biosorbent at optimum pH. Approximately 1 mg each of dried sample of metal unloaded and metal loaded biosorbent were pressed under vacuum into pellets. The pellets were then analyzed in the range $4000 - 600$ cm^{-1}. Comparing the spectra of Cr(III)-loaded biomass with that of the unloaded it was observed that the band around 3280 cm^{-1} shifted after the biosorption. Moreover, the band around 2920 cm^{-1} was more intense and several new bands appeared after adsorption which indicates the formation of new compounds. FT-IR studies before and after the biosorption process indicated the functional groups (O-H, C=C, C=O, C≡C and C≡N) (Table 2, Figure 1-4) might be involved in the sorption of Cr(III) onto waste tea and rice husk biomass which also corroborated with other findings (Overah, 2011).

Table 2. The chemical groups on biosorbent involved for biosorption.

Wave number cm^{-1} Rice Husk		Wave number cm^{-1} Tea Waste		Functional groups
Before treatment	After treatment	Before treatment	After treatment	
3280 (broad)	3339 (broad)	3287 (broad)	3343 (broad)	O-H (alcohols) stretch
-	-	3016	-	O-H (carboxylic acids)
2920	2920	2918	2916	C-H stretch
2850	2851	2850	2851	C-H stretch
-	2102	-	2100	C≡C, C≡N
1649	1637	1627	1634	C=C stretch, C=O stretch
-	-	1516	-	N=O

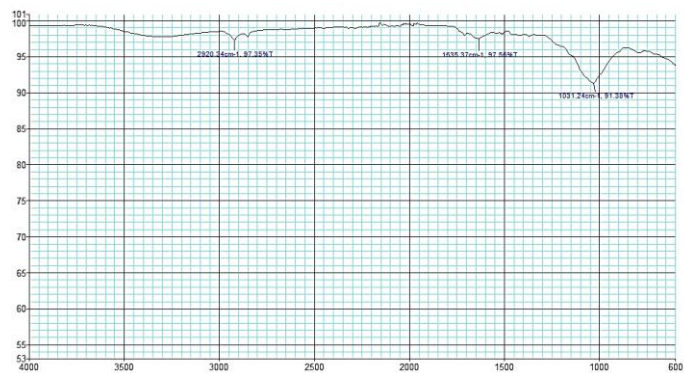Asian Australas. J. Biosci. Biotechnol. 2017, 2 (2)

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Figure 1. FT-IR spectra of rice husk before treatment.
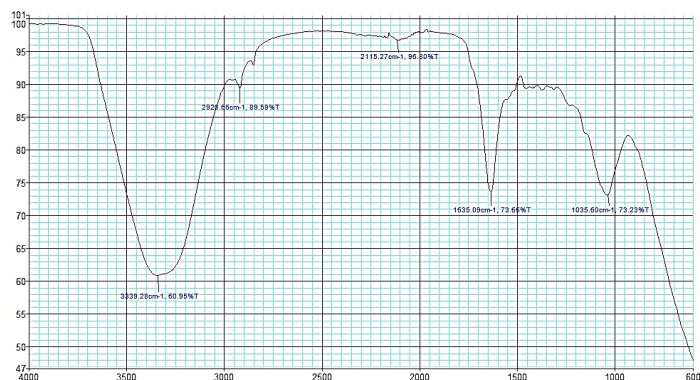

Figure 2. FT-IR spectra of rice husk after treatment.

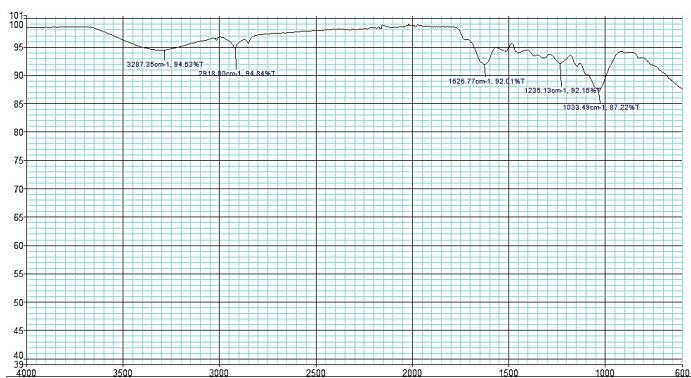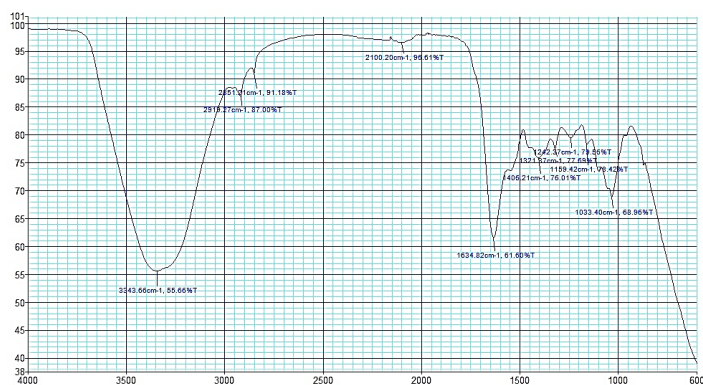**Figure 3. FT-IR spectra of left over tea waste before treatment.**

Figure 4. FT-IR spectra of left over tea waste after treatment.

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In comparison with other popular biomaterials, such as, whole cell like bacteria or algae, the present study used cheap and readily available waste materials like tea waste and rice husk to adsorb chromium from industrial effluent. The overall result of chromium biosorption from both standard solution and tannery effluent by rice husk and waste tea biomass was quite promising. Bhavsar *et al.* (2012) used waste tea biomass to remove Cr(VI) and at optimum condition 88% chromium was removed by tea waste. Dave *et al.* (2011) implemented tea waste and coconut husk to adsorb Cr(VI) from standard solution and at optimum condition maximum adsorption were 86% and 82%, respectively. None of these studies include samples from tannery or environment to compare their findings with standard. However, further analysis such as kinetics, equilibrium and thermodynamics studies of chromium ion biosorption from both Cr(III) and Cr(VI) aqueous solutions should be conducted for better understanding of the efficiency of these two materials.

4. Conclusions
In Bangladesh, tannery industries produce huge amount of waste water containing high concentration of chromium salt daily. The effects of chromium pollution alone with other heavy metal pollution are calamitous. So, measures against heavy metal pollution are a crying need. This study demonstrates rice husk and left over tea biomass could be a potent solution of heavy metal pollution.

Acknowledgements

Conflict of interest
None to declare.

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