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Removal of Zinc and Ferum Ions using *Tilapia Mossambica* Fish Scale

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Abstract: Wastewater contains large amount of contaminants, especially heavy metals, organic toxicants, and human pathogens. Heavy metal contamination had become major problem in water pollution. The use of current treatment causes some drawback even though major pollutant in wastewater already removed. Removal of zinc and ferum from synthetic wastewater using *Tilapia* fish scale as biosorbent was studied. This study was focused on batch method by varying pH, biosorbent dosage, contact time and initial metal ion concentration. Adsorption characteristic of fish scale before and after treatment were analysed by Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF), and Fourier Transform Infrared (FTIR) while concentration of zinc and ferum ions was obtained by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), respectively. The maximum percentage removal was found at 93.52% of zinc ion and 65.9% of ferum ion under best optimum adsorption conditions: pH = 6, 4.5, biosorbent dosage = 0.02 g/100 mL, 0.8 g/100 mL, concentration = 10 ppb, 300 ppb and 3 hours contact time for ferum and zinc. The finding indicated that promising biosorption of zinc and ferum ions using *Tilapia* fish scale as biosorbent.

Keywords: Zinc, ferum, biosorbent, synthetic wastewater

1. Introduction

Heavy metals such as zinc and ferum ions or their compounds have been used by many industrial processes, for example mining, metal plating, chemical industries, and battery manufacturing. The discharge of these industrial effluents into water course resulted in heavy metal contamination in aquatic ecosystems. Due to the fact, the presence of these metals in large quantities will interfere with utilization of water [1,2].

Currently, the uses of conventional method have been applied to remove heavy metal from wastewater. Conventional wastewater treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic matter and, sometimes, nutrients from wastewater. Treatments such as ion exchange, membrane technologies and adsorption on activated carbon are particularly costly. Moreover, such methods create large amounts of sludge to be treated with great problems [3,4].

In recent years, biosorption has emerged as a new technology which has distinct advantages over current treatment methods. Biosorption of heavy metals occurs as a result of physicochemical interactions, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface [5]. It has the natural potential of the biomass to immobilize dissolved components for instance, heavy metal ions, on its surface [2].

Various biosorbents have been applied by using low cost biomaterials for removing heavy metal. However, only biomass with high metal binding and selectively for heavy metal are suitable for biosorption process. The most challenging part is to choose promising biomass from a variety of available and inexpensive biomaterial. A number of fish scale namely *Labeo Rohita*, *Catla catla*, and *Atlanic Cod* had been reported and give promising results of heavy metal removal [6-8]. Although different potential biomasses have been investigated, little research is known for the use of *Tilapia* fish scale in heavy metal removal. Thus, the *Tilapia* fish scale is choosed in this research as a potential biosorbent for heavy metal removal.

2. Characteristic of Municipal Wastewater Treatment Plant UTHM

Table 1 shows the concentration of zinc and ferum ions in municipal wastewater treatment plant UTHM for two months. The concentration of heavy metals was analysed by ICP-MS. The results show concentration follows the order Fe > Zn. Zinc and ferum ions had been selected for further study for heavy metals removal by *Tilapia* fish scale. From the results, normalization of concentration and biosorbent dosage had been made to obtain a suitable working range of parameters for this study.

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Table 1 Concentration of heavy metals in municipal wastewater.

Heavy metal	Concentration of heavy metal (ppb)
Ferum	313.536 – 624.991
Zinc	9.558 – 16.570

3. Materials and Methods

3.1 Preparation of Fish Scales

Fish scales of *Tilapia* were selected as biosorbent in this study. Fish scales were obtained from the fish market in Parit Raja, Batu Pahat. 15% of nitric acid were used to remove adhering dust and soluble impurities from the surface for 24 hours and store in thick plastic container. Fish scales were soaked together with distilled water for further clean up for a minimum of 24 hours and dried at room temperature for a day before kept in an oven at 60 °C. The fish scales were kept in an oven until it became crispy for two months. The dried fish scales were ground by using a mortar grinder at 500 rpm for every 30 minutes. Then, pulverised fish scales were sieved through 100 mesh to obtain 150 µm of particle size [8,9].

3.2 Preparation of Aqueous Solution

Zinc and ferum ions solution were prepared by dissolving 0.440 g of zinc sulphate and 0.484 g of ferric chloride into 100 ml ultra pure water to produce 1000 ppm of each solution, respectively. The aqueous solutions were diluted from 1000 ppm to the desirable concentration. The reagent used in this study was of analytical reagent grade.

3.3 Experimental Design

All experiments were conducted using the batch method of varying pH, fish scale dosage, contact time, and initial metal ion concentration to determine the maximum removal of heavy metals. All samples were shaken at 125 rpm. Table 2 shows the range for each parameter for zinc and ferum ion. Biosorbent were filtered through 0.45 µm filter paper and kept in an airtight container for further analysis of Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FTIR). Finally, the supernatants were kept in airtight plastic bottles and analysed by using ICP-MS.

4. Results and Discussion

4.1 X-Ray Fluorescence (XRF)

Table 3 shows XRF analysis of fish scales use in this study. XRF was conducted to verify the absence of ferum and zinc ions in preparation of biosorbent. From the results, CaO has the highest chemical compound with 63.8% followed by P_2O_5 at 32.0%. The present of CaO confirms that high potential of fish scale to adsorb heavy metals. A clean biosorbent is important to enhance the efficiency of the biosorption process.

Table 2 Working range of zinc and ferum ions.

Heavy metal	pH	Biosorbent dosage (g)	Contact time (hr)	Initial metal ion concentration (ppb)
Zinc	5, 5.5, <u>6</u>, 6.5	0.01, <u>0.02</u>, 0.025, 0.035, 0.040	0.5, 1, 2, 2.5, <u>3</u>, 4	<u>10</u>, 11, 12, 13, 14
Ferum	4,<u>4.5</u>, 5, 5.5, 6	0.6, <u>0.8</u>, 1.1, 1.3, 1.6	0.5, 1, 2, 2.5, <u>3</u>, 4	<u>300</u>, 400, 500, 600, 700

*underline indicate optimum condition [9]

Table 3 Chemical Composition and Concentration of Fish Scales.

Formula	Concentration
original-g	7
added-g	3
CO_2	0.10%
CaO	63.80%
P_2O_5	32.40%
SO_3	2.64%
MgO	0.24%
SiO_2	0.24%
Na_2O	0.21%
SrO	0.17%

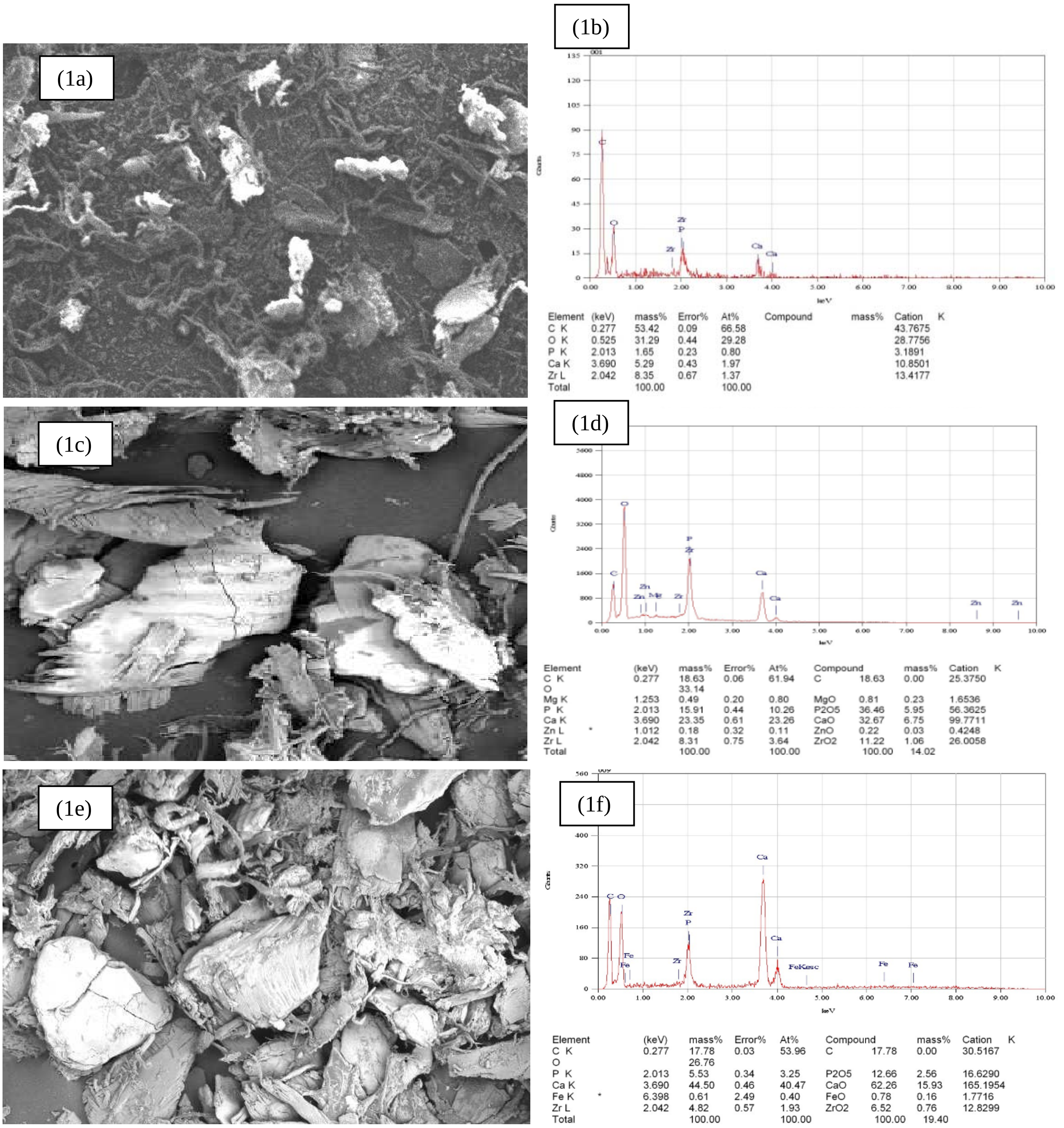
4.2 Scanning Electron Microscopy (SEM)

SEM was used to characterize biosorbent before and after biosorption takes place. Fig. 1a shows SEM micrographs of *Tilapia* fish scale before biosorption of heavy metals (native biosorbent). From the figure, fish scale is characterized by having two regions, one being darker and the other being white. The white region is rich in inorganic material containing a high proportion of calcium and phosphorus whereas the dark region is rich in protein because it has a high proportion of carbon and oxygen. The fish scale also appears to have a rough surface [8]. EDX analysis of native biosorbent biosorption shows no present of zinc and ferum in the biosorbent (Fig. 1b).

Zinc and ferum ions loaded biosorbent is shown in Fig. 1c and Fig. 1e. EDX analysis after biosorption also verifies the presence of zinc and ferum ions in the biosorbent (Fig. 1d and Fig. 1f). This micrograph clearly shows the presence of new shiny bulky particles over the surface of heavy metals loaded biosorbent which is absent in the native biosorbent [8]. These results confirm the binding of metal ion in fish scale through biosorption process.

4.3 Fourier Transform Infrared (FTIR) Analysis

Fig. 2 shows FTIR spectra of fish scale before and after heavy metals adsorption. FTIR spectra of native biosorbent (Fig. 2a) show peaks between the region 1718 cm^{-1} and 1644 cm^{-1}(C=O stretch). The sharp peak observed at 1478 cm^{-1} (N=O stretch) and shows a strong band in the infrared spectrum. Besides, the peaks in the region of wave number 1176 cm^{-1} to 1032 cm^{-1} are representative of ethers (C-O stretch). Fig. 2b shows FTIR spectra of ferum loaded with fish scales. Band ranging from 1490 cm^{-1} to 1432 cm^{-1} refer to C=C ring stretch to aromatic rings while the peaks produced from 1168 cm^{-1} to 1022 cm^{-1} are due to amines (C-N stretch). Fig. 2c shows FTIR spectra of zinc loaded with fish scales. The peaks in the region 1498 cm^{-1} to 1434 cm^{-1} shows the presence of nitro compounds (N=O). This spectra also shows C-N stretching adsorption occurs in the region from 1186 cm^{-1} to 1022 cm^{-1} as a medium to strong band for all amines [10].



Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
C K	0.277	53.42	0.09	66.58				43.7675	
O K	0.525	31.29	0.44	29.28				28.7756	
P K	2.013	1.65	0.23	0.80				3.1891	
Ca K	3.690	5.29	0.43	1.97				10.8501	
Zr L	2.042	8.35	0.67	1.37				13.4177	
Total		100.00		100.00					

Element		(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
C K		0.277	18.63	0.06	61.94	C	18.63	0.00	25.3750	
O			33.14							
Mg K		1.253	0.49	0.20	0.80	MgO	0.81	0.23	1.6536	
P K		2.013	15.91	0.44	10.26	P2O5	36.46	5.95	56.3625	
Ca K		3.690	23.35	0.61	23.26	CaO	32.67	6.75	99.7711	
Zn L	*	1.012	0.18	0.32	0.11	ZnO	0.22	0.03	0.4248	
Zr L		2.042	8.31	0.75	3.64	ZrO2	11.22	1.06	26.0058	
Total			100.00		100.00		100.00	14.02		

Element		(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
C K		0.277	17.78	0.03	53.96	C	17.78	0.00	30.5167	
O			26.76							
P K		2.013	5.53	0.34	3.25	P2O5	12.66	2.56	16.6290	
Ca K		3.690	44.50	0.46	40.47	CaO	62.26	15.93	165.1954	
Fe K	*	6.398	0.61	2.49	0.40	FeO	0.78	0.16	1.7716	
Zr L		2.042	4.82	0.57	1.93	ZrO2	6.52	0.76	12.8299	
Total			100.00		100.00		100.00	19.40		

Fig. 1a Native Biosorbent, Fig. 1b EDX Analysis of Native Biosorbent, Fig. 1c Zinc Ion Loaded Biosorbent, Fig. 1d EDX Analysis of Zinc Ion Loaded Biosorbent, Fig. 1e Ferum Ion Loaded Biosorbent, Fig. 1f EDX Analysis of Ferum Loaded Biosorbent.

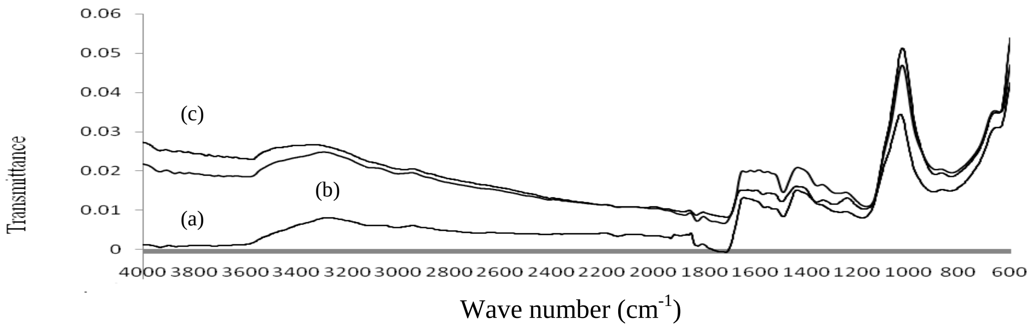


Fig. 2a FTIR Spectra of Native Biosorbent, Fig. 2b FTIR Spectra of Ferum Ion Loaded Biosorbent, Fig. 2c FTIR Spectra of Zinc Ion Loaded Biosorbent.

4.4 Effect of pH on Zinc and Ferum Removal and Uptake Capacity

pH of the aqueous solution is an important factor affecting adsorption process. It is well-known that pH can affect protonation of functional groups (carboxyl, phosphate and amino groups) in the biomass, as well as the chemistry of the metal [11]. The effect of pH on zinc ionsremoval and uptake capacity is shown in Fig. 3a. The optimum zinc ions removal of 91.38% is achieved at pH 6 with uptake capacity 45.69 µg/g. At pH values above the isoelectric point, there is a net negative charge on the cells and the ionic state of ligands such as carboxyl, phosphate, and amino groups will be such as to promote reaction with metal ions. As the pH is lowered, however, the overall surface charge on the cells will become positive, which will inhibit the approach of positively charged metal cations. Protons will then compete with metal ions for the ligands and thereby decrease the interaction of metal ions with the cells [12].

Fig. 3b shows ferum ion removal and uptake capacity depends on the pH of aqueous solution. The optimum ferum ion removal of 63.33% and uptake capacity of 23.75 µg/g is achieved at pH 4.5. Ferum ion shows a gradual decrease in sorption with pH due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and finally cause the reduction in sorption capacity [13]. Increasing pH tend to precipitate biosorbent as insoluble hydroxides or hydrated oxides, thereby lowering its availability for biosorption [14].

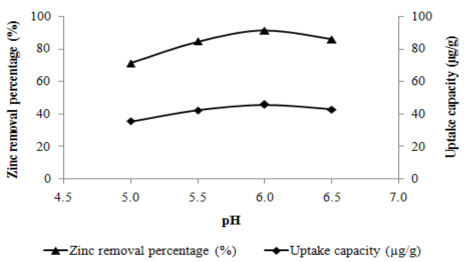


Fig. 3a Effect of pH on Zinc Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

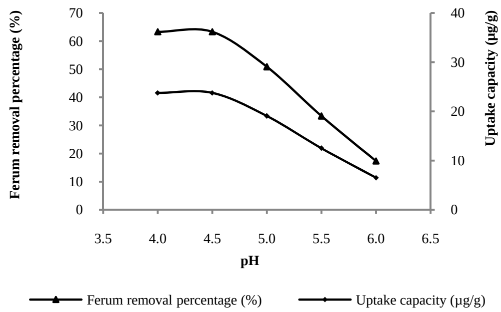


Fig. 3b Effect of pH on Ferum Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

4.5 Effect of Biosorbent Amount on Zinc and Ferum Removal and Uptake Capacity

Biosorbent dose seemed to have a great influence in biosorption process. Dose of biomass added into the solution and determine the number of binding sites available for adsorption [15]. Fig. 4a and Fig. 4b show zinc and ferum ions removal and uptake capacity depended on amount of biosorbent. The results show that zinc and ferum ions reach at the equilibrium state at 0.02 g and 0.8 g with 92.3% and 60.3% respectively. The percentage removal is increased as the increase of biosorbent amount. The uptake capacity is observed at value 45.63 µg/g for zinc ion and 22.63 µg/g for ferum ion. The study by Yu *et al.*, also yielded a similar result where percent removal of metal increases rapidly with increases in the concentration of the biomass due to the greater availability of the exchangeable sites or surface area at higher concentration of the sorbent [16]. Higher uptake at low biosorbent concentrations could be due to an increased metal-to-biosorbent ratio, which decreases upon an increase in dry biomass dose [8]. Moreover, high biomass concentrations can exert a shell effect, protecting the active sites from being occupied by the metal. Therefore, it result a lower specific metal uptake [17].

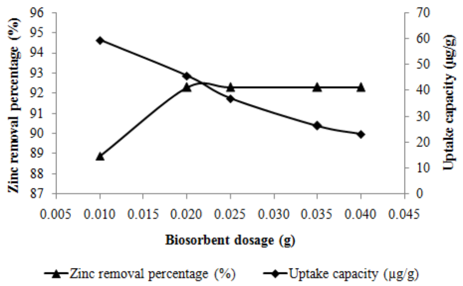


Fig. 4a Effect of Biosorbent Dosage on Zinc Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

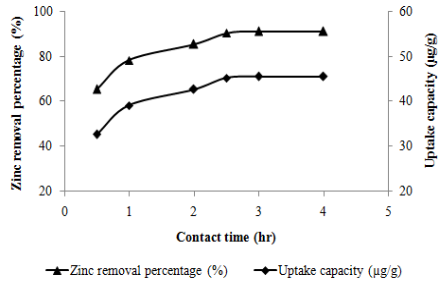


Fig. 5a Effect of Contact Time on Zinc Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

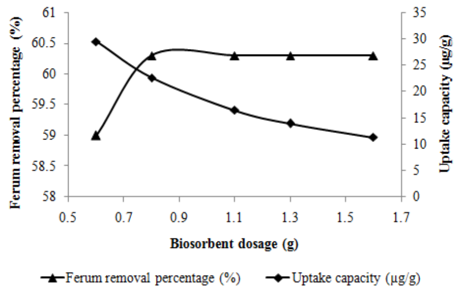


Fig. 4b Effect of Biosorbent Dosage on Ferum Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

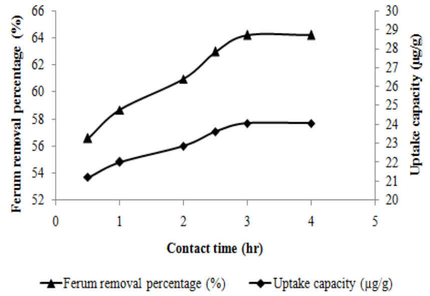


Fig. 5b Effect of Contact Time on Ferum Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

4.6 Effect of Contact Time on Zinc and Ferum Removal and Uptake Capacity

Fig. 5a and Fig. 5b show the biosorption efficiency of zinc and ferum ions removal and uptake capacity by *Tilapia* fish scales as a function of contact time. Increase in contact time leads to an increase in metal removal and uptake capacity. The optimum zinc and ferum ions removal of 91% and 64.2% was achieved at 3 hours of contact time while uptake capacity reaches equilibrium at state 45.5 µg/g and 24.07 µg/g respectively. Initially, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to be occupied. This happens due to repulsive forces between the adsorbate molecules on the *Tilapia* fish scale's surface and in the bulk phase. During the initial stage of adsorption, metal ions are adsorbed into the mesopores that get almost saturated with metal ions. Therefore, the driving force for mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. The metal ions have to traverse further and deeper into the pores encountering much larger resistance and result in the slowing down of the adsorption during the later phase of adsorption. It was possible that a longer contact time allowed the fish scale to be released into the solution. The fish scale needed to be in solution for a longer time in order to absorb heavy metal ions [18,19].

4.7 Effect of Initial Metal Ion Concentration on Zinc and Ferum Removal and Uptake Capacity

Fig. 6a and Fig. 6b show the influence of initial metal ion concentration of zinc and ferum ions removal and uptake capacity by *Tilapia* fish scales. The percentage removal of all heavy metal decreased as the initial metal ion concentration increased. The optimum removal of zinc and ferum ions at 91.33% and 51.67% was obtained at 10 ppb and 300 ppb of initial metal ion concentration while uptake capacity is observed at value 46.67 µg/g and 19.38 µg/g respectively. The number of available binding sites on the biomass surface is high at low concentration of metal ions [20].This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. However, at higher concentrations, metal needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolysed ions will diffuse at a slower rate [15]. The uptake capacity increased with increase in initial concentration, which may be due to the availability of a number of metal ions in solution for sorption [20].

Table 4 Result of zinc and ferum ions under optimum condition.

Heavy metal	pH	Biosorbent dosage (g)	Contact time (hr)	Initial metal ion concentration (ppb)	Percentage removal (%)	Optimum uptake capacity (μg/g)
Zinc	6	0.02	3	10	93.52	46.76
Ferum	4.5	0.8	3	300	65.9	15.2

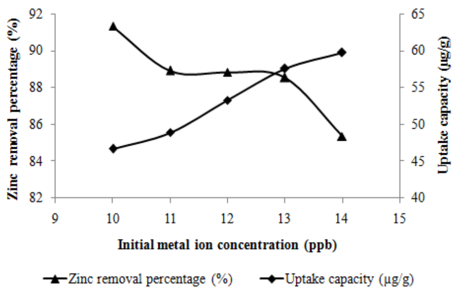


Fig. 6a Effect of Concentration on Zinc Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

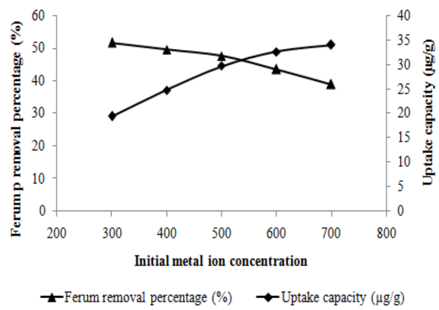


Fig. 6b Effect of Concentration on Ferum Ion Removal and Uptake Capacity using *Tilapia* Fish Scales as Biosorbent.

4.8 Heavy Metals Removal Under Optimum Condition

In order to get optimum condition, four parameters were examined namely pH, biosorbent amount, contact time, and initial metal ion concentration. The optimum values from batch study were applied to obtain maximum removal of heavy metal in aqueous solution. All samples were shaken at speed 125 rpm at room temperature.

Table 4 shows the optimum condition of zinc and ferum ions. From the results,93.52% of zinc ion and 65.9% of ferum ion were removed. The removal of zinc is higher compared to removal of ferum ions. The data revealed that maximum removal of heavy metals can be achieved from optimum condition.

5. Summary

This work shows that *Tilapia* fish scales have a high potential to use as biosorbent for heavy metals removal in aqueous solution. Zinc ion reached the highest removal with 92.3%. This removal achieved at pH 6, biosorbent dose 0.02 g, 10 ppb concentration, and 3 hours contact time. At pH 4.5, biosorbent dosage 0.8 g, 300 ppb concentration and 3 hours reaction time, 65.9% of ferum had been removed from aqueous solution. The biosorbent characterization proved that amide, ester, carboxylic acid, and ketone are the functional group in biosorbent that play important role to reduce zinc and ferum ions. pH, amount of biosorbent, contact time and initial metal ion concentration are the important parameters affecting biosorption process.

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