

Biosorption Studies of Copper, Chromium, Lead and Zinc Using Fins of Catla Catla Fish

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Abstract: *The discharge of heavy metals from industrial effluents into the environment is a major concern today due to its toxicity and persistence in the environment. The present work deals with the removal of heavy metals i.e. Copper, Chromium, Lead and Zinc ions from aqueous solutions using fins of Catla catla fish. The effect of varying conditions in aqueous solution like pH, contact time, temperature, initial metal concentration, turbidity and biosorbent dosage on the biosorption processes was studied. Further, the biosorbent was used to remove heavy metals from different industrial effluents. The percentage removal of heavy metal ions from the industrial effluents using fins of Catla catla fish as a biosorbent were found in the following range: Copper ions (32.95 - 99.34 %), Chromium ions (26.64 - 100 %), Lead ions (19.85 - 56.06 %) and Zinc ions (30.01 - 99.24 %). The heavy metal concentration in aqueous solutions was estimated using ICP-AES and the structural characteristics of the biosorbent was determined by using Fourier Transform Infrared Spectroscopy (FT-IR) analysis. The adsorption isotherm studies were carried out using Freundlich and Langmuir isotherm models. It was observed that fins of Catla catla which is thrown from fish market as wastes, have the capacity to remove heavy metals from aqueous solution and hence it can be used to remove heavy metals from industrial effluents.*

Keywords: *Biosorption, fins of Catla catla fish, Heavy metals, FT-IR, ICP-AES, Freundlich and Langmuir isotherm.*

I. INTRODUCTION

India is rich in water resources, having a wide network of rivers that fulfil water requirements of the country. However, with the rapid increase in the industrialization and urbanization, the water quality has deteriorated. This is due to uncontrolled discharge of industrial effluents which is witnessed by many parts of the world. Among the pollutants, heavy metals discharge in industrial effluents has received special attention because of its toxicity and persistence in the environment.

The various human activities through which heavy metals reach the environment include smelting or processing of ores of metals, mining, discharge of agricultural, industrial and domestic waste, burning of fossil fuels (*viz.* coal, petrol and kerosene oil), auto exhaust, and pesticides containing compounds of heavy metals [1]. Various industries such as mining and smelting, energy fuel production, fertilizer and pesticide industry, metallurgy, electroplating, electrolysis, photography, aerospace, atomic energy installations, etc. produce and discharge wastes containing different heavy metals into the environment. Thus, metals are responsible for serious environmental pollution, threatening human health and environment [2].

In humans, heavy metal toxicity can cause chronic degenerative diseases like mental disorders, pain in muscles and joints, gastro intestinal disorders and vision problems. Genotoxicity and cancer can also occur. Sometimes the symptoms are vague and difficult to diagnose at early stage. Industrial workers, malnourished people, pregnant women and populations living near the polluted industry are more susceptible to show heavy metal toxicity. Data of CPCB shows that in India, Gujarat, Maharashtra and Andhra Pradesh contribute to 80% of hazardous waste including heavy metals [3].

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [4]. But the disadvantages of such techniques include incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal. [5]. The search for new technologies to remove toxic metals from wastewaters has directed attention to biosorption process. Earlier studies in environmental biotechnology have shown that many organic materials occurring in the environment have the capacity to remove heavy metals from solutions by the process called as Biosorption [6]. Biosorption may be simply defined as the removal of substances from solution by using biological material. Such substances can be organic or inorganic and in soluble or insoluble forms [7]. The major advantages of biosorption over conventional treatment methods include low cost, high

efficiency, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent, possibility of metal recovery [5].

Several researchers have reported the removal of heavy metal through algae, marine algae, bacteria, yeast and higher plants in immobilized as well as in free state [8]. Agricultural residues are usually composed of lignin and cellulose as the major constituents with other polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids and ethers that facilitate metal complexation resulting biosorption of heavy metal ions from wastewater [9], [10]. They are economical, eco-friendly and abundantly available and hence are viable option for heavy metal remediation [11].

The removal of Chromium from electroplating industry was carried out successfully using paddy straw, pineapple crown, corn husk, coconut palm fiber as biosorbent [12]. Another study of chromium removal using watermelon rind was reported which showed 176.2 mg/gm of Cr ions [13]. Not much of the work is reported on biosorption of heavy metals using fins of *Catla catla* fish. Hence, the present work aims to explore biosorptive capacity of fins of *Catla catla* fish.

II. MATERIALS AND METHODS

A. Preparation of metal solutions

Stock solutions (1000 mg/l) of heavy metal ions, i.e. Copper, Chromium, Lead and Zinc were prepared by dissolving analytical grade of respective metal salts viz. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, K_2CrO_4 , $\text{Pb}(\text{NO}_3)_2$, ZnO in deionized water. The standard solutions were prepared by diluting the stock solutions to appropriate volumes using deionized water.

B. Preparation of Biosorbent

The fins of *Catla catla* fish were collected from local fish market. The fish fins were washed with distilled water for multiple times to remove adhering dust particles. It was then oven dried at 80°C till crispy (Fig 1a). The dried materials were grounded into fine powder (Fig 1b). The powdered material was stored in airtight polythene bags till further use.



Fig 1 Fins of *Catla catla* fish (a) oven dried (b) powdered form

C. FT-IR characterization

The FT-IR analysis of biosorbent before and after biosorption process was carried out. The powdered sample and KBr was grounded in the ratio of 1:10 and was pressed under vacuum to get thin transparent pellets and analyzed using FT-IR. This study will help us to find the functional groups present on the biosorbent which may help in binding to heavy metals.

D. Biosorption studies

Biosorption experiments were conducted by adding appropriate weight of adsorbent biomass to 100 ml of metal salt solutions of known concentration. The flasks were shaken intermittently to maintain the biosorbent in the solution. The solution was then filtered using Whatmann filter paper No. 1. The metal concentration of the filtrate was then carried out using ICP-AES analysis. The biosorption capacity (Q_e), and the percent removal of metals were calculated as follows:

$$Q_e \text{ (mg/gm)} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\text{Metal Removal (\%)} = \frac{m}{C_0} \times 100 \quad (2)$$

where C_0 = Initial metal concentration before biosorption process (mg/l),

C_e = Final metal concentration after biosorption process (mg/l),

V = Volume of solution (L)

m = Mass of biosorbent (gm) [12].

The effect of different conditions of aqueous solution like pH, temperature, initial metal concentration, turbidity, contact time and biosorbent dose on the biosorption processes were studied by conducting following experiments.

- 1) *Effect of pH:* Stock solutions of heavy metal salts viz. Copper, Chromium, Lead and Zinc were diluted using deionized water to obtain 100 ml of 50 mg/L of each metal solutions. The pH of the metal salt solutions was adjusted to 2, 4, 6, 8 and 10. The biosorption process was studied at room temperature after adding 1% biosorbent to the metal salt solutions for 60 minutes. The solutions were then filtered using Whatmann Filter Paper No. 1 and metal concentration of the filtrate was estimated using ICP-AES.
- 2) *Effect of biosorbent dosage:* 100 ml of 50 mg/L of each metal salt solutions were prepared by appropriate dilution of stock solution of metal salts using deionized water and biosorption process was studied at room temperature at pH 8. The heavy metal solutions were treated with different doses of biosorbent like 0.5, 1, 2, and 3% and kept for 60 minutes. The solutions were then filtered and metal concentrations of the filtrate were estimated using ICP-AES.
- 3) *Effect of contact time:* Stock solutions of heavy metal salts were diluted to obtain 100 ml of 50 mg/L of each metal solutions using deionized water and biosorption process was studied at room temperature. The pH of the solutions was maintained at 8 and 1% biosorbent was added to the solutions. The biosorption process was studied for different time periods like 60, 120 and 180 min. The solutions were then filtered and metal concentrations of the filtrate was estimated using ICP-AES.
- 4) *Effect of initial metal concentration:* Stock solutions of metal salt solutions were diluted using deionized water to obtain 100 ml each of 10, 50 and 100 mg/L of metal salt solutions and biosorption process was studied at room temperature. The other conditions maintained were pH 8, contact time for 60 minutes and 1% biosorbent dose. The solutions were then filtered and metal concentrations of the filtrate was estimated using ICP-AES.
- 5) *Effect of temperature:* Stock solutions of metal salts were diluted using deionized water to obtain 100 ml of 50 mg/L of metal salt solutions and biosorption process was studied by exposing the solutions to different temperatures like 10°C, 30°C and 50°C for 60 minutes. The other conditions maintained were pH 8 and biosorbent dosage as 1%. The solutions were then filtered and metal concentrations of the filtrate was estimated using ICP-AES.
- 6) *Effect of turbidity:* Stock solutions of the metal salts were diluted using deionized water to obtain 100 ml of 50 mg/L of metal salt solutions and biosorption process was studied at 30°C. Turbidity of solution were adjusted to 10-100 NTU using hexamine and hydrazine sulphate solutions mixture. The other conditions were pH 8, contact time for 60 minutes and 1% biosorbent dose. The solutions were then filtered and metal concentrations of the filtrate was estimated using ICP-AES.
- 7) *Application to real Industrial Effluents:* The effluents from different industries like textile industry, paper mill industry, electroplating industry, powder dusting industry and chemical industry were tested for removal of heavy metals under study by using biosorption process. The effluent samples were digested with nitric acid followed by metal analysis using ICP-AES.
- 8) *Adsorption Isotherm Studies:* Batch experiment was carried out at 30°C. 100 ml of each metal salt solutions of known concentration was treated with 1% biosorbent and pH was maintained at 8 for all metal salt solutions and contact time was varied from 30- 240 minutes. After equilibrium was reached the adsorbent was separated from metal solutions using Whatmann filter paper no 1. The metal concentration of the filtrate was estimated using ICP-AES. The Adsorption Isotherm study was carried out using Freundlich and Langmuir Isotherm models.

The linear form of Freundlich Isotherm is

$$\text{Log (Ce/m)} = \text{log } K_f + (1/n) \text{ log } C_e \quad (3)$$

Where, (C_e/m) = Moles sorbed at equilibrium per mass of sorbent (mg/g)

K_f = Freundlich isotherm constant (L/g)

$1/n$ = Measure of adsorption intensity

C_e = Sorbate concentration in solution at equilibrium (mg/L)

The linear form of Langmuir isotherm is

$$Ce/Qe = 1/q_m K_L + Ce/q_m \quad (4)$$

Where, Q_m = Maximum sorption capacity of the sorbent (mg/g)

K_L = Adsorption constant related to binding energy of sorbate (1/mg)

Q_e = Moles sorbed at equilibrium per mass of sorbent (mg/g)

III. RESULTS AND DISCUSSION

A. FTIR Characterization

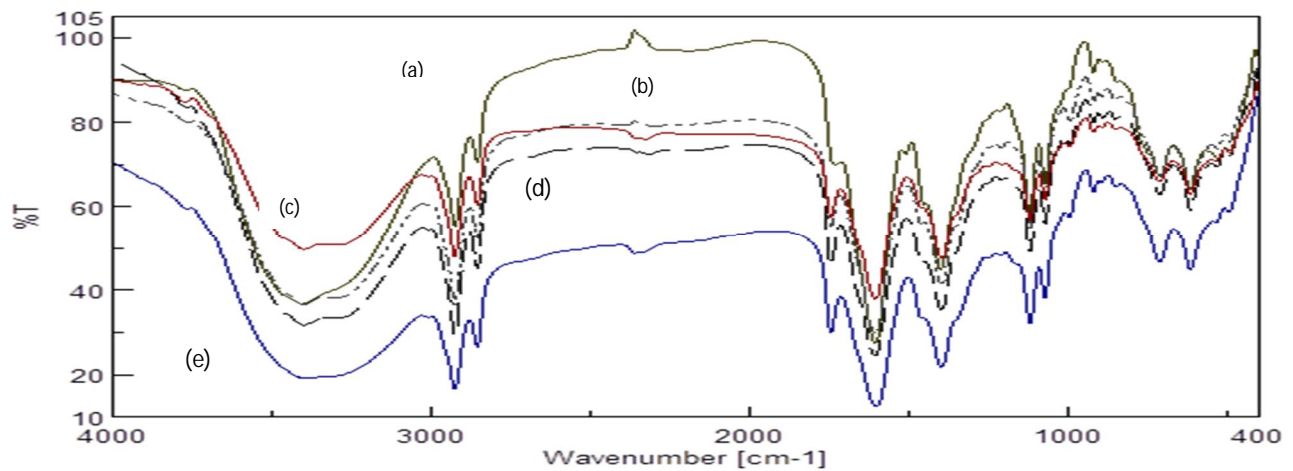


Fig. 2 FTIR spectra (a) Initial biosorbent (b) Lead (c) Zinc (d) Chromium (e) Copper, loaded biosorbent

The following table shows shift in the wavenumbers which may be due to binding of metal ions to the functional group present on the surface of biosorbent.

Table 1: Shift in Wavenumbers Due To Biosorption Process

Wavenumber (cm ⁻¹)					Functional group (str.)
Intial	Lead loaded	Zinc loaded	Chromium loaded	Copper loaded	
3406.64	3396.99	3401.82	3402.78	3402.78	-NH-
2925.48	--	--	2926.45	--	-CH ₂ -
2854.13	2855.1	2855.1	2855.1	2855.1	
1729.83	1743.33	1743.33	1743.33	1743.33	>C=O bending
1604.48	1601.59	--	1603.52	1603.52	
1449.24	--	--	1460.81	--	
1399.1	1396.21	1396.21	1393.32	1393.32	
1118.51	1116.58	1117.55	1117.55	1117.55	
917.95	--	916.986	--	--	-CH-
889.023	847.561	848.525	847.561	847.561	trans bending
708.712	--	709.676	--	--	-CH- cis bending
614.217	613.252	613.252	613.252	613.252	>C=O bending
527.436	--	529.364	--	--	Mineral carbonates
488.886	490.795	--	--	--	

The above table shows shift in the wavenumbers of the peaks associated with the metal load on the surface of the biosorbent as shown in the FTIR plots (Fig 2) by comparing the initial adsorbent with metal loaded adsorbents. These shifts in the wavenumbers showed that there was a metal binding process taking place at the surface of the adsorbent. In some cases, the unsaturated group like alkene, carbonyl group was also responsible for adsorption of metals on the foresaid adsorbents which was

inferred from the shift of the peak more than 10cm^{-1} like vibration of 1449.24 cm^{-1} to 1460.81 cm^{-1} due to binding of chromium to $>\text{C}=\text{O}$ group present on the surface of the biosorbent. The adsorption of metals on the said adsorbent was also confirmed by increase in the absorbance of metals at the respective wavenumbers (Fig 2).

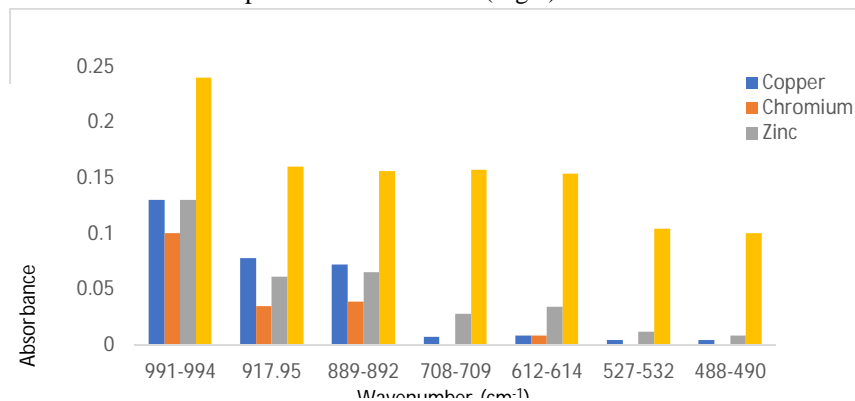


Fig 2 showing change in absorbance w.r.t. wavenumber due to treatment with metal ions

B. Effect of pH

Metal adsorption depends on the nature of the adsorbent surface and species solution. At lower pH, H^+ competes with metals for the exchange sites in the system thereby partially releasing the latter. The heavy metals are completely released under circumstances of extreme acidic conditions [14]. The amount of adsorption was minimum at pH 2 and increased with increase in pH of the solution. The maximum adsorption occurred at pH 8 for all four metal ions under study. But the adsorption was decreased with increase in pH to 10 (Fig. 4f). The minimum adsorption at low pH may be due to the higher concentration and high mobility of H^+ ions leading to H^+ ions preferentially adsorbed over metal ions. Further increase in pH increases the hydroxyl ion concentration in the solution thereby precipitating metals as their hydroxides. Hence, solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent.

C. Effect of adsorbent dose

The dosage of biosorbent was also found to be the factor influencing biosorption process. It was observed that as the dose of the biosorbent increased up to 1%, the biosorption rate increased. Further, the biosorption rate decreased with increase in biosorbent dose to 3% (Fig. 4e). This may be probably due to high biomass which led to the crowding and thus protecting the active sites from being occupied by the metal [15].

D. Effect of Contact time

Studies have shown that as contact time between biosorbent and metal solution increases, the biosorption efficiency also increases [16]. Here, the biosorption efficiency of fish fins increased with contact time from 60 min to 180 min (Fig. 4a). This may be because the more the biosorbent is in contact with the metal solution, the more is the chance of the metal to bind to the adsorbent. This indicates that contact time also influences biosorption process.

E. Effect of temperature

According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier tend to desorb from the surface at elevated temperature [17]. This was found to be true in the present study. The biosorption process increased with temperature rise from 10°C to 30°C but further increase in temperature to 50°C led to decrease in biosorption process (Fig. 4c). This may be because with the increasing temperature the attractive forces between biomass surface and metal ions are weakened and sorption decreases.

F. Effect of turbidity

As the turbidity of the metal solution increased from 10 NTU to 100 NTU, there was decrease in biosorption process (Fig. 4d). This may be due to positively charged metal ions getting adsorbed to the negatively charged ions of the turbid solution, thereby rendering them unavailable for the biosorption process. Similar observation was reported by [18].

G. Effect of initial metal concentration

The initial metal concentration plays an important role in biosorption process. As the metal concentration increased from 10 ppm to 100 ppm, there was decrease in biosorption process (Fig. 1b). This may be probably due to saturation of binding sites on biosorbent beyond the particular metal concentration. Similar result was obtained by [15] using *Spirulina platensis* biomass for biosorption of copper ions.

H. Application to real effluents

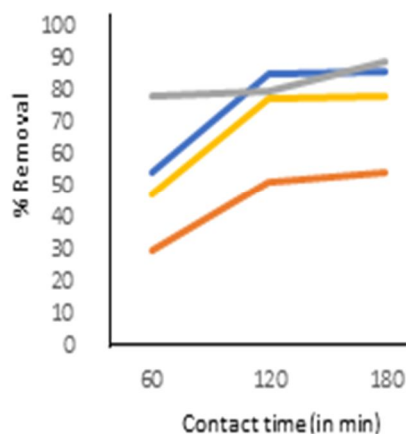
The fish fins of *Catla catla* was capable of removing heavy metals from all five industrial effluents. The removal of heavy metals was 100% in the case of effluents bearing low metal concentration. The electroplating industry showed less removal of metals as compared to other samples. This may be because of other metal ions present in the effluent samples which might have interfered with the biosorption process.

I. Adsorption Isotherm study

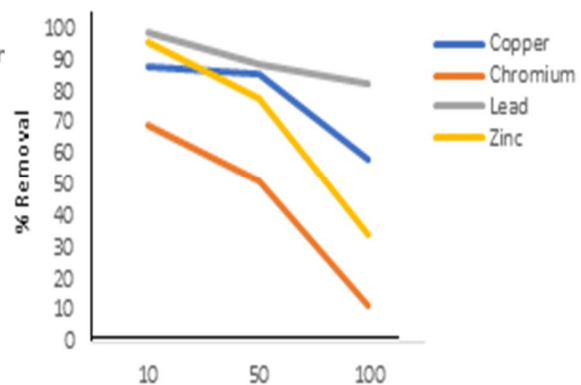
Equilibrium sorption isotherms are used to describe the capacity of the biomass in terms of the constants whose values expresses the surface characteristics and affinity of the biomass. This study helps us to understand equilibrium correlation between adsorbate concentration, mass loading, adsorbent dose and equilibrium concentration of the adsorbate at selected temperature [19]. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface [20]. The graphs are not included in the paper. The following table shows Freundlich and Langmuir constants

Table 2: Table Showing Constants For Isotherm Studies

	Freundlich Isotherm		Langmuir Isotherm	
	R_F^2	K_f	R_L^2	Q_{max}
Copper	0.8599	1.3598	0.9013	1.7232
Chromium	0.905	2.1528	0.853	0.9851
Lead	0.8789	0.9034	0.9782	3.003
Zinc	0.8939	1.5274	0.9275	2.4783



(a)



(b)

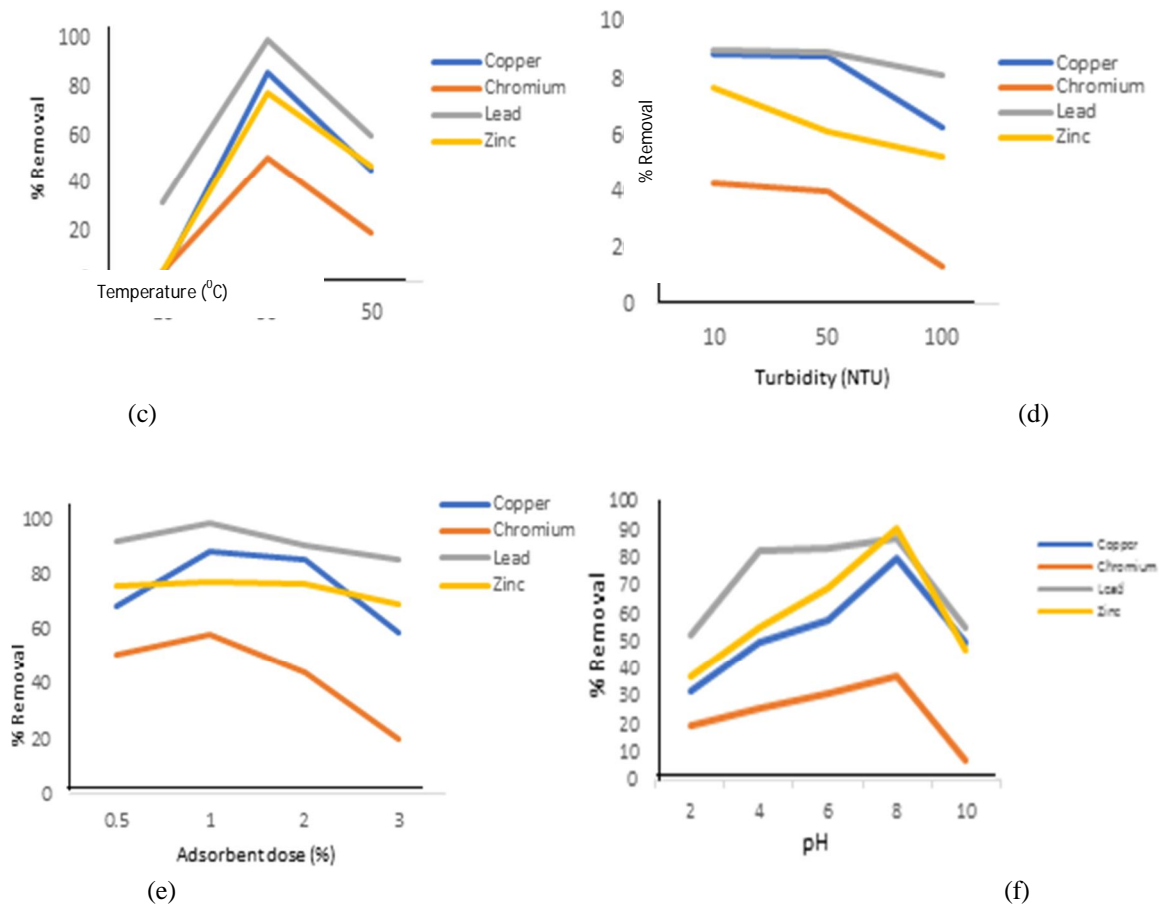


Fig. 4 Effect of different parameters on biosorption process (a) Contact time (b) Initial metal Concentration (c) Temperature (d)zTurbidity (e) Adsorbent dose (f) pH

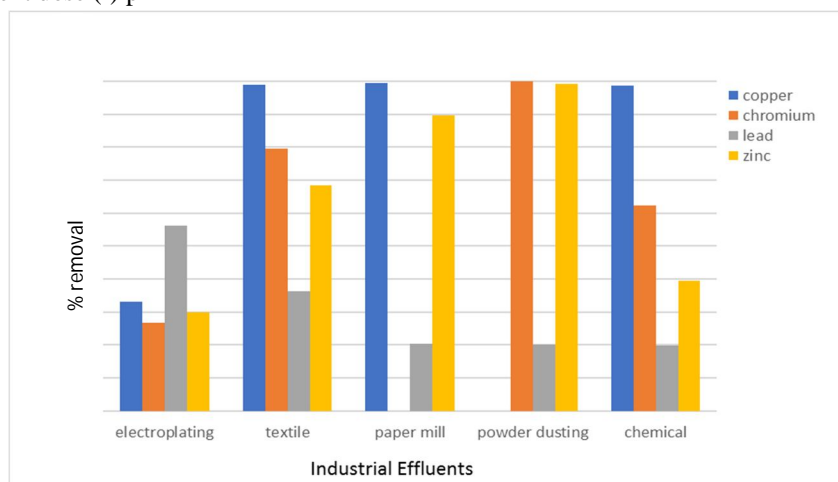


Fig. 5 Removal of Heavy metals from industrial effluents by biosorption process

IV. CONCLUSION

The removal of heavy metals (Copper, Chromium, Lead, Zinc) from aqueous solutions were studied using fins of *Catla catla* fish which was collected from local fish market. The present study showed that biosorption process was dependent on different



conditions like pH, temperature, adsorbent dose, turbidity, contact time, initial metal concentration in the aqueous solution. The optimum removal of heavy metals was shown at pH 8, temperature 30°C, contact time 180 min and using 1% adsorbent dosage for all the heavy metals. Also, the removal of Lead was found to be maximum while that of Chromium removal was minimum. The application of biosorbent to different industrial effluents showed removal of heavy metals from all the industrial effluent samples under study. The Adsorption isotherm studies showed that Freundlich model fits for biosorption of chromium showing heterogenous adsorption whereas Langmuir model showed good fit for biosorption of Copper, Lead and Zinc using fins of *Catla catla* fish. Hence, it can be concluded that fish wastes such as fishfins of *Catla catla* discarded from fish markets have the potential to adsorb heavy metals and this may help in finding the industrial application of solid wastes like fishfins for the removal of heavy metals.

V. ACKNOWLEDGMENT

The authors are thankful to the SAIF Department, Indian Institute of Technology-Bombay for their kind support during the analysis of heavy metals using ICP-AES and Department of Nanotechnology, Birla College of Arts, Science and Commerce, Kalyan for using FT-IR.

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