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Bioaccumulation of heavy metal chromium from Titanium industry effluent using egg shells as an adsorbent

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ABSTRACT

Egg shells was used as biosorbent to remove chromium from Titanium industry effluent, located in Trivandram. Laboratory experimental investigation was carried out to find out the binding of Chromium ions by eggshell was influenced mainly by pH with maximum sorption 13.07 ± 0.52 found in the effluent after adsorption at pH 7. The maximum was 28.18 ± 0.72 ppm metal up take by egg shell powder at room temperature and increasing temperatures decreased the Cr ion uptake.

Keywords: Titanium Industry effluent Biosorption; egg shell powder; Chromium uptake.

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INTRODUCTION

Heavy metals released into the environment by industrial activities tended to persist indefinitely circulating and eventually accumulating through the food chain, becoming a serious threat to the environment [1]. Adsorption has been found to be an efficient and inexpensive method for removing dyes, pigments, heavy metals and other colourants and for controlling. The biochemical oxygen demand. Activated carbon, inorganic oxides, mineral and natural adsorbents have been extensively used as adsorbents to treat wastewater [2]. Egg shells are a very reliable adsorbent due to its calcium carbonate content [3].

Investigations have been conducted to explore the possibility of useful applications of eggshells, especially for wastewater. The porous nature of egg shells makes it an attractive material to be used as an adsorbent. Each eggshell is estimate contain between 7000 and 17,000 pores [4]. Novel adsorbents based on eggshell functionalized with iron oxyhydroxide for phosphorus removal from liquid effluents [5]. Valorization of eggshell biowaste for sustainable environment remediation [6].

The main objective of this study was how efficient egg shell powder was in adsorbing heavy metal Cr at various different parameters such as pH and temperature.

MATERIAL AND METHODS

Egg shell powder was employed as biosorbent for the removal of Cr from titanium industry effluent.

Preparation of eggshell powder

Eggshells of common fowls were washed with tap water for several times and afterwards with distilled water for three times. Then, they were placed in the over at 40^{o}C to dry. The dried eggshells were ground to a powder and sieved to obtain 60 – 100 mesh size (0.025 – 0. 104 mm) particles. This powdered material was used as an adsorbent for the removal of chromium from titanium industry effluent.

Experimental Design

The experimental was designed to analyze the adsorptive potential of cheap bioresource, capable of entrapping Fe ions in the aquatic and semi aquatic media. The powdered adsorbent was mixed with the two different types of effluents (raw untreated and partially treated) in 5 different concentrations of 1, 2, 3, 4 and 5 mg/l. The medium was separately maintained at six different pH levels (0.5, 2, 4, 7, 8 and 9). The adsorbent was thoroughly mixed with the toxicant solution and the mixture was agitated once in 2 h. The initial concentrations of Fe were estimated in the two different effluents. The treatment was run for a period of 30 days. The Fe content of the treated effluents was estimated after 30 days of interaction with the adsorbent. The difference between the initial and final metal levels indicated the quantity adsorbed by the bioresource used.

The effect of temperature on the adsorptive potential of the materials used was estimated at pH7. For assessing the effect of temperature, the reaction mixtures were allowed to interact in a 250ml Erhlen-Meyer flask. The flasks were placed inside separate incubators maintained at 42, 32 and 28^{o}C. The experiments were continued for more than 60 days and the quantities of Fe was analyzed in the raw and partially treated effluent.

Estimation of heavy metal (Fe)

Samples were estimated for iron using atomic absorption spectrophotometer. A shimadzu type Atomic Absorption Spectrophotometer (AAS) 6300 model with Air-C2H2 flame type of an average fuel flow rate of between 0.8-4.0 L min-1 and the support gas flow rate between 13.5-17.5 L min-1 was used for sample analysis and operated as per the equipment manual. The single element hollow cathode lamps for respective metals were of Hamamatsu photonics co. Ltd-L24 33 series. The atomic absorption analysis standards for the given elements were purchased from Inorganic ventures Inc. and Sisco Research Laboratories Ltd. Calibration curves for various elements obtained from these standards were of first order reaction. The samples for Fe analyses were aspirated with the help of an Automatic sampler for Atomic Absorption Spectro photometer measurements. Series of reference standards -1, 2 and 3 ppm for the metal were prepared from the purchased stock solution. The standards were prepared by pipetting 0.1, 0.2 and 0.3 mL respectively of the metal reference standards and made up to 100 mL and mounted on the automatic sampler for standard calibration curve measurement. Percentage recovery rates of metals ranged from 94.8 to 102.3%. The samples were finally injected into the flame AAS and the readings were directly measured in a computer.

RESULTS AND DISCUSSION

Egg shell adsorbed maximum quantity of chromium at pH 7 and when 2g of the adsorbent was used, leaving behind 19.68 $\pm$ 0.84 ppm of chromium in the raw untreated effluent. At pH 9, adsorption of Cr was minimum and at 2 g egg shell concentration, the Cr concentration of the raw untreated effluent was 38.46 $\pm$ 0.75 ppm. At pH 7 adsorption with egg shell powder left behind 13.07 $\pm$ 0.52 ppm Cr in the raw untreated titanium industry effluent (Table 1).

Table 1: Adsorption of Cr from raw untreated titanium industry effluent by egg shell powder at different pH levels

S. No.	Amount (in g) of egg shell powder	Chromium in effluent (ppm) control	Cr concentration (ppm) in effluent					
			pH					
			0.5	2	4	7	8	9
1	1	51.87 ± 1.18	46.09 ± 0.45	43.80 ± 0.62	42.73 ± 0.49	23.03 ± 0.65 (-55.66)	32.31 ± 0.58	41.89 ± 0.85
2	2		44.27 ± 0.39	41.50 ± 0.58	39.52 ± 0.51	19.68 ± 0.84 (-62.13)	29.02 ±0.73	38.46 ± 0.75
3	3		41.21 ± 0.43	34.22 ± 0.78	32.14 ± 0.85	18.16 ± 0.91 (-65.06)	25.79 ± 0.74	36.14 ± 0.44
4	4		39.11 ± 0.56	35.25 ± 0.81	32.44 ± 0.58	14.75 ± 0.46 (-71.64)	23.81 ± 0.77	33.93 ± 0.79
5	5		36.71 ± 0.39	35.32 ± 0.66	31.64 + 0.47	13.07 ± 0.52 (-74.88)	21.49 ± 0.77	31.88 + 0.20

Note : Percent decrease in Cr concentration in parentheses

Deviations significant at P $\leq$ 0.05 (t-test)

When 3g of egg shell powder was used at 32^{o}C, 34.12 $\pm$ 0.69 ppm of chromium found in the raw untreated effluent after adsorption by the adsorbent. Adsorption was maximum at 28^{o}C only 7.46 $\pm$ 0.72 ppm found in the effluent compare to other temperatures (32^{o} C and 42^{o}C) (Table 2).

Dose of egg shell affected the removal of lead, because the removal efficiency of solutes increased with increasing dose of adsorbent [7]. Numerous studies have reported that the pore structure particularly affects by adsorption capacity [8]. Rivin and Kendrick [9] observed that the adsorption of Chromium increases with the decreases in temperature.

Das *et al.* [10] observed that egg shells were able to remove Cr (III) ions (100 mg/kg) at 40^{o}C at the adsorbent (egg shell) concentration of 15g. Egg shell powder is a cost effective with high adsorption capacity [11].

Egg shell powder effectively adsorbed chromium from the titanium industry effluent. Higher dosages of the adsorbent removed more quantities of Cr compared to low dosages. At acidic pH levels, the quantity of Cr adsorbed much less compared to neutral and alkaline pH levels. Thus pH plays a vital role and pH should be maintained at 7.0 to achieve maximum adsorption of Cr.

Temperature was another significant factor determining adsorption of heavy metals. At higher temperatures (42^{o}C) even 1g of adsorbent removed 55.1 percent of Cr from the titanium industry effluent at the ideal pH of 7.

Awual [12] observed that due to their porous structure eggshells have large specific surface areas; therefore, they are excellent biosorbents. The eggshell structure is uneven and granulated. One eggshell, which consists of 95 – 97% $CaCo_3$ crystals contains approximately 17,000 pores. Biotechnological applications of eggshell: recent advances was analysed by Ahmed *et al* [13].

Table 2: Adsorption of Cr from raw untreated titanium industry effluent at pH 7 egg shell powder at different temperature levels

S. .No	Amount (in g) of egg shell powder	Chromium in effluent (ppm) control	Cr Concentration (ppm) in effluent		
			Temperature (° C)		
			28	32	42
1	1	51.87 ± 1.18	18.92 ± 0.67 (-63.59)	38.60 ± 1.06	45.18 + 0.77
2	2		17.04 ± 0.81 (-67.22)	36.95 ± 0.69	43.82 ± 0.91
3	3		13.98 ± 0.67 (-73.13)	34.12 ± 0.69	40.14 ± 0.83
4	4		10.96 ± 0.59 (-78.96)	32.08 ± 0.53	37.69 ± 0.72
5	5		7.46 ± 0.72 (-85.71)	28.18 ± 0.72	36.05 ± 0.56

Note : Percent decrease in Cr concentration in parentheses
Deviations significant at $P \leq 0.05$ (t-test)

CONCLUSION

Titanium industry produces effluents rich in sulfuric acid, which affects the flora and fauna inhabiting the aquatic ecosystem that receive the effluent. The Titanium industry effluent is discharged as raw effluent from the main factory and it is subjected to primary waste treatment. Eggshells are cheaply refuses and hence were cost effective and accumulate chromium metal. So, from the results we can concluded that eggshell powder accumulated Cr ions. Only after the effluent becomes totally non -toxic it can be allowed into lotic or lentic habitats.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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