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RESEARCH ARTICLE

Modification of Nile tilapia fish scales as one of the best biosorbent for the determination, preconcentration and removal of Mn(II) and Cd(II) from Bahr Yousief

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Abstract

Fish scales a globally available natural waste material was used for determination, preconcentration and removal of Mn(II) and Cd(II) from Bahr Yousief and underground water. The results clearly demonstrate the effect of important experimental parameters on the sorption process. The effect of biosorbent dose, shaking time, pH, initial metal ions concentration and sample volume were studied. Modification of Nile tilapia fish scales using cheep and safe sod. acetate resulted in enhancement of the removal capacity of the fish scales than the unmodified one. The capacities of the detergent treated fish scales are estimated to be 76.5 and 133.2 mg g^{-1} for Mn(II) and Cd(II), respectively. While the capacities of Sod. acetate modified fish scales are estimated to be 126.1 and 154.6 mg $g^{-1}$for Mn(II) and Cd(II), respectively. The high adsorption capacity of Nile tilapia fish scales places this biosorbent as one of the best sorbent materials for the removal of Mn(II) and Cd(II) from aqueous effluents. The results confirmed relevant analytical parameters which enable the feasible applications of this method in analyzing natural samples. This study indicated that the novel modified fish scales presents high affinity for Cd(II) and Mn(II) ions.

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INTRODUCTION

One of the main problems of the society in this century is the environmental pollution. The main pollutants include toxic metal, the quantity of which permanently increases in the environment as the result of increased industrial activity. Once toxic metal ions are present in the environment they undergo cycles between its abiotic and biotic elements, posing toxicity in the latter group. Since it is impossible to degrade those pollutants by any means, the only way to remove them from environment is to exclude metal ions from cycling through concentration with a possible recovery and reuse (Volesky, 1997). This would also reduce the consumption of non-renewable resources (Chojnacka, 2010). The problem is of particular significance to human as the final consumer, since on each level of the trophic chain biomagnifications occurs. If toxic metals become bioaccumulated by an organism of human, several disadvantageous symptoms form eg. neurological, gastrointestinal and immunological systems are observed. Among toxic heavy metals, cadmium is one of the most dangerous for human health (Mandjiny et al., 1998). The industrial uses of cadmium are increasing in plastics, paint pigments, mining, electroplating, batteries and alloy industries (Al-Asheh and Duvnjak, 1997). Cadmium is a highly toxic element and considered as a carcinogen. It can enter the human body by drinking water, eating food, breathing or smoking. Most of the cadmium that enters the

body goes to kidney and liver and can remain there for many years and can cause serious damage to kidney and bones (U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, 1999).

Manganese presence in groundwater from leaching processes varies widely depending on rock types. Thus, it has been reported that the groundwater used as drinking water supply up welled from the Etna Volcano aquifer exceeds the maximum contaminant level more than 30 times (Roccaro et al., 2007).

Some methods for the removal of heavy metals e.g., precipitation and coagulation produce concentrated and further toxic wastes. Moreover, there are concentration limits to which these methods are economical and become ineffective or too expensive. Hence, there is a constant need to search for an optimal technology for the removal of metal ions from water at least below the regulatory level while considering its cost materials employed and its efficiency and selectivity. As a consequence, the search for effective new technologies has directed attention to biosorption, a technically feasible and economically attractive approach using biological material as sorbents.

Metal biosorption is the removal of metal ions by inactive, nonliving biomass due to highly attractive forces present between the two (Volesky and Holan, 1995). Particularly, it is due to the presence of certain functional groups, such as amine, carboxyl, hydroxyl, phosphate, sulfhydryl etc., on the cell wall of the biomass (Wang, 2002). The process involves a solid phase (biomass) and a liquid phase containing metal ions (solution of metal ions/waste-water). Metal ions are attracted and bound to the biomass by a complex process that comprises of a number of mechanisms like adsorption on the surface and pores, ion-exchange, surface precipitation, complex formation and entrapment in capillaries and spaces of polysaccharide network, due to the concentration causing diffusion through the cell wall and membrane (Chojnacka et al., 2005; Crist et al., 1981; Kuyucak and Volesky, 1989; Miretzky et al.,2006; Muraleedharan and Venkobachar, 1990; Murphy et al., 2009; Tsezos and Mattar, 1996; Veglio and Beolchini,1997 and Yang and Volesky, 1999).

Research in biosorption suggests the following advantages over other techniques (Modak and Natarajan, 1995). The materials can be found easily as wastes or by-products and at almost no cost, there is no need of costly growth media, the process is independent of physiological constraints of living cells, Process is very rapid, as non-living material behaves as an ion exchange resin, metal loading is very high, the conditions of the process are not limited by the living biomass, no aseptic conditions required, process is reversible and metal can be desorbed easily thus recycling of the materials is quite possible, and chemical or biological sludge is minimized (Farooq et al., 2010). However, there are certain disadvantages as well; irrespective of the value of the metal, it needs to be desorbed from the material to be further re-employed, the characteristics of the biosorbents can not be biologically controlled, and the limitations include first of all a shorter life time of biosorbents when compared with conventional sorbents (Gadd, 2009).

In this study our attention was focused on the preparation of novel chelating sorbents by immobilizing chelating biomass with good metal ions sorption characteristic. Thus, in this work Nile tilapia fish scales were pretreated by shaking with 0.5 M Sod. acetate solution to enhance the uptake capacity for the tested metal ions. Characterization by different techniques and sorption studies with both detergent washed and modified fish scales were used as solid sorbents in an off-line pre-concentration system for Mn(II) and Cd(II) determinations. The method was successfully applied to different natural waters.

2. Experimental

2.1. Apparatus and reagents

UV/Vis. Spectrophotometer: Buch-Lomb, spectronic 20 "UV/Vis. Perkin Elemer Lambada 3B spectrophotometer using 1cm quartz cell" was used in the determination of metal ions standard and in the eluents during preconcentration studies. Flame atomic absorption spectrometer model AA-6200 (Shimadzu, Japan) equipped with single element hollow cathode lamps and air-acetylene burner was used for the determination of the metals. Air-acetylene flame (fuel 1.8 L min^{-1}, oxidant 8 L min^{-1}) and 0.7 mm slit width were used. The wavelength and lamp current selected for the Cd(II) determination was as follows: 228.56 nm and 8 mA. The pH measurements were carried out using the microprocessor pH meter BT 500 BOECO, Germany, which was calibrated against two standard buffer solutions at pH 4 and 9, and a mechanical shaker with up to 200 rpm (SL 350 NU¨ ve san. Malz). Doubly distilled water (DDW) was obtained from two successive distillations using Hamilton laboratory glass instrument (Europe House, Sandwich Industrial Estate, Sandwich Kent, England).

Stock solutions (1000 μgmL^{-1}) of cadmium were prepared by dissolving appropriate amounts of analytical reagent grade cadmium nitrate in a 0.1 mol $L^{-1}HNO_3$ (Panreac, Spain) solution, appropriate weight of anhydrous $MnSO_4$ (Aldrich) in a doubly distilled water containing 2mL of conc. H_2SO_4, appropriate weight of ammonium ferrous sulphate (Aldrich) in a doubly distilled water containing 5mL of con H_2SO_4, and diluted as required. Sodium hydroxides were received from Winlab

Company, UK for reagents fine chemicals. Hydrochloric acid used was delivered from Merck (Germany). All liquids were used without any further purification.

2.2. Sorbent preparation

The Nile tilapia fish scales were collated from El-Fayoum market. The scales were washed repeatedly with detergent followed by bidistilled water to eliminate impurities and dried in an air oven at 65^{o}C till constant weight. The dried scales were stored in airtight polypropylene jars in desiccated condition to avoid moisture.

2.2.1 Fish scales modification

The detergent washed fish scales (50g) were shaking with 500mL of 0.5M Sod. acetate for 3h at mechanical shaker then filtrated and washed by bidistilled water, till free from any hydroxide then heated at 65^{o}C till constant weight.

2.3. Recommended procedure

2.3.2. Batch measurements

The optimum pH of the metal ion uptake was determined by using the batch equilibration technique. Twenty five milliliters of metal ion solutions containing 20µg of Mn(II) and Cd(II), from single element aqueous solutions, were shaken with 0.2 g of the fish scales for 3h. The pH of the metal ion solution was adjusted before equilibration with fish scales over a range of 1–9. After the equilibration, the remained metal ions were determined by the recommended method.

In order to determine the optimum sorbent dose on the extraction of Mn(II) or Cd(II) onto the fish scales, 25mL solution containing varying scales weight from 0.1- 0.8 g and 20µg of individual metal ion was adjusted to the optimum pH, and the mixture was shaken for 3h on a mechanical shaker, the amount of the metal ions remained in the solution was measured using the recommended method after separation of the scales by filtration. The extracted amount of the metal ions retained in the scales was determined by the difference.

The effect of shaking time on the extraction efficiency of Mn(II) and Cd(II) was studied using the batch experiment. For that purpose, 0.2 g of fish scales was added to 25mL of the samples containing 20µg the metal ions at the optimum pH and automatically shaking for different time intervals. The percentage of sorption (E %) was determined by using the following formula:

$E\ \% = [(C_0 - C)/C_0] \times 100$.

C_0 and C are the initial and remaining concentrations (µg L^{-1}) of the metal ion, respectively.

Determination of the sorbent capacity was carried out by the sorption of the selected metal ions; namely, Mn(II) and Cd(II) from separate element aqueous solutions. Typically, 0.2 g of fish scales was equilibrated with 4000 µg metal ion solution adjusted to different pH_s using NaOH or HCl in a 25mL volumetric flask, which was automatically shaken for 3 h at room temperature. After equilibration, the mixture was filtered and the remaining metal ion in the filtrate was determined. The sorption capacity per gram (Q, mgg^{-1}) was calculated from the equation:

$Q = [(C_0 - C) \times V]/m$

Where V is the sample volume in liter and m is the weight of fish scales in gram.

2.3.2. Dynamic measurements

Glass columns (10 cm long and 1.0 cm in diameter) were packed with 2.5 g of fish scales. The column was successively rinsed with 20 mL of water, 5 mL of a 2 M solution of HCl, and finally with DDW till the effluent was free from any acid.

The effect of the sample flow rate on the extraction of Mn (II) and Cd(II) on the scales was studied in the flow rate range of 2.0–6.0 mL min^{-1}. Breakthrough capacity was studied as follows: a 100 mL volume of separate metal ion solution (10 mg metal ion) was percolated through the column at the optimum flow rate. Five milliliters portions of the effluent were collected and analyzed. Saturation of the scales was reached when the concentration of the metal ion in the effluent aliquot was the same as in the original solution loaded onto the column.

Pre-concentration of the studied metal ions was investigated from model solutions prior to the determination in the real samples. Solutions containing Mn(II) and Cd(II) at a concentration of 20µgL^{-1} each, were passed through the column after adjusting to the optimum pH value and a flow rate. The stripping of the metal ions from the scales column was carried out by 10mL 0.5M hydrochloric acid solution and the amount of each metal ion in the eluent was determined by the recommended method. The concentration factor (CF) could be calculated from the ratio of the initial volume of sample to the final volume after concentration. Separation of the metal ions from the column, previously loaded with 10mL solution at concentration of 1.0 µgmL^{-1} and a flow rate of 3.0 mLmin^{-1}, was carried out. Each metal retained on the column was eluted using the suitable stripping solution. The amount of the metal in every 5mL portion of the collected eluate aliquot was determined by the recommended method, and the recovery was evaluated.

The effect of diverse ions on the recovery of the studied metal ions from the column was investigated. Solutions containing 20 µg of Mn(II) and Cd(II) were added to solutions containing interfering ions and adjusted to the optimum sorption conditions. The metal ions held to the sorbent were desorbed by 10 mL 0.5 M hydrochloric acid and the

concentration in the eluate was determined by the recommended method. The recovery (R) percentage for each metal was calculated from the amount of metal ion added to the sample and the amount found by the elution.

The Breakthrough capacity of the biosorbent material is very important since it determine the maximum amount of the extracted analyte ions that could be quantitatively pre-concentrated in the column. There, 1000 mL blank or sample solution for each studied ions were prepared separately at concentration (5 mg L^{-1}) were passed through the fish scales column, at flow rates 4 mL min^{-1}. Each solution was adjusted to the optimum pH value and the effluent was collected in 5ml fractions where the amount of the analyte ions in each fraction was determined by the recommended method. The percentage of the metal ions in each effluent aliquot could be calculated and plotted against the volume of the effluent (Bed volume) and the dynamic capacities with each analyte ions could be calculated. The breakthrough studies were carried out by 2.5 g of different fish scales each in a separated column.

3. Results and discussion

3.1. Characterization of fish scales by IR

The IR Spectroscopy is an important analytical technique which detects the vibration characteristics of chemical functional groups in a molecule. On interaction of an infrared light with the matter, chemical bonds will stretch, contract and bend. As a result, chemical functional group tends to absorb infrared radiation in a specific wavelength range regardless of the structure of the rest of the molecule. Based on these principles, the surface functional groups of fish scales were adequately studied in the range of 400–4000 cm^{-1}. The main functional groups present on surface of fish scales were carboxylic at 2344 - 2362 cm^{-1}, carbonyl at1659 - 1559 cm^{-1}, -NH group at 3500–3000 cm^{-1} and -COONH group at1070-1630 cm^{-1} a shown in Fig. 1

3.2. Batch measurements

3.2.1. Effect of initial pH solution

It is well documented that the pH of the metal ions solution affects the metal solubility and the concentration of the counter ions on the functional group of the cell wall of the biomass, consequently, the pH is considered as the most important parameter that could affect the biosorption of metal ions from solutions (Gaur and Dhankhar, 2009 and King et al., 2007). The pH effect on the removal of the studied metal ions by the modified fish scales was studied by the batch method. The results demonstrated that the extraction of the analyte ions on the detergent treated scales is reached a maximum value at pH 3.5 and 4 for Mn(II) and Cd(II), respectively while pH 6 and 5 for Sod. acetate treated fish scales for Mn(II) and Cd(II), respectively. These results can be seen in Figs. (2a & b).

The effect of the pH on the removal Mn(II) and Cd(II) can be explained due to the ionization of the weakly acidic groups on the surface of fish scales such as amino, carbonyl, carboxylic, phosphate and hydroxyl which enhance the binding of the tested metal ions. Similar studies were carried out for the biosorption of Cu(II) and Ni(II) by Bueno et al. and Cayllahua et al.

3.2.2. Effect of biosorbent dose

Experiments were carried out to find the effect of biosorbent dose on the removal of Mn(II) and Cd(II) by the batch method. The results demonstrated that the removal of the tested ions on the detergent treated scales and Sod. acetate treated fish scales is maximum at sorbent dose 0.2and 0.1 g for Mn(II) and Cd(II), respectively as shown in Figs.(3a & b). Therefore, the dose 0.2 g/ 25 mL for Mn(II) and0.1 g/ 25 mL for Cd(II) were selected as the optium dose of the biomass for the rest of the study.

It is obvious that with increasing the fish scales weight from 0.05 to 0.1 g more binding sites are available and thus, the removal efficiency increase for the modified scales then decrease. This decrease could be explained by the formation of aggregates of the biomass at higher doses, which decreases the effective surface area for biosorption (Sari and Tuzen, 2008 and Karthikeyan et al., 2007).

3.2.3. Effect of shaking time

The metal ions retained by the extract depends on the time at which equilibrium is attained, this is considered as the equilibrium time. The removal of the tested metal ions onto the modified fish scales with different time intervals (1-180 min) at the optimum pH values was studied. It is found that the removal is very rapid and reached a value between (81-88%) for the modified scales and 61% for the detergent treated scales within the first 10 min. This indicates the availability of the modified sites.

From the Figs.(4a & b), the extraction of Mn(II) and Cd(II) increases with lapse of time and reaches the equilibration time between (40-140 min) for detergent treated scales and Sod. acetate treated scales. Typical biosorption kinetics a rapid initial uptake fallowed by a slower process. It has been observed that the maximum extractions took place within the first 40 min Figs.(4a & b). After this period, the amount of the extracted ions showed a little increase, after a period of 80-120 min the amount of the removed ions did not change during the biosorption process. The removal of the tested metal ions was concentration dependant.

It is cleared that the rate of the extraction is rapid and then attains the equilibrium state. This equilibrium is achieved easily when the initial metal ions concentration is low. As the contact time increases the available surface of the extractor in gradually decreases until it attains equilibrium.

The relativity faster uptake of the tested ions on the new modified scales reflects the excellent accessibility of the studied analyte ions to the new sites built on the fish scales.

3.2.4. Effect of initial metal ion concentration

The initial concentration manganese (II) and cadmium (II) on the extraction of the tested metal ions by the pretreated scales was studied by the batch method. The results given in Figs.(5a & b) indicate that the metal uptake percentage values increased with increasing in initial metal ions concentration up to 40 µg /25 mL. The results demonstrated that the extraction of Mn(II) and Cd(II) on the detergent treated scales were less than sod. acetate treated scales.

The obtained results reflect also the high efficiency of the new modified material for the removal of Mn(II) and Cd(II) from aqueous solution over a wide range of metal ions concentration.

The enhancement in metal ions sorption could be due to an increase in electrostatic interactions involving the sites of progressively lower affinity for the metal ions (Asheh and Duvnakz, 2007). But decreasing in the metal uptake percent at higher metal ion concentration may be due to rapid saturation of the metal binding sites of the biosorbent (Nadeem et al., 2008 and Kapoor and Viraraghavan, 1995).

This behavior was also attributed to the fact that, initially all the binding sites on the fish scales surface were vacant resulting in high metal ions removal at the beginning. After that, with increasing the metal ions concentration, the removal of ions was decreased because of the few active sites were available on the surface of the fish scales.

3.2.5. Extraction isotherm and determination of the capacity

The capacity of the biosorbent is an important factor because it determines how much solid phase is required quantitatively to remove a specific amount of the studied ions from the solution. Isotherm studies provide information about the capacity of the new modified fish scales material or the amount required to extract a unit mass of pollutants like Mn(II) and Cd(II) from aqueous solution. The extraction capacities were between 176-303 mg g^{-1} for the detergent treated scales and Sod. acetate treated scales, at the optimum conditions.

From Figs. (6a & b) it is clear that the extraction isotherm for the tested metal ions by the modified biomass increase when metal ion concentration increased from 100 to 2000 µg/25 mL. This confirms the new modified fish scales have greater affinity to Cd(II) and Mn(II) ions.

3.2.6. Effect of sample volume by the batch method

The measurement of breakthrough volume is important in the removal because breakthrough volume represents the sample volume that can be preconcentrated without any loss of analyte during elution of the sample (Mester and Sturgeon, 2003). From Fig. 7a it is clear that the quantitative Mn(II) extraction until sample volume 70 and 140 mL for detergent treated scales and Sod. acetate treated scales, respectively.

During studying the effect of the sample volume on the removal of Cd(II) on the modified fish scales, the results obtained was reported and drawn as in Figs.(7 b). From the results, it is clear that the quantitative Cd(II) removal until sample volume 110 and 170 mL for the detergent treated fish scales and Sod. acetate treated scales, respectively.

3.3. Dynamic measurements

3.3.1. Effect of the flow rate on the recovery of the analytes

The retention of sorbent depends on the flow rate of the sample solution (Mester and Sturgeon, 2003). Thus, the effect of flow rates of the sample and elution solutions on the retention and uptake of ions is an important

parameter, since it not only affects the recovery of the analyte, but also controls the time of analysis, because a large volume of sample solution is needed in the preconcentration. It is also expected that sample solutions can be passed through the column at a higher flow rate without sacrificing the recoveries. So, sample flow rate investigated under the optimum conditions to obtain quantitative retention and elution of the studied metal ions. The influence of the flow rate of the samples and eluent solution on the retention of Mn(II)and Cd(II) were also investigated in the flow rate ranges of 1-6 mL min^{-1} keeping other conditions constant. The results obtained for the effect of the flow rate on the extraction of Mn(II) and Cd(II) onto pretreated fish scales were plotted as in Figs.(8a &b). From Fig. 8a we can conclude that quantitative retention of the Mn(II) ions on the column is at flow rate from 1-5 mL min^{-1} in case of Sod. acetate treated scales and from 1-2 in case of detergent treated scales. The proposed procedure recommended flow rates of 2 mL min^{-1} and 4mL $min^{-1}$is suitable for the retention on column packed with 2.5 g of detergent treated scales and Sod. acetate treated scales, respectively.

3.3.2. Effect of eluent type

Acids are recommended in desorption of the metal ions from biosorbent because they rapidly decrease the pH of the medium and assist the H^+ exchange to replace the bounded metal ions in the biosorbent. In order to choose the proper eluent for desorbing the metal ion from the scales surface, a series of selected eluent solutions such as 0.1 M hydrochloric acid, 5.0 M sod. chloride or 0.1M acetic acid each were examined individually. Aliquots of 25mL solution containing 20µg metal ions were passed through the fish scales minicolumn at flow rate 4 mL min^{-1}. The amount of metal ion back recovered into eluate by 15 mL in the individual eluent was measured using FAAS and the recovery was calculated for each sample. The results are given in Table(1), quantitative recovery was obtained when 0.1M hydrochloric acid was used, while the recovery values by using 5 M sod. chloride and 0.1 M acetic acid as eluent were not quantitative. After these results, the recoveries were carried out by using 0.1 M hydrochloric acids.

3.3.3. Effect of eluent volume on the recovery (%)

During studying the effect of the eluent volume on the removal of Mn(II) onto pretreated fish scales, the results obtained was drawn in Figs.(9a &b). From Fig. 9a it is clear that the appropriate eluent volume is from 10-20 mL for eluting Mn(II) onto detergent treated scales, while the appropriate eluent volume for eluting Mn(II) on Sod. acetate treated scales is from 8-20 mL. The proposed procedure recommends that the extraction of Mn(II) onto the pretreated fish scales give maximum retention of the metal ions when 10 mL eluent volume of 0.1M HCl is used. Therefore, this volume was used in all experiments of elution.

To investigate the effect of the eluent volume on the removal of Cd(II) ions on to the modified fish scales, the results are depicted in Figs.(9b). From the figures it is clear that Cd(II) ions could be quantitatively removed (96-100%) by using eluent volume 10 mL of 0.1 M HCl, respectively.

3.3.4. Interfering effect of foreign ions

Matrix effects are important problems in the determination of metal ions in real samples. In order to assess the potential interference effect for the selective extraction of the investigated ions, a selected group of foreign ions was tested to assess the possible analytical applications of the recommended procedure. The effect of some foreign ions which interfere with the determination of the analyte ions was examined under the optimized conditions to asses the possible analytical applications of the proposed procedure Table (2). The added ions were (Na, K^+, Ca^{2+}, Mg^{2+}, Cl^-, F^-, Br^-, NO_3^-, SO_4^{2-}, CO_3^{2-} or Po_4^{3-}). The percentage recovery (R) of Mn (II) and Cd (II) wasn't affected by the added ions. Tolerable limit was defined as the highest amount of the foreign ions that produced an error not exceeding ±5% in the recovery of the investigated analyte metal ions. As it is seen in Table (2) all the interfering ions used have no considerable effect on the removal of the studied analyte ions.

3.3.5. Breakthrough capacity

Column capacity is an important parameter that determines if the solid phase is capable of quantitatively uptake of the analyte from a given solution or not. The breakthrough capacity for the column packed with 2.5 g of fish scales can be calculated from the relation:

Capacity = $(V_{50}\%C_0)/m)$

Where C_0 the concentration of the feed solution (mgL^{-1}), m is the weight of biosorbent (fish scales) in grams and $V_{50}\%$ is the effluent volume at 50% breakthrough.

The breakthrough curve of Mn(II) and Cd(II) biosorption was obtained in Figs.(10a & b), by plotting the amount of metal ion emerged from the column against the bed volume (volume of effluent collected). From Fig. 10a we can see that Mn(II) appears in the effluent after passing of 5mL solution for the column packed by 2.5 g detergent treated fish scales while Mn(II) appears in the effluent after passing of 10 mL solution for column packed by 2.5 g Sod. acetate treated fish scales. Saturation of the column reaches after passing of 55 mL solution containing 5 mgL^{-1} Mn(II) and flow rate of 2 mL $min^{-1}$for column packed by detergent treated fish scales, 95 mL solution containing 5 mgL^{-1} Mn(II) and flow rate of 4 mL $min^{-1}$for column packed by Sod. acetate modified fish scales.

From Fig. 10 b we see that Cd(II) appears in the effluent after passing of 10 mL solution for column packed by 2.5 g detergent treated scales while Cd(II) appears in the effluent after passing of 10 mL solution for column packed by modified fish scales. Saturation of the column reaches after passing of 80mL solution containing 5 mgL^{-1} Cd(II) at flow rate of 2 mL $min^{-1}$for column packed by detergent treated fish scales, 95 mL solution containing Cd(II) at flow rate of 5 mL $min^{-1}$for column packed by Sod. acetate modified fish scales.

From Figs.(10a & b) it is clear that the steep curves at the breakthrough point for the studied metal ions on the sod. acetate modified fish scales suggest the better ability of the modified biomass for the separation and the determination of the studied analyte ions.

The capacity of the detergent treated fish scales are estimated to be 76.5 and 133.2 mg g^{-1} for Mn(II) and Cd(II) Table(3), respectively. While the capacity of Sod. acetate modified fish scales are estimated to be 126.1, and 154.6 mg $g^{-1}$for Mn(II) and Cd(II), respectively. It is obvious that, the uptake capacity of the new Sod. acetate modified biosorbent is generally good, it can be used to extract Mn(II) and Cd(II) from diluted aqueous solutions

The difference in the extraction capacity of Sod. acetate modified fish scales and detergent treated fish scales may be attributed to the chemical stability between the studied ions and the new modified sites built on the fish scales and the difference in the ionic sizes of the studied ions.

3.4. Preconcentration of metal ions

Of all the preconcentration methods, chelating extractor recovery method is one of the most effective multi element preconcentration methods, because it can provide more flexible working conditions together with good stability, high concentration ability, selectivity, high capacity of metal ions, and simple operation (Tuzen et al., 2005 and Soylak et al., 2005). However, at the same time, there are demands for trace element determination and concentration using the new modified extractors are ever increasing.

For this purpose 100-1250 mL solution containing 20 µg from each metal ion adjusted to the optimum conditions, and then passed through the column. Using 8-12 ml. of 0.1M HCl solution as eluting agent, the amount of each metal ion in the eluate was measured by the recommended method. The percentage recovery (R) was calculated from the initial concentration of the metal ions in solution and the amount found in the eluate. The results obtained are listed in Table (4). These results show that Mn(II) and Cd(II) ions can be concentrated effectively from the diluted aqueous solution using the modified fish scales.

3.5. Limit of Detection and Limit of Quantification

The limit of detection (LOD) was calculated as three times standard deviation of five measurements of the blank (SD_b) divided by the slope of the calibration curve. LOD was found to be 0.17and 0.05 µg/mL for Mn(II) and Cd(II) respectively. Similarly the limit of quantification (LOQ) was calculated as the concentration that gives a signal height equivalent to ten times of five measurements of the blank (SD_b) was found to be 0.56, and 0.16 µg/mL for Mn(II) and Cd(II) respectively. Those data confirmed relevant analytical parameters which enable the feasible applications of this method in analyzing natural samples.

3.6. Analytical applications of the method to real Samples

The analytical procedure was used for the removal of the tested metal ions from natural water samples, Bahr Youseif water and underground water. The results obtained are shown in Tables (5&6). Recoveries (R) of the spiked ions to water samples were quantitatively removed. R (%) was calculated as follows:

$$R\ (\%) = [C_{found} / C_{Certified} + C_{add}] \times 100$$

Where C_{found} is the total value of the metal ions in the spiked sample, $C_{Certified}$ is the value of the metal ions in the sample and C_{add} is the amount of the metal ion spiked. The results also proved that the procedure is not affected by

high concentration of alkaline earth metals and can be employed successively for the extraction of Mn(II) and Cd(II) ions in natural water samples.

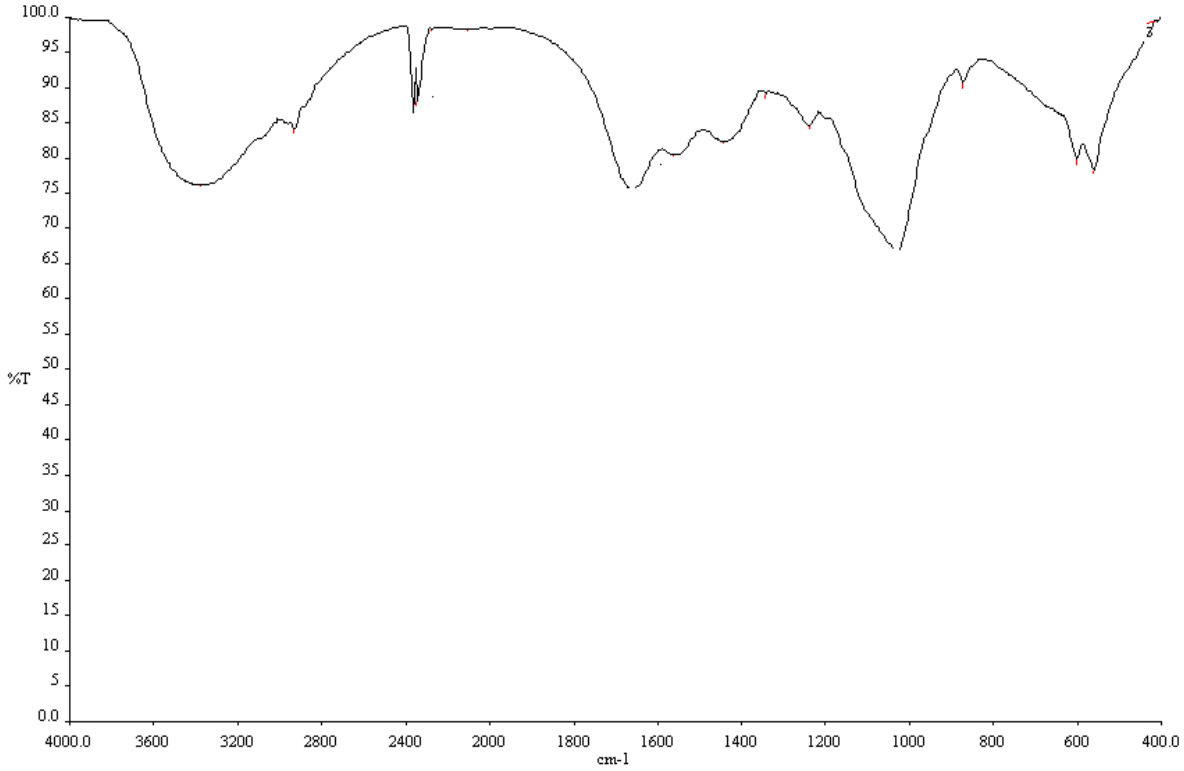

Fig. 1 IR of characteristic group in fish scale

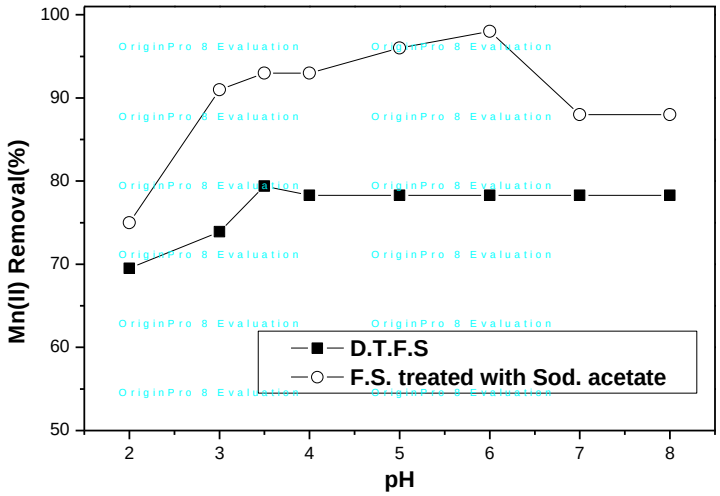

Fig. 2a Effect of the pH on the removal of Mn(II) by fish scales.

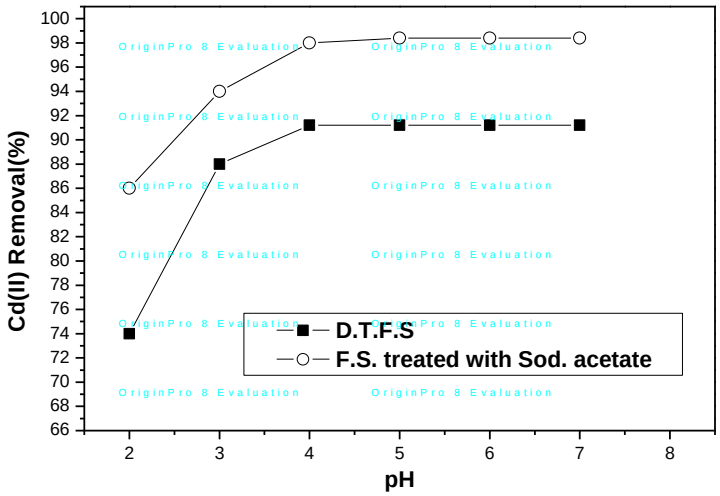

Fig. 2b Effect of the pH on the removal of Cd(II) by fish scales.

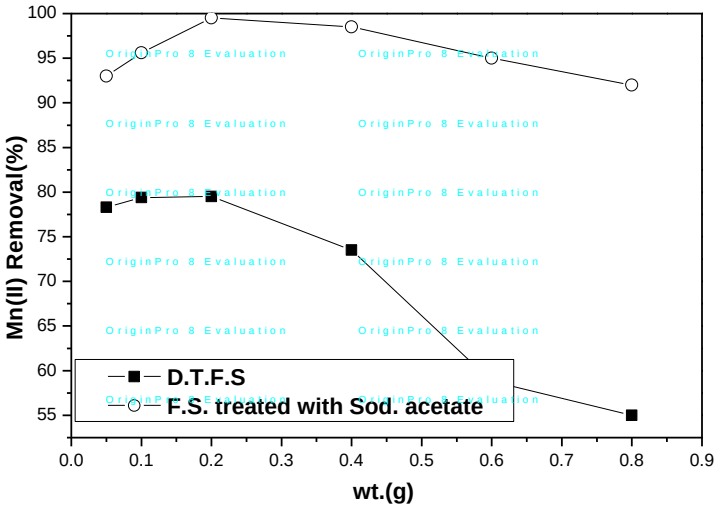

Fig. 3a Effect of the sorbent dose on the removal of Mn(II) by fish scales.

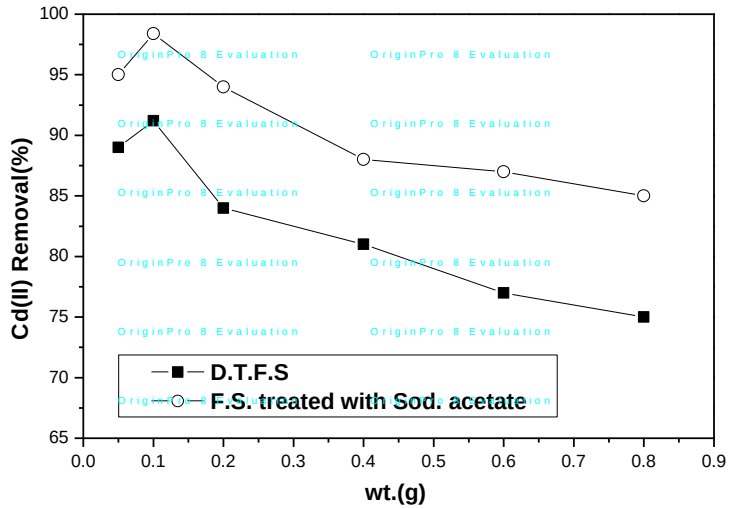

Fig. 3b Effect of the sorbent dose on the removal of Cd(II) by fish scale

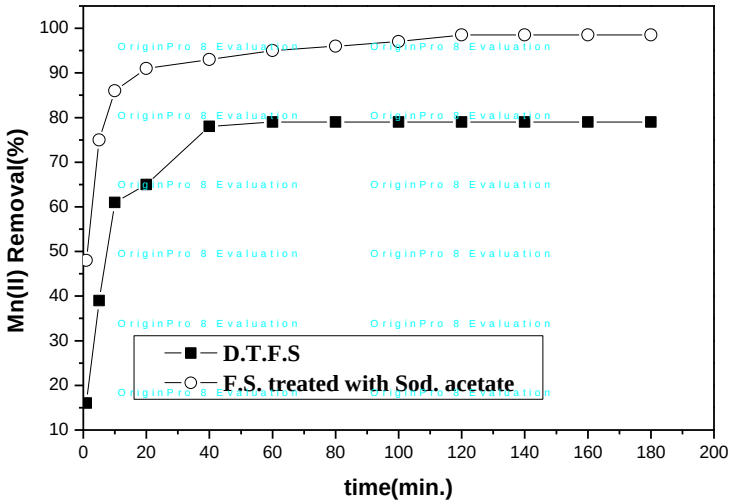

Fig. 4a Effect of shaking time on the removal of Mn(II) by fish scales.

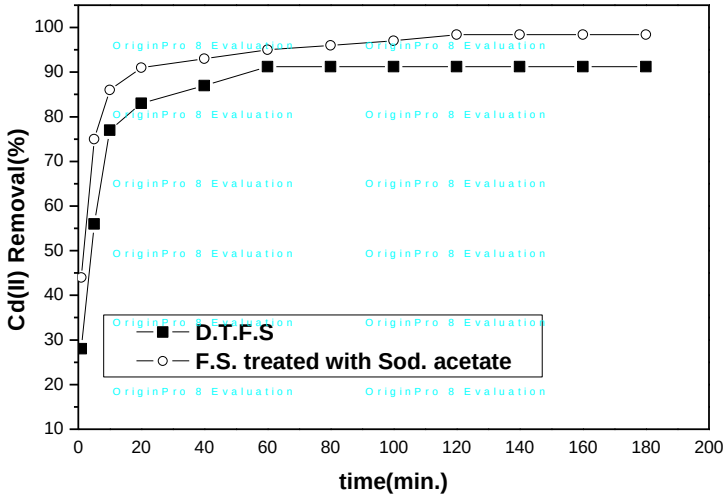

Fig. 4b Effect of shaking time on the removal of Cd (II) by fish scales.

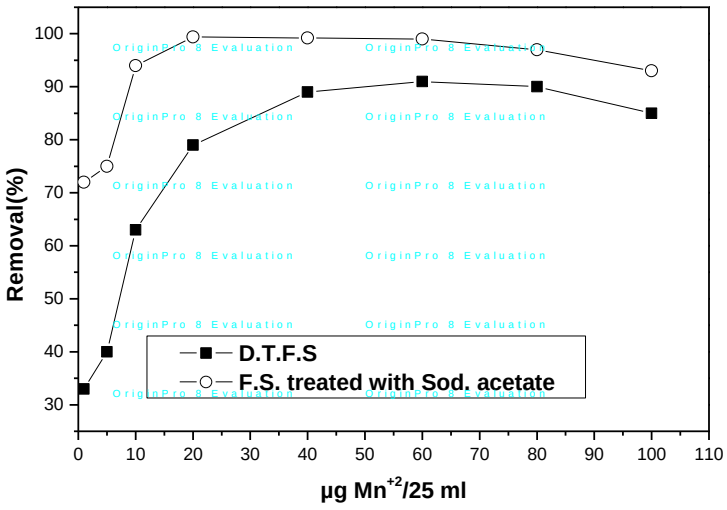

Fig. 5a Effect of Mn (II) concentration on Mn (II) biosorption.

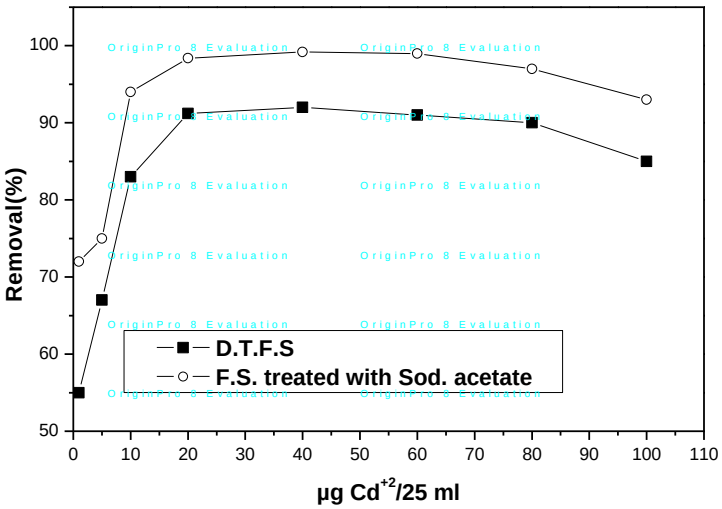

Fig. 5b Effect of Cd (II) concentration on Cd(II) biosorption.

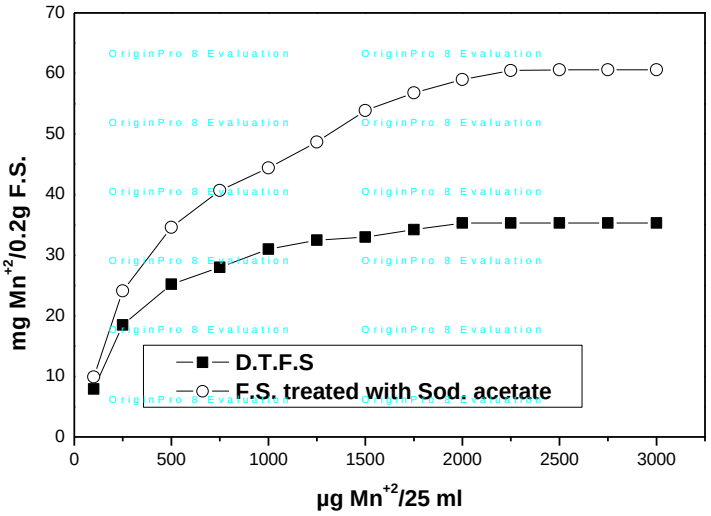

Fig. 6a Extraction isotherm of Mn(II) using fish scales.

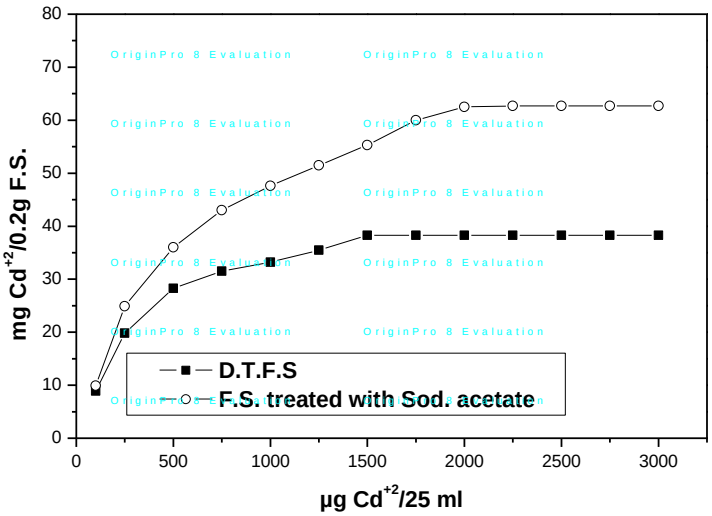

Fig. 6b Extraction isotherm of Cd(II) using fish scales.

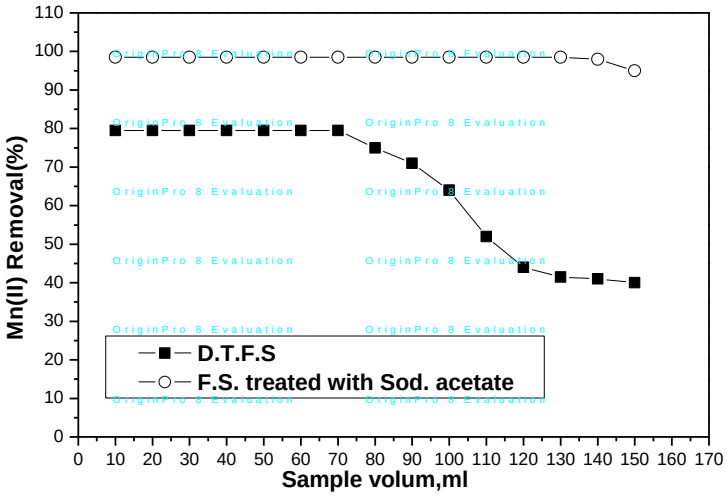

Fig. 7a Effect of sample volume on Mn (II) biosorption using fish scales.

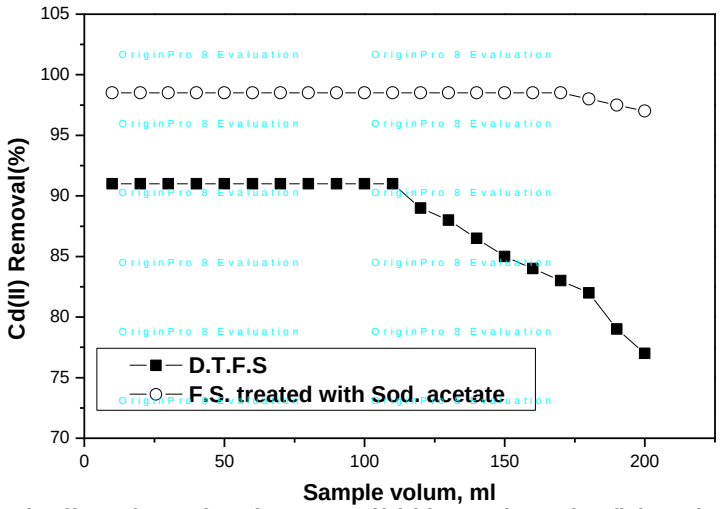

Fig. 7b Effect of sample volume on Cd(II) biosorption using fish scales.

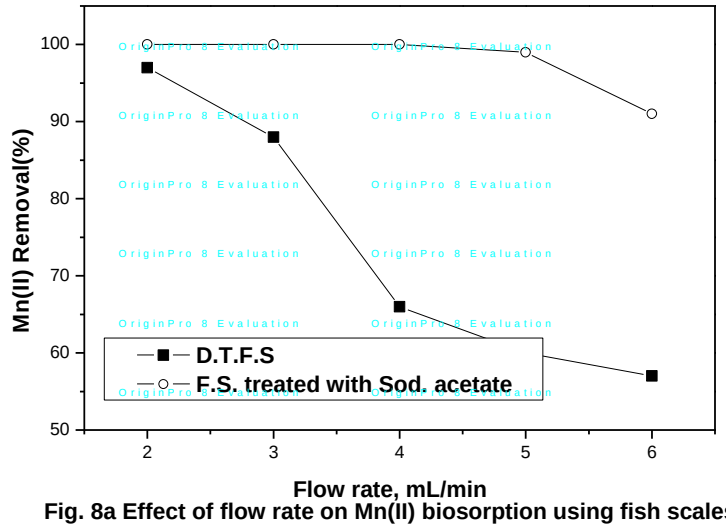

Fig. 8a Effect of flow rate on Mn(II) biosorption using fish scales.

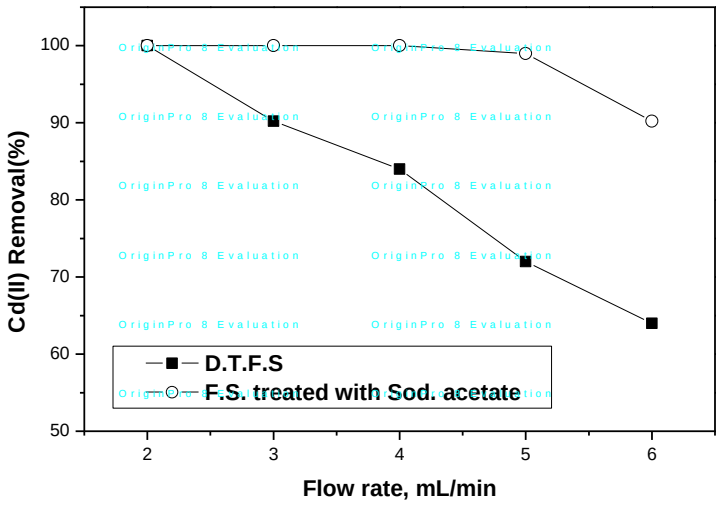

Fig. 8b Effect of flow rate on Cd(II) biosorption using fish scales.

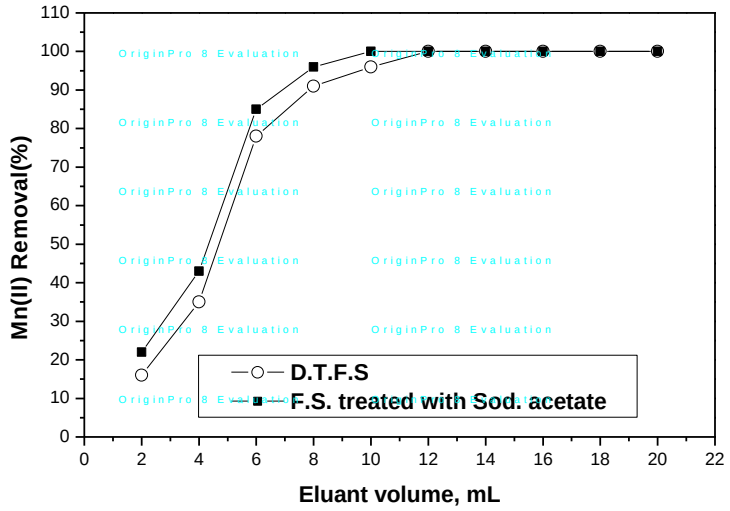

Fig. 9a Effect of eluant volume on Mn(II) biosorption using fish scales.

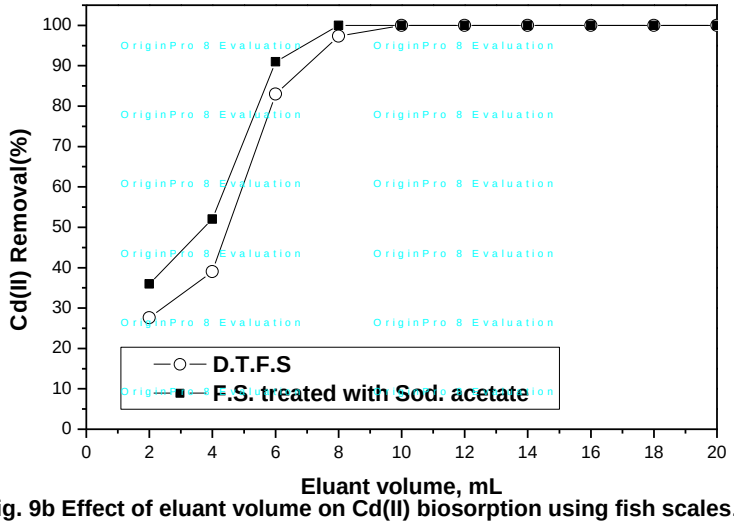

Fig. 9b Effect of eluant volume on Cd(II) biosorption using fish scales.

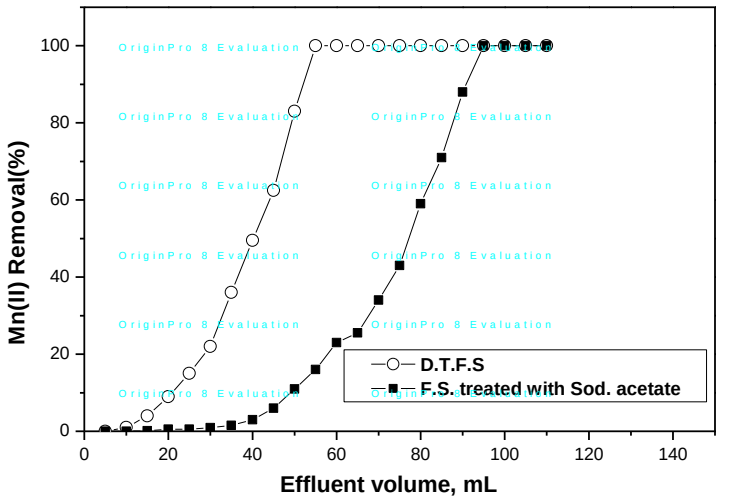

Fig. 10a The breakthrough curve of Mn(II) biosorption using fish scales.

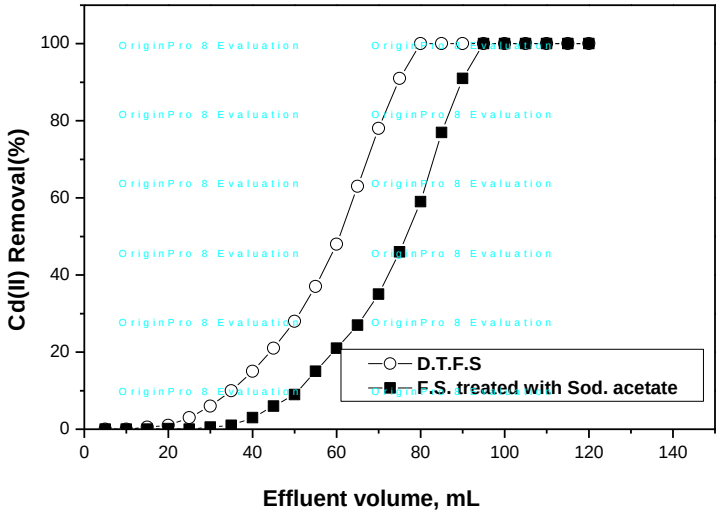

Fig. 10b The breakthrough curve of Cd(II) biosorption using fish scales.

Table 1

Effect of different eluents on eluating Mn(II) and Cd(II) from pretreated fish scales.

Eluent	Fish scales type	%R[1]	
		Mn(II)	Cd (II)
0.1M HCl.	Detergent treated scales.	96.5%	98%
	Sod. acetate treated scales.	100%	100%
5.0 M NaCl.	Detergent treated scales.	35%	44%
	Sod. acetate treated scales.	53%	71%
0.1M CH_3COOH.	Detergent treated scales.	63%	71%
	Sod. acetate treated scales.	86%	95%

%R[1] : Removal percent.

Table 2

Effect of interfering ions on the recoveries of Mn(II) and Cd(II) from detergent treated scales and sod. acetate treated scales.

Ions	Add as	Conc. (mg/L)	R (%)used D.T.F.S[1]		R(%)used Sod.acetate T.F.S[2]	
			Mn(II)	Cd(II)	Mn(II)	Cd(II)
Nil.	-	-	97	98	100	100
Na^+	NaCl	15000	96.5	97	99.5	100
K^+	KCl	1000	96.8	97.8	99.5	99.5
Ca^{2+}	$CaCO_3$	50	96.8	97	99	99
Mg^{2+}	$MgCO_3$	50	95.8	97	98.5	98.5
Cl^-	NaCl	1500	96.5	97.5	99	99
F^-	NaF	100	96.5	97	99	99
Br^-	NaBr	100	95.8	96.5	99	99.5
NO_3^-	$NaNO_3$	1000	95.8	95.5	98.5	98
SO_4^{2-}	Na_2SO_4	50	95	96	98.5	98
CO_3^{2-}	Na_2CO_3	1000	94.8	96	98	98.5
PO_4^{3-}	Na_3PO_4	150	95.5	96	98	98.5

D.T.F.S[1]: detergent treated scales.

Sod.acetate T.F.S[2]: sod. acetate treated scales.

Table 3

Capacity of column packed with 2.5 g fish scales.

Biosorbents	Batch capacity(mg g^{-1})		Column capacity(mg g^{-1})	
	Mn(II)	Cd(II)	Mn(II)	Cd(II)
Detergent treated scales.	176	191.5	76.5	133.2
Sod. acetate treated scales.	303	313.5	126.1	154.6

Table 4

Preconcentration of Mn(II),and Cd(II) and using detergent treated scales and sod. acetate treated scales.

Scales type	Metal ions	Intial volume (mL)	Final volume (mL)	Recovery (%)	CF[1]
Detergent treated scales	Mn(II)	100	12	98	8.33
		250	12	97.5	20.8
		500	12	96	41.6
		750	12	95.2	62.5
		1000	12	91.5	-
	Cd(II)	100	10	99	10
		250	10	98	25
		500	10	97.5	50
		750	10	96	75
		1000	10	94.5	-
Sod. acetate treated scales	Mn(II)	100	10	100	10
		250	10	99	25
		500	10	98.5	50
		750	10	97	75
		1000	10	95.8	100
	Cd(II	100	8	100	12.5
		250	8	100	31.3
		500	8	99.5	62.5
		750	8	98	93.8
		1000	8	97.5	125
		1250	8	95.8	156

CF[1]: concentration factor

Table 5

Recovery data for the preconcentration of Mn(II) and Cd(II) ions from Bahr Yousief water using modified Nile tilapia fish scales.

Biosorbents	Metal ions	Add (ppm)	Found (ppm)	R (%)	R.S.D (%)[1]

Detergent treated Scales	Mn(II)	0.2	0.33	91	2.3
	Cd(II)	0.2	0.267	95	1.8
Sod. acetate treated scales	Mn(II)	0.2	0.358	98.5	1.2
	Cd(II)	0.2	0.278	99.1	4.1

R.S.D(%)[1]: relative standard deviation.

Recovery data for the preconcentration of Mn(II) and Cd(II) ions from underground water using modified Nile tilapia fish scales.

Biosorbents	**Metal ions**	**Add (ppm)**	**Found (ppm)**	**R(%)**	**R.S.D (%)[1]**
Detergent treated Scales.	Mn(II)	0.2	0.305	93	2.2
	Cd(II)	0.2	0.24	94.6	3.4
Sod. acetate treated scales.	Mn(II)	0.2	0.326	99	1.7
	Cd(II)	0.2	0.253	99.8	2.8

R.S.D(%)[1]: relative standard deviation.

4. Conclusion

Fish scales are an environmentally friendly potential biosorbent for heavy metals in water samples. This work examined the efficiency of this sorbent in removal of Cd(II) and Mn(II) ions from aqueous environment. The results indicated that several factors such as pH of solution, initial metal ions concentration, biomass dose and flow rate affect the biosorption process. Based on these results it can be concluded that fish scales are an effective green and alternative biomass for the removal of Cd(II) and Mn(II) from aqueous solutions because of its good biosorption capacity, renewable and low-cost nature.

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