

# Detoxification of chromium (VI) in coastal water using lignocellulosic agricultural waste

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## Abstract

Development of new economically feasible eco-friendly products from natural plants/agricultural wastes for removal of pollutants from coastal aquaculture systems is the objective of our continued research. In the present study, attempts have been made to harness lignocellulosic agricultural waste material (bagasse) for the removal of chromium (VI) from highly saline coastal water used for aquacultural practices using brackish water. Five different products prepared from bagasse were evaluated for the detoxification of Cr(VI) from high saline coastal water. The maximum removal capacity for Cr (VI) was found for the material charred with sulphuric acid. Dried bagasse powder was the second most effective product. These substrates are efficient for Cr removal from coastal water owing to their very low cost.

**Keywords:** phytoremediation, reduction, chromium, bagasse, coastal waters

## Introduction

The successful growth, propagation and harvest of aquatic animals, whether freshwater or marine, are heavily dependent upon the quality of the surrounding water. Coastal water receive a heavy influx of sewage, industrial effluents, domestic and agricultural waste which consists of varying hazardous chemical and causing deleterious effects on fish and other aquatic organism. Heavy metals are among the conservative pollutants that are not subject to bacterial attack or other breakdown and are permanent additions to the marine environment (El-Nady and Atta, 1996). The primary sources of heavy metals pollution in coastal lagoons are input from rivers, sediments and atmosphere, which can affect aquaculture profitability in certain areas. In recent years, chromium concentrations have been increasing in coastal waters through the electroplating industry, metal finishing, leather tanning and chrome preparation. In the United States, it is the second most common inorganic contaminant in waters, after lead (Wielinga et al., 2001). However, Cr is necessary for normal life processes; it can be toxic to organisms at elevated concentrations. Free metal ionic activity in seawater is a function of metal toxicity, rather than the total concentration of the metal (Viarengo, 1989). Chromium usually exists in both trivalent and hexavalent oxidation states in soils and aqueous systems. The hexavalent form is of particular concern because of its great toxicity resulting from its powerful oxidation properties. The Cr (VI) is a U.S.EPA classified group A carcinogen based on its chronic effects (Nkhalambayausi-Chirwa and Wang, 2001). This has adverse impact on aquatic species as it accumulates in fish tissues and causes reduction in fish production at high concentrations (Cutter, 1991; Krishnani et al., 2003). The trivalent form of chromium, namely Cr (III), on the other hand, is about 1 000 times less toxic than Cr(VI). Furthermore, it has a limited hydroxide

solubility making it relatively immobile and less available for biological uptake. As a result, Cr (VI) toxicity could be reduced and then become less bio-available when reduced to Cr(III).

Among available conventional processes used to remove hexavalent Cr, the most commonly used are precipitation as chromium hydroxide or ion exchange using macroporous resins (Jianlong et al. 2000). However, these methods suffer from some disadvantages due to their relatively high operational costs and cannot be recommended for Cr removal from coastal waters. Conversely, in recent years, a promising alternative method for removal of Cr(VI) uses the sorption by lignocellulosic solid wastes such as sugar-beet pulp (Reddad et al. 2003), wheat bran (Dupond and Guillon, 2003) and saw-dust (Raji and Anirudhan, 1998). Sugarcane bagasse is a highly fibrous lignocellulosic material, which is the residue remaining after sugar cane has been pressed to remove sucrose. Sugar-cane mills produce more bagasse than can be utilised as a fuel source for sugar processing; few commercial uses for the excess bagasse have been developed and its accumulation presents a waste problem for the sugar industry. One potential use of bagasse is as a feedstuff for shrimps (Freeman et al. 1992). However, reports on its use for the detoxification of Cr (VI) from high saline coastal water are not available. This study reports the use of five different products prepared from bagasse for detoxification of Cr (VI) in high saline coastal waters under laboratory conditions.

## Materials and methods

### Preparation of bagasse products

Five different kinds of materials were prepared from bagasse:

- Raw bagasse filaments (BRF)
- Dried bagasse filaments (BDF): Raw material was thoroughly washed with water and then dried in sun light
- Dried bagasse powder (BOP): Material dried in sunlight was dried in an oven at 75°C for 6 h and then powdered.
- Charred bagasse powder (BCP): Dried material was charred at 250°C in a muffle furnace and then powdered.

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- Bagasse charred with sulphuric acid (BSP): Dried material was charred with concentrated sulphuric acid for 24 h. After complete charring, charred materials were thoroughly washed with water to remove sulphuric acid, dried at 100°C and then powdered.

### Experimental and analytical procedures

Standard stock solution was prepared from potassium dichromate. For each experimental run, a solution of Cr metal ion was added to 1 l of coastal water (salinity 35±1 g/l) in a glass jar in order to obtain a known concentration of the metal. The resulting solution was treated with five different products of bagasse at concentrations of 3, 6 and 10 g/l with a separate set of control. In addition, water samples were analysed for Cr concentrations at daily intervals for a period of 6d. At the end of the experiment, water samples were collected from all the treatments and other water quality parameters such as pH, salinity, alkalinity, ammonia, nitrite, phosphate and total bacterial counts were analysed by standard methods [Strickland and Parson, 1972; *Standard Methods*, 1989]. Hexavalent Cr in coastal water was determined spectrophotometrically [*Standard Methods*, 1989] by measurement of the intense red-violet complex formed by reaction of Cr (VI) with 1,5-diphenyl carbazide in an acidic medium. A Hitachi UV-Visible spectrophotometer was used to obtain measurements of the chromophore complex at its absorbance maximum of 540 nm.

### Statistical analysis

The data were statistically analysed using 5 (duration) x 5 (materials) factorial completely randomised design with two replications for each dose. Duncan's multiple range test was applied to identify significant differences between main effects and interaction effects. M-STATC statistical software was employed to perform statistical analyses.

### Results and discussion

#### Determination of effective bagasse product and dose for detoxification of Cr (VI)

The effect of five different products of bagasse at the dose of 3 g/l on the removal of initial Cr(VI) concentration of 8.126 mg/l is presented in Fig. 1. This shows that bagasse charred with sulphuric acid (BSP) is most effective in detoxifying Cr(VI) as this product removed initial Cr(VI) concentration of 8.126 mg/l within 24 h, whereas, in the treatments with charred bagasse powder (BCP), dried bagasse powder (BOP), raw bagasse filaments (BRF) and dried bagasse filaments (BDF), per cent Cr(VI) removal was 12.6%, 14.6%, 8.27% and 11.3% in 24 h respectively. There was a further decline in Cr concentrations and after 48 h, per cent Cr (VI) removal was 22.8%, 22.3%, 13.9% and 11.9% in 48 h, 34.3%, 22.4%, 14.9% and 12.6% in 72h and 38.5%, 22.6%, 15.1% and 13.4% in 96 h respectively. Bagasse filaments dried in sun light (DBF) were least effective.

The effect of five different products of bagasse at a concentration of 6 g/l on 8.126 mg/l Cr(VI) is presented in Fig. 2. This shows that BCP, BOP, BRF and BDF decreased initial Cr concentration of 8.126 mg/l to the extent of 16.3%, 19.5%, 10.6% and 9.33% in 24 h and 31.8%, 27.9%, 16.1% and 10.8% in 48 h and 40.3%, 37.9%, 17.4% and 11.1% in 72 h respectively. There was a further decline and after 96 h, the per cent Cr removal was 57.9%, 47.8%, 18.8% and 12%.

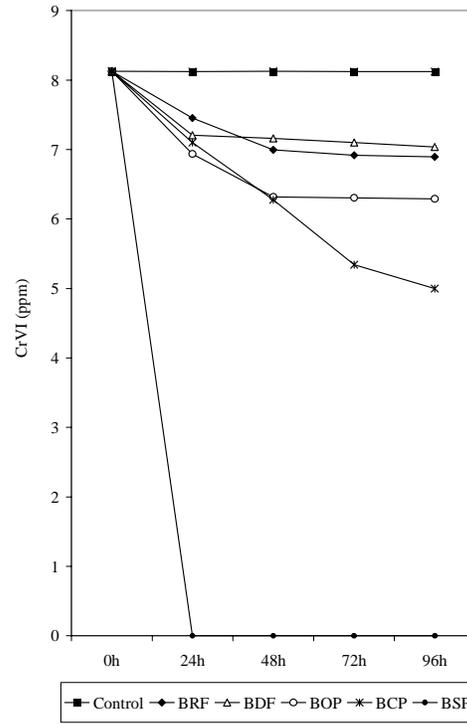


Figure 1  
Effect of bagasse products @ 3 g/l on chromium(VI) removal

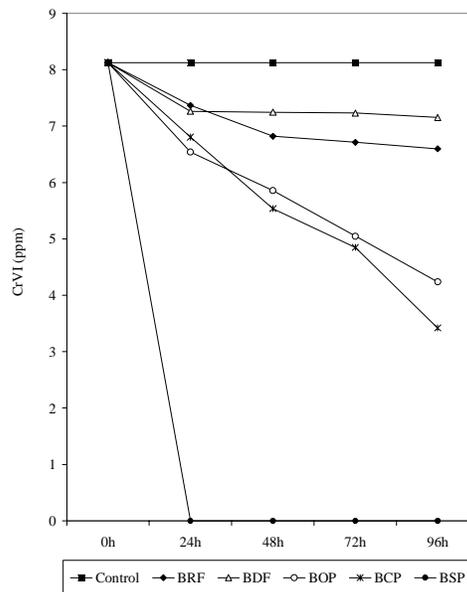


Figure 2  
Effect of bagasse products @ 6g/l on chromium(VI) removal

The effect of five different products of bagasse at the concentration of 10 g/l on 8.126 mg/l Cr shows (Fig.3) that BOP, BCP, BRF and BDF, decreased Cr to the extent of 36.2%, 19.7%, 11.6% and 17% in 24 h and 61.4%, 38.7%, 25.4% and 20.2% in 48 h and 85.2%, 62.3%, 34.6% and 20.6% in 72 h respectively. There was a further decline and after 96 h, the per cent Cr (VI) removal was 96.1%, 79.7%, 43.6% and 21.3%.

TABLE 1 Comparison of efficacies of bagasse products for the removal of hexavalent chromium from coastal waters				
Materials	3 g/l	6 g/l	10 g/l	
BRF	7.278 <sup>B</sup>	7.125 <sup>B</sup>	6.255 <sup>B</sup>	
BDF	7.326 <sup>A</sup>	7.402 <sup>A</sup>	6.840 <sup>A</sup>	
BOP	6.795 <sup>C</sup>	5.962 <sup>C</sup>	3.595 <sup>D</sup>	
BCP	6.368 <sup>D</sup>	5.747 <sup>D</sup>	4.868 <sup>C</sup>	
BSP	1.625 <sup>E</sup>	1.625 <sup>E</sup>	1.625 <sup>E</sup>	
Materials	Hours	Initial Concentration 8.126 <sup>A</sup>		
		3 g/l	6 g/l	10 g/l
BRF	24	7.454 <sup>B</sup>	7.368 <sup>B</sup>	7.186 <sup>B</sup>
	48	6.996 <sup>G</sup>	6.820 <sup>E</sup>	6.064 <sup>G</sup>
	72	6.918 <sup>H</sup>	6.712 <sup>F</sup>	5.315 <sup>H</sup>
	96	6.869 <sup>H</sup>	6.598 <sup>G</sup>	4.582 <sup>K</sup>
BDF	24	7.206 <sup>C</sup>	7.262 <sup>C</sup>	6.742 <sup>C</sup>
	48	7.162 <sup>D</sup>	7.245 <sup>C</sup>	6.486 <sup>DF</sup>
	72	7.098 <sup>E</sup>	7.227 <sup>D</sup>	6.452 <sup>EF</sup>
	96	7.038 <sup>F</sup>	7.152 <sup>H</sup>	6.396 <sup>F</sup>
BOP	24	6.936 <sup>H</sup>	6.540 <sup>I</sup>	5.184 <sup>I</sup>
	48	6.316 <sup>J</sup>	5.856 <sup>K</sup>	3.140 <sup>L</sup>
	72	6.306 <sup>I</sup>	5.048 <sup>M</sup>	1.204 <sup>O</sup>
	96	6.290 <sup>I</sup>	4.240 <sup>E</sup>	0.320 <sup>P</sup>
BCP	24	7.100 <sup>E</sup>	6.804 <sup>J</sup>	6.524 <sup>D</sup>
	48	6.274 <sup>I</sup>	5.538 <sup>J</sup>	4.980 <sup>J</sup>
	72	5.341 <sup>J</sup>	4.847 <sup>L</sup>	3.062 <sup>M</sup>
	96	5.000 <sup>K</sup>	3.420 <sup>N</sup>	1.646 <sup>N</sup>
BSP	24	0.0001 <sup>L</sup>	0.0001 <sup>O</sup>	0.0001 <sup>Q</sup>
	48	0.0001 <sup>L</sup>	0.0001 <sup>O</sup>	0.0001 <sup>Q</sup>
	72	0.0001 <sup>L</sup>	0.0001 <sup>O</sup>	0.0001 <sup>Q</sup>
	96	0.0001 <sup>L</sup>	0.0001 <sup>O</sup>	0.0001 <sup>Q</sup>

Means in the vertical row with different superscripts are significantly different (pd<sup>0.05</sup>)

### Comparison of efficacy of bagasse materials

Statistical analysis for the comparison of efficacies of five different types of bagasse with respect to 8.126 mg/l Cr concentration is given in the Table 1. This shows that efficacies of all the five bagasse products with all the three doses were significantly different. From these analyses, it is evident that Cr removal was highest with BSP followed by BCP and BOP throughout the experiment. The interaction effect between duration and materials for Cr removal was also observed and it was found that in the case of BSP at all the three doses, there was no significant effect of duration on Cr removal and maximum removal was achieved at 3 g/l within 24 h. In the case of BOP at 3 g/l, Cr removal in 24 h was significantly different from other durations and there was no Cr removal during 48 to 96 h. Amount of Cr removal by BRF at 3 g/l after 72 h can be achieved using BOP at 3 g/l in 24 h.

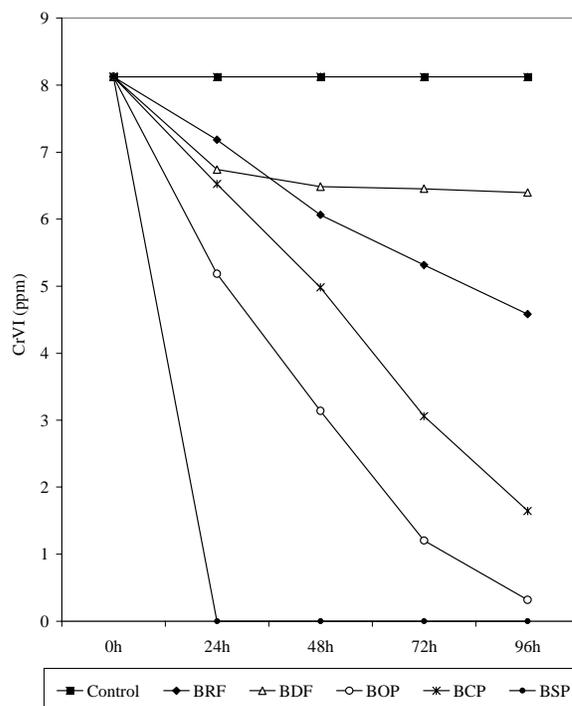


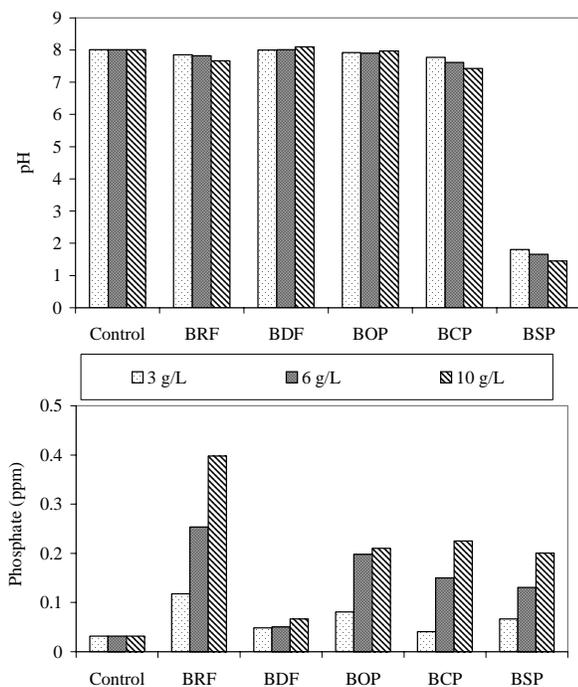
Figure 3

Effect of bagasse products @ 10 g/l on chromium(VI) removal

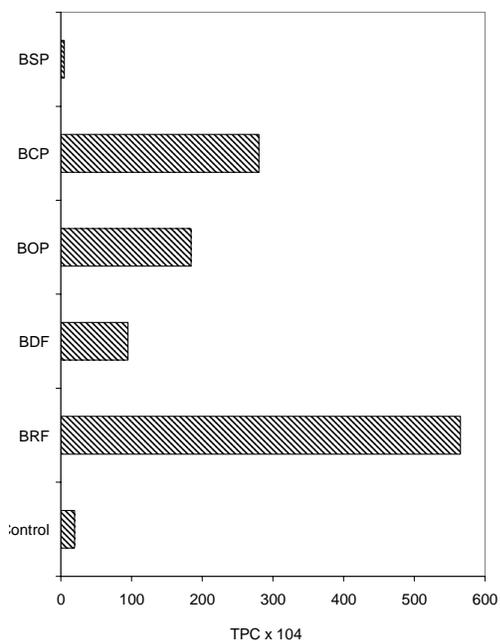
### Effect of bagasse materials on other water quality parameters

During the course of experiment, other water quality parameters such as salinity, nitrite and ammonia did not show many changes with treatments with BRF, BDF, BOP, BCP and BSP throughout the course of the experiment and they ranged from 34 to 36 g/l, 0.002 to 0.02 mg/l and 0.029 to 0.329 mg/l respectively. Effect of bagasse materials on pH and phosphates is presented in Fig. 4. This shows that there were not many changes in pH with the treatment with BRF, BDF, BOP and BCP at 3 to 10 g/l and it ranged from 8.01 to 7.42, whereas BSP at 3, 6 and 10 g/l decreased the pH from 8.01 to 1.8, 1.66 and 1.45 respectively. From this figure, it is evident that BRF, BDF, BOP, BCP and BSP at 3 g/l increased phosphate from 0.032 mg/l to 0.118, 0.049, 0.081, 0.041 and 0.067 mg/l. Phosphate levels were 0.254, 0.051, 0.198, 0.15 and 0.131 mg/l in the treatments with these materials at 6g/l and they were 0.398, 0.067, 0.21, 0.225 and 0.201 mg/l with the dose of 10 g/l respectively. Highest increase in total plate counts (TPC) was observed with BRF followed by BCP and BOP in alkaline medium, whereas in the case of BSP, TPC decreased in the acidic medium (Fig. 5).

Previous studies (Gerente et al., 2000; Reddad et al., 2002) have revealed that the lignocellulosic substrate is constituted by lignin and cellulose as its major constituents. Lignins bear functional groups such as alcohol, ketones and carboxylic groups that can be involved in complexation reactions with metallic cations. The removal of Cr (III) and Cr(VI) from aqueous solutions using sugar-beet pulp as a biosorbent substrate was performed by Reddad et al. (2003) under various experimental conditions and they found that Cr(VI) removal was largely involved in a reduction mechanism with the appearance of Cr(III) ions in the solution and the carboxylic groups of the biosorbent is the main reduction sites of Cr(VI) species. They also found that Cr (III) ions are adsorbed onto the biosorbent by ion-



**Figure 4**  
Effect of bagasse products on pH and phosphate in coastal water



**Figure 5**  
Total plate counts in coastal water treated with bagasse products

exchange mechanism with Ca<sup>2+</sup> cations neutralizing the carboxyl groups of the material. The influence of solution pH greatly affected the adsorption efficiency of Cr (VI) and the optimum removal resulting from the reduction mechanism was achieved at acidic pH values (Reddad et al., 2003).

In the present study also, bagasse charred with sulphuric acid (BSP) has been found to be most effective for the detoxification of

Cr(VI) in the acidic medium, which can be attributed to the reduction of Cr(VI) into Cr(III), whereas the removal of Cr(VI) in the treatments with other bagasse products in alkaline medium may be due to the reduction by increase in native microbial community. Oliver et al. (2003) have conducted a study to assess the potential for immobilising Cr (VI) using a native microbial community by reducing soluble Cr(VI) to insoluble Cr(III) under conditions similar to those in the vadose zone, and to evaluate the potential for enhancing biological Cr(VI) reduction through nutrient addition, and they have found that native microbial communities in subsurface sediments with no prior Cr(VI) exposure were shown to be capable of Cr(VI) reduction. In both the batch and column experiments conducted by Oliver et al. (2003), Cr(VI) reduction and loss from the aqueous phase were enhanced by adding high levels of both nitrate (NO<sub>3</sub>) and organic C (molasses).

## Conclusion

The present study showed that bagasse can be used for the effective removal of Cr (VI) from coastal waters. The removal of this carcinogenic toxicant was found to depend on materials, dosage and time. Bagasse charred with sulphuric acid (BSP), oven-dried bagasse powder (BOP) and charred bagasse powders (BCP) at 3 to 10 g/l are effective in decreasing Cr (VI) level within 24 to 96 h. Statistical data shows that amount of Cr (VI) removal by BRF and BDF at 3 g/l in 72 h can be achieved using BOP and BCP at 3g/l in 24 h respectively. Hence, from this study, it may be concluded that oven-dried bagasse powder (OBP) and charred bagasse powder (BCP) are effective products for the detoxification of Cr(VI) and there was no significant effect of these products on any of the other water quality parameters. Furthermore, bagasse is a biodegradable substrate, which harbours higher periphytic biomass than non-degradable ones. This could be because biodegradable substrates provide a better surface structure for periphytic species to attach to or they may leach nutrients beneficial for the growth of periphyton, which has more than one role in aquaculture. It improves fish/shrimp production and water quality, thus enhancing the efficiency of aquaculture systems. The very low cost of this lignocellulosic material is a real advantage that renders it a suitable alternative for the detoxification of Cr (VI) and successful studies on this material could be beneficial for the treatment of coastal water being used for aquaculture practices.

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