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A Biosorption of Heavy Metal Ions from Aqueous Solutions Using Fish Scale (*Catla catla*)

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Abstract: In recent years, heavy metals pollution has become one of the most serious environmental problems. With rapid development of many industries, wastes containing heavy metals are directly or indirectly being discharged into the environment. Biosorption is a cost effective excellent tool for removing heavy metals from the wastewater aqueous solutions. In this study, freshwater fish scale, inexpensive biowaste offers potential for the removal of metal ions by biosorption.

Key words: Fish scale % Wastewater % Biosorption % Heavy metals % Biosorbent

INTRODUCTION

Biosorption is a physico-chemical adsorption whereby metal ions become attached to the biomass surface [1]. The ability to adsorb metals has been investigated for many materials, including wool, rice, straw, coconut husks, peat moss [2], fungi [3], algae [4] and yeast [5]. The feasibility of using fish scale as a biosorbent to remove heavy metals was examined by Mustafiz [6]. Biological effects on adsorption of heavy metals such as lead, arsenic and chromium were studied using Atlantic cod scale [7]. Biosorption of Pb (II) by fish scale was studied by Raziya Nadeem *et al*., [8]. Metals are non-biodegradable and are considered as major environmental pollutants [9]. Literature survey reveals that several biological materials such as non living biomass like bark, lignin, peanut hulls as well as living biomass like fungi, bacteria, yeast, moss, aquatic plants and algae, were investigated for the removal of heavy metals [10-16]. Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake. Heavy metals released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment [17]. Biosorption is proven to be quite effective for the removal of metal ions from contaminated solution in a low cost and environment friendly manner [18]. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough to warrant further research [19]. In the present work, *Catla catla* fish scales are used as the biosorbent. More amounts of these scales are being generated from fish markets everyday and are thrown away as it is. This paper reports the potential of this biosorbent for removing the heavy metals from the synthetic wastewater aqueous solution. The biosorption activity of the fish scales was studied under various parameters such as effect of dosage, effect of time and the effect of pH. FTIR spectroscopy and SEM was used to find out the various functional groups present on the cell wall of the biosorbent as well to study the surface morphology of biosorbent.

MATERIALS AND METHODS

All the chemicals reagents used in these studies were of Analytical Reagent Grade, including concentrated reagents; HNO3, H_2SO_4, HCl, H_3PO_3 and Ca $(OH)_2$, NaoH (Merck) and Al $(OH)_3$.

Preparation of Biosorbent: *Catla catla* fish scales were collected from the local fish market, Chidambaram. Mature fish scales were washed repeatedly with water to remove adhering dust and soluble impurities from their surface. The fish scales were allowed to dry in sunshine for 2 days. The scales were then kept in an oven at 70°C till the fish scales became crispy. The dried scales were then converted into 100-150 mesh by grinding in a mechanical grinder. Then preserve the sample in polythene container for further use as biosorbent.

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Chemical Pretreatment of Fish Scales: For chemical pretreatment, 10 gm of sample was soaked in 150 ml of 0.1 M HCl, H_2SO_4, H_3PO_3, NaOH, Ca $(OH)_2$ and Al $(OH)_3$ for 2 hr in rotary shaker in 100 rpm at room temperature. The fish scales were filtered and washed with generous amount of deionised water until neutral pH was attained. Resulting biomass is used for the biosorption study.

Preparation of Synthetic Wastewater: The initial concentration used was 50 ppm for each of (chromium, iron, cobalt, zinc, cadmium, manganese, nickel, lead) and 100 ml in the standard flask. The pH of the synthetic wastewater was adjusted to a pH 5 to prevent hydrolysis.

Heavy Metals Analysis: The experiments were carried out for measurement of adsorption capabilities. The bottles with 500 ml capacity were filled with synthetic wastewater (50 ml) was mixed with fish scale. The bottles were shaken at room temperature in a reciprocating shaker for 24 hr at 300 rpm. Then the separation of the biosrobent and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans for determine the metal ion concentrations using an ICP-OES, Perkin Elmer (OPTIMA 2100 DV). This experiment is carried out by different concentration of dosage, pH and incubation time.

Instruments: The FTIR spectrum of the biosorbent was measured by using Perkin Elmer spectrum -RX1 system in the range of 400-4000 cm-1 and the scanning electron microscopy of the biosorbent was analyzed using JEOL-JSM-5610LV.

RESULTS AND DISCUSSION

Effect of Biosorbent Dosage in Wastewater Treatment: Various dosages of the prepared fish scales biosorbent have been used to treat the synthetic wastewater treatment. The parameters such as chromium, iron, cobalt, zinc, cadmium, manganese, nickel and lead has been decreased drastically with the increase in the biosorbent dosage. Hence 5 mg was found to be the optimum dosage in treating the wastewater (Table 1).

Table 1: Effect of biosorbent dosage in synthetic wastewater (50 ml) treatment

		Sample dose (mg/ml)				
Parameter	Initial concentration (mg/l)	1	2	3	4	5
Chromium (mg/l)	50	17.4	8.5	5.2	3.2	2.9
Iron (mg/l)	50	26	17	13	9	5
Cobalt (mg/l)	50	27	19	15	12	7
Zinc (mg/l)	50	26.7	22.5	12.5	8.4	5.5
Cadmium (mg/l)	50	29	21	15	9	7
Manganese	50	39	33	18	11	8
Nickel	50	44	35	31	26	22
Lead	50	41	32	26	22	17

Table 2: Effect of time in synthetic wastewater (50 ml) treatment

		Time (hrs)				
Parameter	Initial concentration (mg/l)	1	2	3	4	5
Chromium (mg/l)	50	17.4	8.2	5.3	2.8	2.1
Iron (mg/l)	50	22	18	14	8	6
Cobalt (mg/l)	50	25	16	11	7	6
Zinc (mg/l)	50	25.6	21.2	13.8	7.6	3.4
Cadmium (mg/l)	50	44	33	26	17	8
Manganese	50	36	31	16	10	6
Nickel	50	42	33	30	24	17
Lead	50	44	37	24	20	16

Table 3: Effect of pH in synthetic wastewater (50 ml) treatment

		pH				
Parameter	Initial concentration (mg/l)	5	6	7	8	9
Chromium (mg/l)	50	27.4	20.3	9.3	12.2	18.3
Iron (mg/l)	50	33	21	6	12	18
Cobalt (mg/l)	50	26	15	8	11	14
Zinc (mg/l)	50	29.4	21.4	8.4	10.4	15.5
Cadmium (mg/l)	50	34	29	12	14	18
Manganese	50	42	36	15	18	20
Nickel	50	43	37	22	25	28
Lead	50	40	35	19	23	26

Effect of Time in Wastewater Treatment: Effect of time on the treatment of wastewater treatment by the fish scales. On increasing the time, the initial concentration reduces. After the treatment for 5 hours all the heavy metals concentration at significant level. Hence 5 hours was found to be an optimum treatment time (Table 2).

Effect of pH on Wastewater Treatment: The reduction of all the heavy metals in the wastewater by the fish scale biosorbent was found to be pH dependent. Results showed that there was maximum adsorption of all the parameter in the effluent by fish scale biosorbent at pH 7 and hence pH 7 was found to be better on treating the wastewater (Table 3).

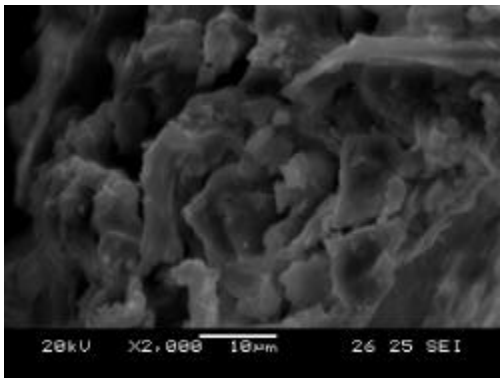

Fig. 1: Scanning electron microscopy structure of *Catla catla*

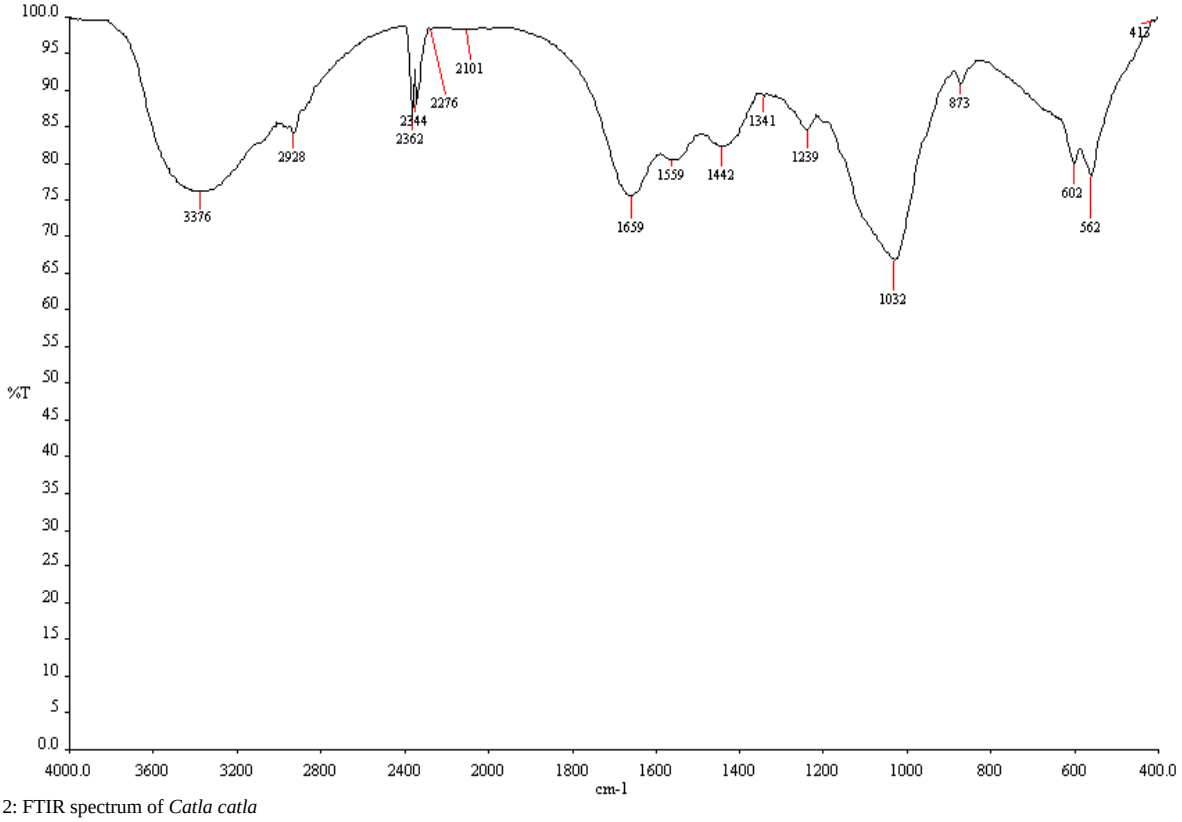

Fig. 2: FTIR spectrum of *Catla catla*

Table 4: FTIR spectrum represented functional group

S. No	Band position	Functional groups
1	3376 cmG¹	Stretching vibration of O-H and N-H groups
2	2928 cmG¹	C-H stretching vibrations of -CH3 and -CH2
3	2344 - 2362 cmG¹	Carboxylic
4	1659 - 1559 cmG¹	Carbonyl
5	1442 - 1341 cmG¹	C-H, -CH3 and -CH2
6	1032 cmG¹	C-O
7	873 cmG¹	Sulphonate group
8	562 cmG¹	Alkanes

Scanning Electron Microscopy: Scanning electron microscopy has been used by many researchers for the characterization of the biosorbent. SEM micrographs obtained for catla scales as seen in the micrograph (Fig.1). The white region is rich in inorganic material containing high proportions of calcium and phosphorus whereas the dark region is rich in proteins, because it has a high proportion of carbon, oxygen and sulphur.

Fourier Transforms Infrared (FTIR) Spectroscopy: Different chemical functional groups such as carboxyl, hydroxyl, amide etc. are responsible for biosorption of metal ions [20-23]. These functional groups are the potential sites for adsorption and the uptake of metal depends on various factors such as abundance of sites, their accessibility, chemical state and affinity between the adsorption site and metal. The FTIR spectroscopy is an important analytical technique which detects the vibration characteristics of chemical functional groups present on adsorbent surfaces. The biosorbent spectra were measured by using Perkin Elmer spectrum -RX1 system in the range of 400-4000 cmG¹. FTIR spectra of *Catla catla* scale is shown in Figure (2). The represented functional group in the FTIR spectrum was given in the Table (4).

CONCLUSION

This paper reports the potential of this fish scale (*Catla catla*) biosorbent for removing the heavy metals from the synthetic wastewater aqueous solution. The biosorption activity of the fish scales was studied under various parameters such as effect of dosage, effect of time and the effect of pH. At pH 7 in the dosage of 5 mg/l and at the time of 5 hour, the biosorbent show significant result has been found. FTIR spectroscopy and SEM was used to find out the various functional groups present on the cell wall of the biosorbent as well to study the surface morphology of biosorbent. So the fish scale act as a biosrobent and it can be used for wastewater treatment at industrial level.

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