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Novel and Green Modification of Shrimp Shells for the Determination and Extraction of Some Toxic Metal Ions from Real Water Samples

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Abstract

In the present work, raw shrimp shells were modified by sodium chloride, sodium carbonate and sodium acetate. Bioextraction of Cd (II), Mn(II) and Fe(III) ions from real water by the new and safe modified shrimp shells were studied as a function of initial solution pH, shaking time and initial metal ions concentration. The bioextraction is more efficient in pH ≤ 6 for all the three modified extractor than the unmodified shrimp shells. The adsorption capacities of the three modified shells for Cd (II), Mn (II) and Fe (II) were evaluated using static mode and they are found to be 556,478 and 438 for sod.chloride, 557,492 and 502 for sod. Carbonate and 537,437 and 417 for sod.acetate modified shells, respectively. The results also revealed that the modified extractor show high selectivity toward the analyteions in the presence of Cl^-, Br^-, I^-, SO_4^{--}, NO_3^- ,K^+, Ca^{++}, Mg^{++} and Na^+ ions. Based on these results the use of such bioextractor for the environmental application is encouraged.

Key words: Absorption; chitin; shrimp shells; heavy metal.

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1. Introduction

Contamination by metal ions is one of the most serious environmental problems today. Industrial processes including battery manufacturing electroplating and mining release several toxic metal ions in the ecosystem [1-3].Heavy metal ions are considered as pollutants, due to their accumulation in fish, plants and animals. This accumulation cases different diseases. Also the accumulated metal ions are non-biodegradable, so that, they must be extracted from the aqueous system and keep their abundance at the minimum level [4]. The treatment of metals ions is of special concern due to their adverse effect on the environment. In recent years, various methods for metal ions extraction from wastewater have been extensively studied such as electrochemical treatment [5], membrane separation [6], adsorption [7] and ion exchange [8]. Adsorption is extensively used because it is simple, economical and effective. However many sorbents always suffer from low efficiency and extraction capacity [9]. Therefore, it is highly desirable to develop a new sorbent with high extraction capacity, simple operation in treatment process, green, good and easy modifiability and recoverability [10]. Biosorption is a relatively new process that has proven to be very promising for the removal of heavy metals from wastewater. Biosorption can be carried out either by immobilized biosorption or in suspension. Many biosorbents have been applied for heavy metals removal including agricultural weeds wastes [11], biomasses of bacteria, algae, yeast and fungi [12]. Among efficient biosorbents, Chitin is a potential biosorbent for many toxic ions, because of its high extraction capacity, good and easy modifiability and reusability [13]. Recent studies have shown that chitinous materials are effective in removing metal ions such as cadmium, arsenic, iron, cobalt, copper, manganese, zinc and lead, from aqueous systems [14-22]. Chitin molecule consists of (1-4)-2-acetamido- 2-deoxy-d-glucose units, some of which are deacetylated. The acetamido groups are able to act as non-specific chelators and form hydrogen bonds with many metal ions [23]. The production of chitin however, requires large amounts of acid and alkaline, therefore; other natural sources of chitin should be evaluated rather than lab preparation. Among potential materials, the low-cost fresh shrimp shells can be one of the choices [24]. Shrimp shells contain chitin (15% -20%), protein (25% - 40%), and calcium carbonate (45% -50%).As they contain good amount of chitin, shrimp shellsare considered as an alternative biosorbent to extract toxic metal ions from aqueous solutions [25] .An important strategy for metal ions extraction is the incorporation of complexing agents in the solid to extract and preconcentrate toxic ions from aqueous solution. The objective of this study was to evaluate the extraction of some metal ions from natural water by the modified shrimp shells as a novel biosorbent.

2. Experiment

2.1. Apparatus and reagents

Flame Atomic Absorption Spectrometer: measurements were recorded on AAS-5 FL instrument (Carl Zeiss Technology, Germany), equipped with standard burner for air–acetylene flame. 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.Mechanical shaker: A mechanical shaker with up to 200 rpm (SL 350, Nuve, Akyurt, Ankara, Turkey) with speed control was used. Polyethylene bottles: 125 ml polyethylene bottles were soaked in chromic acid for 24 hours, then washed by doubly distilled water (DDW) and dried at 60-80 ºC in drying oven. Glass columns: 25 cm long and 1.1 cm in diameter glass columns were used in the dynamic experiments.

2.2. Chemicals and solution

Standard solutions (1000 µg mL^{-1}) of iron, manganese and cadmium were prepared by dissolving an accurately weighed portions for of $MnHCl_2.4H_2O$ (*Aldrich*), [$FeNH_4(SO_4)_2.12H_2O$] (Merck) in DDW containing 5ml of conc. $H_2SO_4$and $Cd(NO_3)_2.4H_2O$ obtained from Panreac (Barcelona, Spain) in DDW and addition of 2 mL from concentrated HNO_3 acid(Adwic, Egypt). Working solutions (10 µg mL^{-1}) were prepared daily using ml of stocks and dilution with 99 ml of standard solutions with DDW.

2.3. Modification of Shrimp Shell

100 gram of the dried shrimp shells were immersed in 0.5 M of NaCl , Na_2CO_3or CH_3COONa and shacked for 5h, then washed with DDW till free from Cl^-,CO_3^{2-} or CH_3COO^-. The washed sorbents were oven dried at 60 $^{\circ}$C till constant weight.

2.4. Recommended procedures

2.4.1. Batch procedure

In the batch method a quantity of sorbent is added to the sample metal ions and the mixture is shaken for a specified time. Then the sorbent was separated from the sample solution by filtration. Finally the resultant solution is analyzed by an appropriate method.

2.4.1.1. Effect of pH and acidity

In order to investigate the effect of pH on the extraction of both Fe(III), Mn (II) or Cd (II) ions onto the modified shrimp shells, 25 ml solution containing 20 µg of the individual metal ions was adjusted to a pH range of 2 to 8 using NaOH or HCl solution, and the mixture was shaken with 0.4 g of shrimp shells for 3 hours on a mechanical shaker, the amount of the metal ions remained in the solution were measured using the recommended method after separation of the shrimp shells. The extracted amount of the metal ion retained on the biosorbent was determined by the difference. The uptake percent of the metal ions on the sorbent were calculated from the equation (1).

$$\%uptake = \frac{C_{\circ} - C}{C_{\circ}} x100 \qquad (1)$$

Where C_o and C are the initial and final concentrations, respectively, of metal ions in the solution (µg/l).

2.4.1.2. Effect of shaking time

Aliquots of the metal ions (20µg /25ml) adjusted at the optimum pH in 25ml solution were shaken with 0.4g modified shrimp shells for various time intervals in 125ml bottles, and then the remaining metal ions after equilibration with the shells were determined spectrophotometrically,the amounts of metal ions extracted were calculated.

2.4.1.3. Extraction isotherm and Sorbent Capacity

Determination of the sorbent capacity was carried out by the sorption of the selected metal ions from separate metal ions solutions**.** Typically 0.4g of the modified shrimp was equilibrated with 10 to 100 µg metal ions adjusted at the optimum pH, which were automatically shaken for3 hours at room temperature. After equilibration, the remaining metal ions in the filtrate were determined. The sorbent capacity was calculated from equation (2).

$$q = \frac{C_{\circ} - C}{m} xV \qquad (2)$$

Where q is the sorbent capacity (µg/g), C_o and C are the concentration of the ion in the initial and final solution, respectively, V is the volume of the aqueous phase in liters and m is the mass of sorbent in grams (g)**.**

2.4.1.4. Kinetic Study

To obtain the efficient removal, for this purpose, the effect of shaking time on the extraction by the different modified shrimp shells were studied, where 0.4g of the modified shrimp shells was added to 25 ml of the tested metal ions solution containing 20 µg of Fe (III), Mn (II) or Cd (II) ions at the optimum pH and automatically shaking for different time intervals on a mechanical shaker. The uptake percent of the metal ions on the biosorbent was calculated from equation (1).

2.4.2. Dynamic method

Column method applied by off-line. In an off-line method the solution sample is passed through a suitable column and the resultant solution is analyzed by a suitable procedure. In the dynamic experiments 1.5 g of the novel modified shrimp shells was packed into the column with gentile pressure by a glass rode on the biosorbent plugs onto the column filled with DDW to avoid air bubbles then added glass beads on the top of the shrimp shells bed to prevent shrimp shells floating upwards. The bed high of the shrimp shells column was about 60 mm. it was washed successively with DDW then stored in DDW for the next experiment. Working solutions were passed through the shrimp shells column at a flow rate 3 ml/min. the stripping of the metal ions from the shrimp shells column were carried out with the suitable eluting agent and the mount of the metal ion was determined by the recommended procedure.

2.4.2.1. Effect of sample flow rate

Determination of the sample flow rate is an important step where it determines the time needed for contacting of the analyte and biosorbent. This carried out by percolating 25 ml solution containing 20 µg of Fe (III), Mn (II) or Cd (II) ions onto 1.5 g different modified shrimp shells column at the optimum pH at different flow rates ranging from 1 to 10 ml/min. the % uptake was calculated from the initial and final concentration of metal ion in the solution from equation (1).

2.4.2.2. Effect of eluent concentration

The following considerations should be taken into account to select an appropriate eluent for effective desorption of the metal ion complexes from the sorbent: (i) the eluent should desorbs the metal ion complexes; (ii) the eluent should not destroy the sorbent, and (iii) the eluent should be suitable for the subsequent determination technique**.** Extraction of analyte ions onto chelating sorbent depends on eluent concentration, and this was investigated. For this purpose 25 ml solution containing 20 µg of each metal ion was percolated onto 1.5 g different modified shrimp shells column, desorption of the metal ion was carried out by using various concentrations of hydrochloric acid ranging from 0.1 to 1.5 mol. The amounts of metal ions in the eluate were determined by the recommended method, and the % uptake was calculated from the initial and final concentration of metal ions in solution from equation (1).

2.4.2.3. Effect of eluent volume

Different volumes of 1 mol HCl ranging from 2 to 14 ml were used to test the effect of the eluent volume on the extraction of the analyte. For this purpose 25 ml solution containing 20 µg of each metal ion was percolated onto 1.5 g different modified shrimp shells column. Ions in the eluent were determined by the recommended method, and the % uptake was calculated from equation (1).

2.4.2.4. Breakthrough Curve (Capacity)

The amount of the metal ions taken by the column is called the breakthrough capacity. For this purpose 500 ml sample solution containing 5 µg/ml of each metal ion separately was passed through the column. Each solution was adjusted to the optimum pH and the effluent was collected in 5 ml fractions where the amount of metal ions in each fraction was estimated by the recommended method. The percentage of metal ions in each effluent aliquot can be calculated and plotted against the volume of effluent (Bed volume). The breakthrough studies were carried out by 0.4g of the modified shrimp shells.

2.4.2.5. Preconcentration of the metal ion

By placing 20µg of the metal ion adjusted to the optimum extraction conditions in different volumes of the samples (100 – 1000ml) were passed through the modified shrimp shells column at 3ml min^{-1} flow rate, the column was then washed by suitable solutions and the metal ion retained in the column was recovered a suitable eluting agent, the amount of the eluted metal ion was determined and the percentage of the recovery was then calculated.

2.4.2.6. Interfering effect of foreign ions

In order to study the interfering effect of some foreign ions by the column method, 25 ml solution containing 20 µg of Fe (III), Mn (II) or Cd (II) ions at the optimum pH percolated onto the column loaded with 1.5 of the different modified shrimp shells column at a flow rate of 3 ml/min in the presence of varying concentrations of the foreign ions. The taken amount of each metal ion by this biosorbent was desorbed by 10ml of 1 mol/l HCl solution and the concentration of the metal ion in the eluate was determined by the recommended method. The recovery percent (% R) of each metal ion was calculated from equation (3).

$$\%R = \frac{C}{C_{\circ}} x100 \qquad (3)$$

Where, $C_{\circ}$ and C are the initial and final concentration of metal ion in solution (µg/l), respectively.

2.5.Real Sample preparation

2.5.1Baher yossef and Qarun lake water

Baher yossef and Qarun lake water samples were collected from Fayoum City. A 1.0 L from each sample was spiked with 20 µg of each analyte ions, adjusted to the pH 6 and passed through the modified shrimp shells column at flow rate 3 mL min^{-1}. The column was rinsed with few portions of DDW to remove the physically bounded metal ions and the retained metal ions were desorbed from the column by 10 mL of 1 mol L^{-1}HCl solution and measured by the FAAS method.

3.Result and discussion

3.1.Extraction of the metal ion as a function of the pH

Sample pH is a very important chemical parameter that has to be investigated, because it plays an important role in analyte biosorption process and ions speciation. From Fig[1-4],it is found the extraction % increase by rising the pH value till reaching a maximum value then leaving off within a certain range of pH range which is usually followed by a decrease. At pH 2 ,the extraction efficiency of NaCl modified shrimp shells is found 62% , 63% and 68 % and sod.carbonate modified shrimp shells are 71% , 67 % and 55% while, the extraction % of sod.acetate modified shrimp shells are 66% , 73% and 77% for Mn (II),Cd (II) and Fe (III) respectively. In general the amino groups of the chitosan present in the shrimp shells are protonated in strong acidic solutions pH≤2and consequently the shrimp shells material becomes positively charged [26].

The uptake percent of the three modified shrimp shells for Mn (II), Cd (II) and Fe (III) is strongly dependent on the variation of the initial solution pH. In strong acidic solution pH 2, more protons will be available to protonate the amino groups of chitosan to form NH_3 groups, this reduce the number of chelating binding sites for the extraction of the analyte ions [27]. The minimum extraction at low pH 2 may be also due to the fact that high concentration and high mobility of hydrogen ions are preferred initially bioextracted rather than the studied ions. On the other hand, at weakly alkaline solutions, quantitative extraction% more than 95% is observed. Higher pH values, resulting more negative binding sites. Consequently, the attraction of the positively charged ions would be enhanced. Another aspect that must be considered is the ions speciation in the solution, which is also strongly pH dependant. So, the correct adjustment of the pH is necessary to improve the formation of complexes between the analyte ions and the ligand built on the biosorbent which leads to better retention. Compared with the unmodified shrimp shells, the extraction % of the three modified biomass increased. In the unmodified shrimp shells the maximum extraction% for Mn (II) is 89.5 at pH 3 and 90 for Cd (II) at pH 4 and for Fe (III) is 90.4 at pH 5. The results clearly show the novel modified shrimp shells are more effective than the unmodified one. The high efficiency of the modified shrimp shells may be related to the structural change brought through the modification process.

Thus, the new modified shrimp shells are promising materials to be applied in metal ions extraction from aqueous solution. Finally, the modified shrimp shells is an effective and alternative bioextractor for the removal of Mn(II),Cd(II) and Fe(III) ions from aqueous solutions in terms of high uptake capacity ,natural abundant availability and low cost.

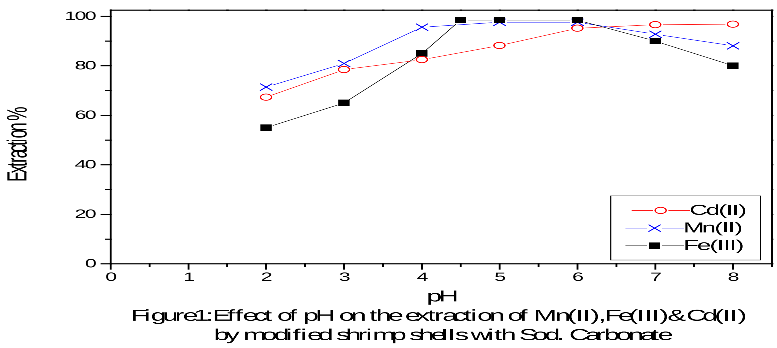

Figure 1

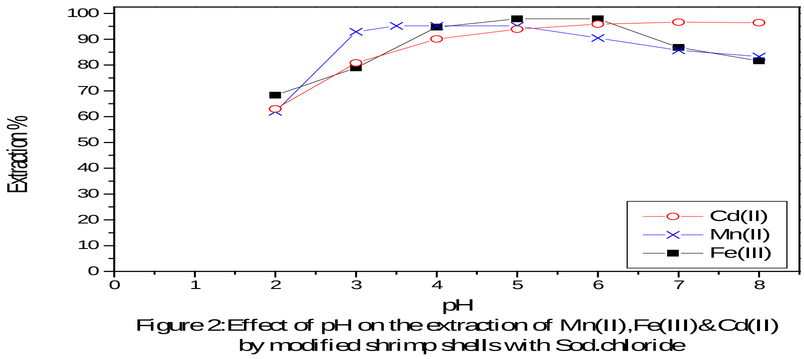

Figure 2

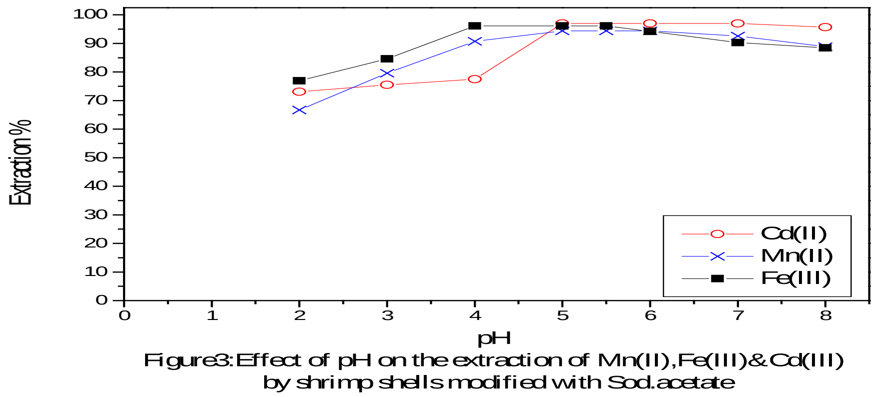

Figure 3

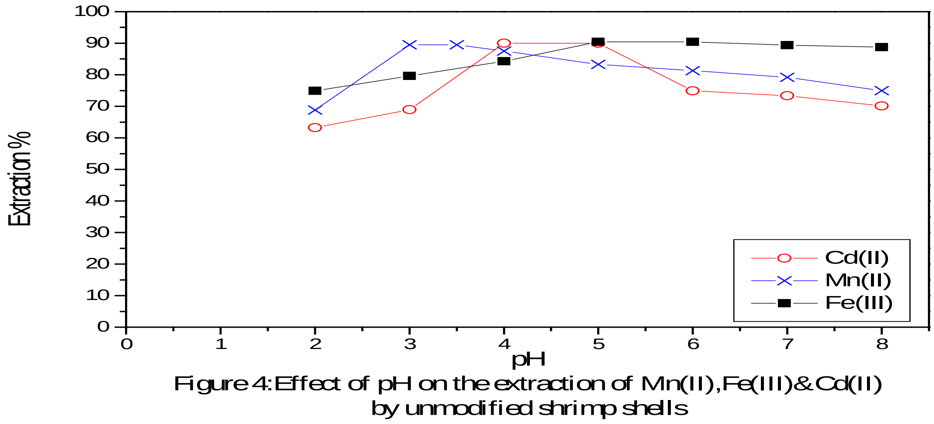

Figure 4

3.2. Effect of shaking time

Figs [5-8] show the kinetics of biomass of 20 µg /25ml Mn (II), Cd (II) and Fe (III) ions by the unmodified and modified shrimp shells. The kinetic curves for the studied ions showed that the removal amount by the biosorbent sharply increases to reach an equilibrium value in 50, 60 and 80 min at sod.acetate modified shrimp shells, 120,110 and 110 at sod.carbonate modified shrimp shells and 100, 110 and 90 at sod.chloride modified shrimp shells for Mn (II), Cd (II) and Fe (III) ions respectively. A further increase in the contact time had a negligible effect on the extracted analyte. According to these results, the contact time is fixed at 3h for all batch experiments to make sure that the equilibrium was reached. The bioextraction of Mn (II), Cd (II) and Fe (III) ions by the novel modified extractors were relatively rapid for the first hour as a result of the free binding sites on the shrimp shells. The bioremoval of the studied ions seems to follow two-phase removal mechanism [28-29]. The initial is fast phase which occurs due to the large surface area of the extractor. The subsequent slow phase occurs due to quick exhaustion of the extraction sites. The quick removal of sod.acetate modified shrimp shells for Mn (II),Cd (II) and Fe (III) ions reflects their higher affinity to the new modified shells ,also the better accessibility of the studied ions to the chelating sites , and therefore strong bond formation with the modified shrimp shells. This investigates the accessibility of the modified shrimp shells in column technique where quick chelation is a pronounced factor.

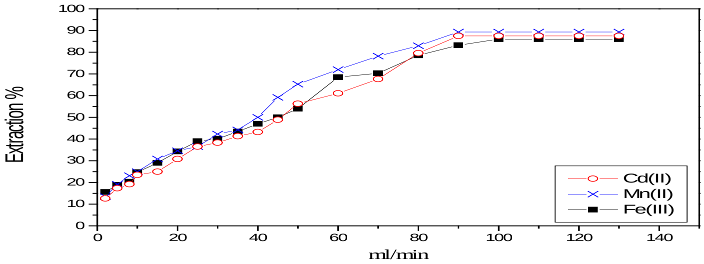

Figure 5:Effect of shaking time on the extraction of Mn(II),Fe(III)&Cd(II) by unmodified shrimp shells

Figure 5

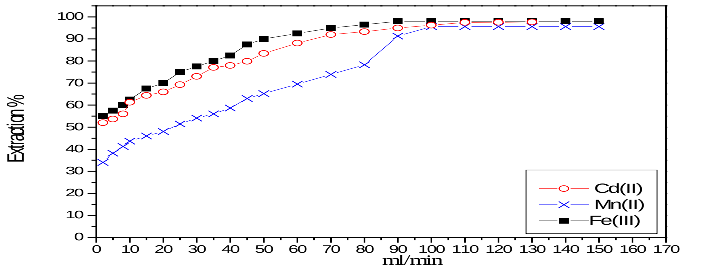

Figure 6:Effect of shakingtime on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shell modified with Sod.chloride

Figure 6

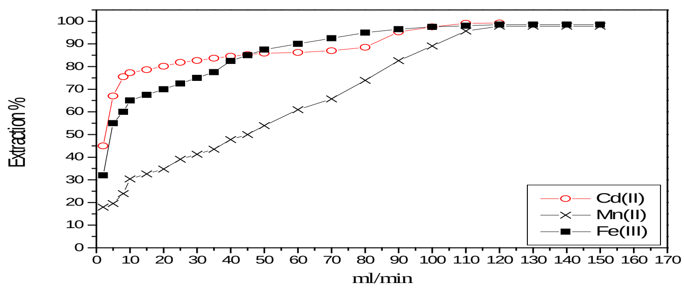

Figure 7:Effect of shaking time on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modified with Sod.Carbonate

Figure 7

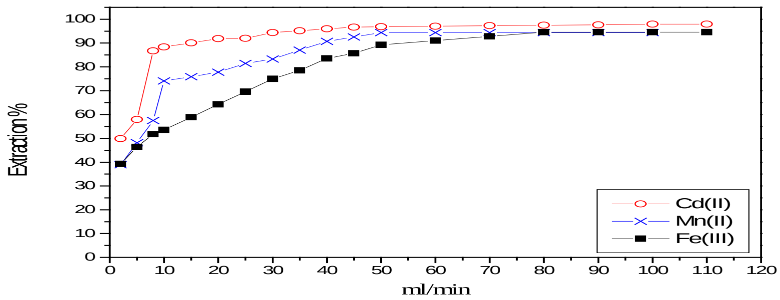

Figure 8:Effect of shaking time on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shell modifieded with Sod.acetate

Figure 8

3.3. Effect of the shell dose

The effect of bioextractor dose on the extraction efficiency of Mn (II),Cd (II) and Fe (III) are studied by varying the biomass weight at fixed experimental parameters, pH, shaking time and metal ion concentration. As it could be seen Fig[9-11],the extraction % of Mn (II),Cd (II) and Fe (III) increases with increase the extraction weight from 0.1 to 0.4 g

. when the modified shrimp shells dose beyond 0.4g there is no significant increase in the uptake percentage of the studied ions by all the three modified shrimp shells. This behavior suggests that after a certain dose of the biomass, the maximum uptake is attained and hence the amount of the ions remains constant even with further increasing of extractor dose.

The increase of the extractor weight prevents the analyte ions from reaching the various sites of the biomass [30].

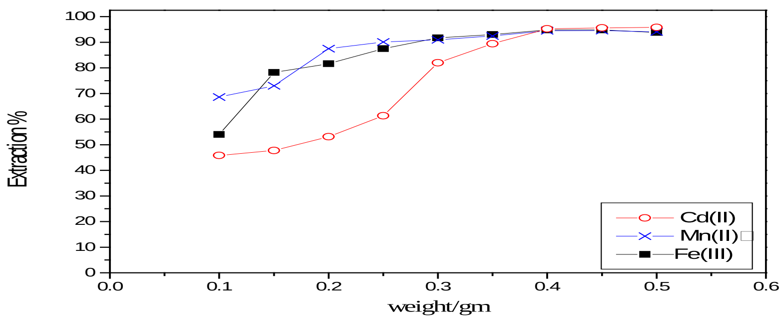

Figure 9:Effect of sorbent weight on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modified with Sod.chloride

Figure 9

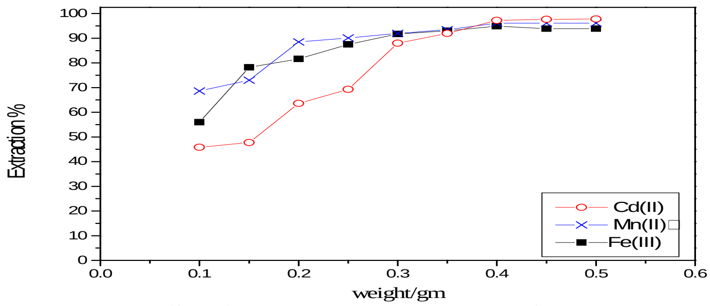

Figure 10:Effect of sorbent weight on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modified with Sod.carbonate

Figure 10

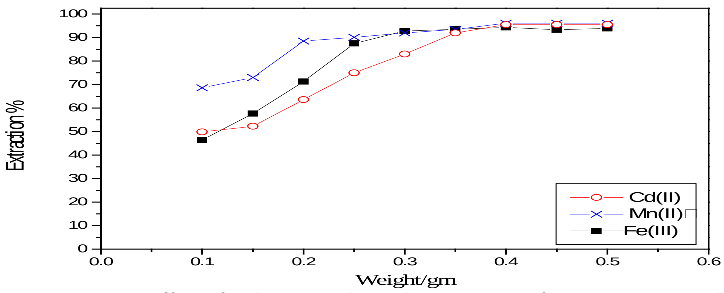

Figure 11:Effect of sorbent Weight on the extraction of Mn(II),Fe(III)& Cd(II) by shrimp shells modified with Sod.acetate

Figure 11

3.4. Effect of interfering ions

Cations, like Sodium, Potassium, and Magnesium, Calcium and Iron and anions like Chloride, Bromide, Iodide, Sulphate, Nitrate and Phosphate are known to exist in natural water samples.

These ions have the capability to complex or interfere with lot of ions. Therefore, the effect of these interfering metal ions on the uptake of studied ions with the three types of the new modified shrimp shells was studied using the recommended batch method under the optimum uptake condition. Foreign ions concentration added to the sample according to the method reported previously**.** A species is considered to interfere when it affects the uptake by≥±5%. The presences of the most of these devers ions do not cause any interfering effect on the uptake of the studied ions as showen in tables [1-3].

However, among the interfering ions which strongly reduce the uptake% are SO_4^{--},NO_3^- ,while only (I^-) reduce strongly the extraction of Mn (II) and Cd (II) in case of sod.acetate modified shrimp shells. These results demonstrate the three modified shrimp shells are capable to extract Mn (II),Cd (II) and Fe (III) ions from real water samples, moreover ,sod.acetate modified shrimp shells is more efficient in the selective extraction of the tested analyte ions in the presence of all interfering ions.

This confirms the betterment in the uptake affinities and selectivity of the three modified shrimp shells especially in case of sod.acetate modified shrimp shells.

Table 1: Effect of Interfering Ions by shrimp shell modified with Sod.acetate

Ion	**Formof interfering ion**	**Conc.of interfering ion mg/25ml**	**Recovery Mn (II)**	**Fe(III)**	**Cd(II)**
Non	-	---------	100	100	100
Cl^-	NH_4Cl	$37.5x10^{-3}$	95.6	100	98.2
Na^+	NaCl	$375x10^{-3}$	95.6	95	98.8
Br^-	100	95			95.8
I^-	NaI	$2.5x10^{-3}$	91.3	100	92.5
SO_4^{-2}	Na_2SO_4	$12.5x10^{-3}$	97	100	90
NO_3-	$NaNO_3$	$25x10^{-3}$	100	95	98.8
Mg^{+2}	$MgSO_4$	$1.25x10^{-3}$	95.6	100	95.2
Ca^{+2}	$Ca(NO_3)_2$	$2.5x10^{-3}$	95.6	97	98.2
K^+	KCl	$25x10^{-3}$	100	100	98.2

Table 2: Effect of Interfering Ions by shrimp shell modified with Sod.carbonate

Ions	**Form of interfering ion**	**Conc.of interfering ion mg/25ml**	**Recovery Mn (II)**	**Fe(III)**	**Cd(II)**
Non	-	---------	100	100	100
Cl^-	NH_4Cl	$37.5x10^{-3}$	95.7	100	98.27
Na^+	NaCl	$375x10^{-3}$	100	100	99.2
Br^-	NaBr	$2.5x10^{-3}$	95.7	90	96.3
I^-	NaI	$2.5x10^{-3}$	91.3	97	94.8
SO_4^{-2}	Na_2SO_4	$12.5x10^{-3}$	100	90	97.6
NO_3-	$NaNO_3$	$25x10^{-3}$	91.3	93.7	93.7
Mg^{+2}	$MgSO_4$	$1.25x10^{-3}$	95.7	95	97.1
Ca^{+2}	$Ca(NO_3)_2$	$2.5x10^{-3}$	100	97	97.9
K^+	KCl	$25x10^{-3}$	95.7	100	96.1

Table 3: Effect of Interfering Ions by shrimp shell modified with Sod.chloride

Ions	Formof interfering ion	Conc.of interfering ion mg/25ml	Recovery		
			Mn (II)	Fe(III)	Cd(II)
Non	-	---------	100	100	100
Cl^-	NH_4Cl	$37.5x10^{-3}$	100	95	97.8
Na^+	NaCl	$375x10^{-3}$	100	100	100
Br^-	NaBr	$2.5x10^{-3}$	93.1	85	90.4
I^-	NaI	$2.5x10^{-3}$	96.5	95	96.9
SO_4^{-2}	Na_2SO_4	$12.5x10^{-3}$	96.5	90	93.5
NO^{3-}	$NaNO_3$	$25x10^{-3}$	96.5	90	97.7
Mg^{+2}	$MgSO_4$	$1.25x10^{-3}$	96.5	95	97.7
Ca^{+2}	$Ca(NO_3)_2$	$2.5x10^{-3}$	96.1	95	99.3
K^+	KCl	$25x10^{-3}$	93.1	100	97.7

3.5. Effect of Sorbent Capacity

The capacity of the extractor is an important factor because it determines how much solid phase is required quantitatively to extract a specific amount of the analyte ions from the eluted solution. The capacity q (µg/g) of adsorbed ion at 25°C was calculated using equation (2).

Extraction isotherm was studied for individual ions by the static mode. By shaking 25 ml metal ions solution containing metal ion concentration varying from 10 to 100 µg at the optimized conditions.

It is clear that the extraction capacity of Fe (III), Mn (II), and Cd (II) ions probably differ due to their ionic size.

The results indicate also that Fe, Mn, and Cd ions are directly coordinated on the modified shrimp shells, probably by using sulfur and nitrogen donor atoms, without other transfer mechanism [31-32].

The gradual increase in the amount of metal ions extracted with increasing the metal concentration reveals the gradual saturation of the sorbent binding sites. When complete saturation of the binding sites is fully occupied, no further extraction occurs.

The total uptake capacity of the modified shrimp shells are listed in Tables [4].

Table 4: Capacity of modified shrimp shells

Metal ion	(q ± SD*) (µg/g)Capacity of shrimp shells modified with Sod.acetate	(q ± SD*)(µg/g) Capacity of shrimp shells modified with Sod.Carbonate	(q ± SD*)(µg/g) Capacity of shrimp shells modified with Sod.Chloride
Cd(II)	537±1.04	557±0.7	556±0.3
Mn (II)	437 ±1.3	492 ±0.7	478 ±2.2
Fe(III)	417 ±1.6	502 ±0.9	438 ±1.3

SD*****: Standard deviation Basedon three replicate measurements

3.6. Column procedure

3.6.1. Dynamic Capacity

The saturation capacity of the three modified shrimp shells column is estimated by feeding the studied ions solution at concentration 20µg/25 ml of each metal separately at the optimum conditions, While the sample is percolated in the novel modified shrimp shells, the effluent is collected into 5ml successive volumes fraction and the analyte ions are estimated by the recommended method.

From the breakthrough Figures [12-14] it is clear that, the shape of the dynamic capacity curves depend on the type of the shrimp shells modification and the metal ions.

The breakthrough point was assigned when the metal ions is detected in the effluent.

The saturation of sod.acetate modified shrimp shell column was achieved after passing 120ml, 110 ml and 150 ml while saturation of sod.carbonate modified shrimp shell was achieved after passing 150ml, 170ml and 210ml and saturation of sod.chloride modified shrimp shell was achieved after passing 120ml, 120ml and 130 ml of Mn (II),Cd (II) and Fe(III),respectively from the feeding solution.

3.6.2. Effect of Sample flow rate

The uptake extent on the novel modified shrimp shells was studied at varying sample flow rate (0.5-8) ml/min .The maximum flow rate at which extraction more than 95% estimates the range allowed for the extraction of the analyte ions onto the column. The results showed optimum range of flow rate for all the studied metal ions with sod. acetate,sod. chloride and sod. carbonate modified shrimp shells are (0.5-2 min), (0.5-2 min) and (0.5-3 min) for all the studied metal ions respectively. The flow rates 0.5 or 1 ml/min is excluded since it requires too long extraction time. However at flow rate greater than the maximum limit the retention efficiency decreases due to the insufficient phase content between the shells and the studied ions. Based on the above results, the optimum flow rate is 3 ml/min for Mn (II),Cd (II) and Fe (III), respectively which is used in subsequent experiments.

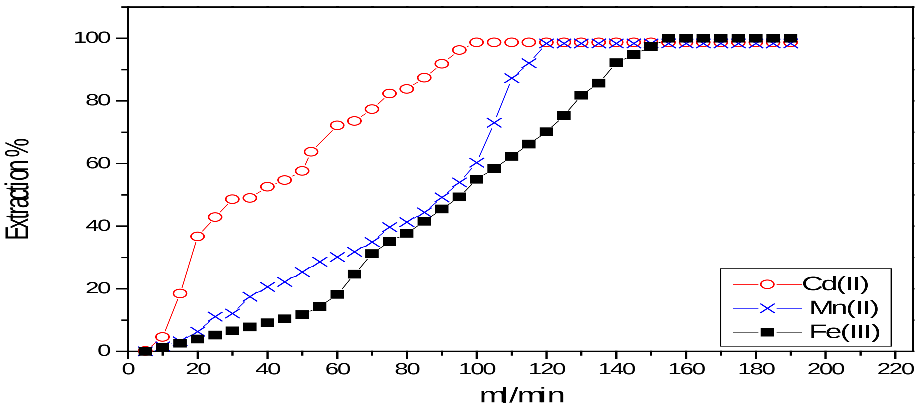

Figure 12:Effect of Breakthrough on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shells modified with sod.acetate

Figure 12

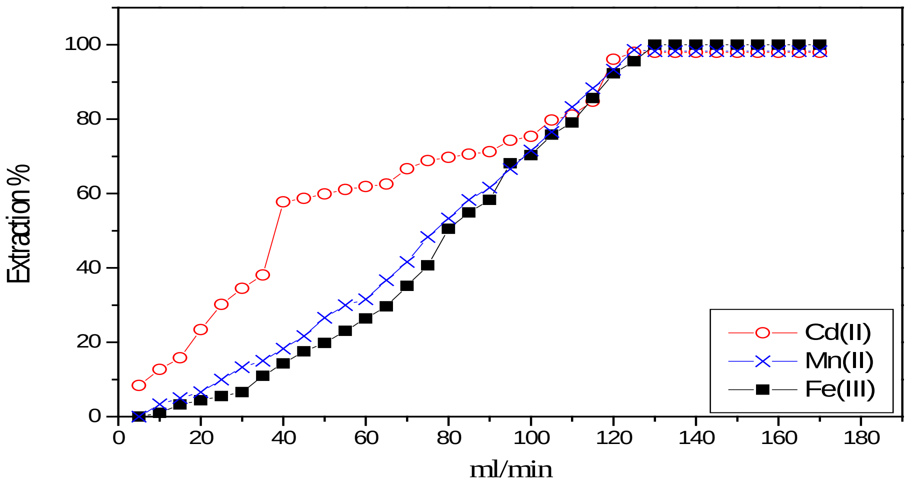

Figure 13:Effect Breakthrough on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shells modified with Sod.chloride

Figure 13

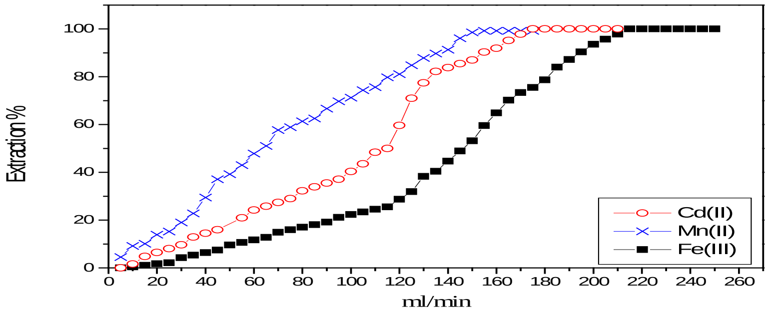

Figure 14:Effect of breakthrough on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modified with Sod. Carbonate

Figure 14

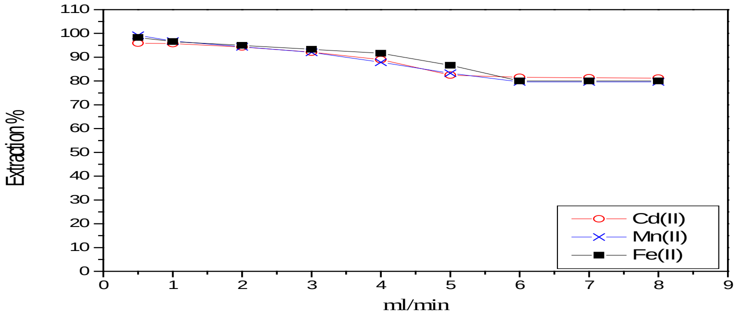

Figure 15:Effect of flow rate on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modifieded with Sod.chloride

Figure 15

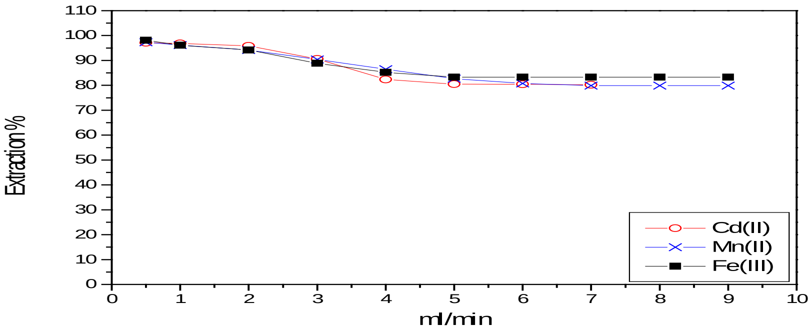

Figure 16:Effect of flow rate on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modifieded with Sod.acetate

Figure 16

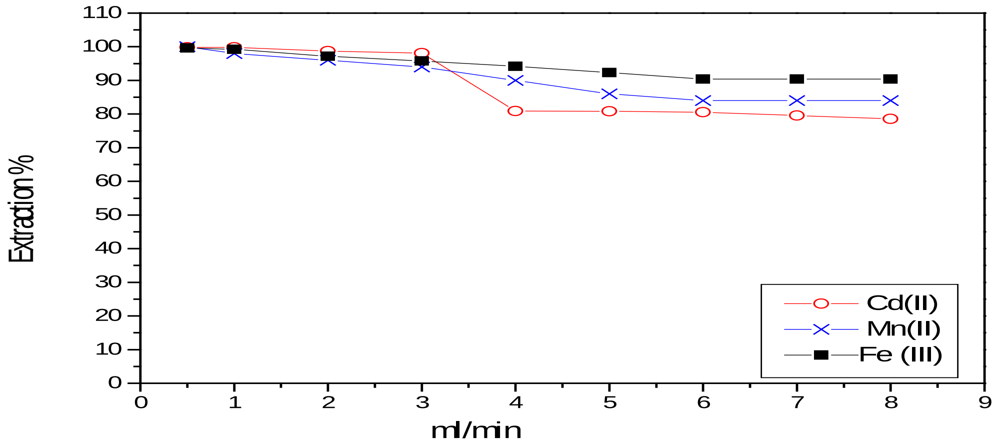

Figure 17:Effect of flow rate on the extraction of Mn(II),Fe(III)&Cd(II) by shrimp shells modifieded with Sod.Carbonate

Figure 17

3.6.3. Eluent volume

The volume necessary for quantitative extraction more than 95 % of the analyte ions should be carefully studied for the estimation of the prconcentration factor. Fig[18-20] showed the data obtaind when 20 µg of Mn (II), Cd (II) and Fe (III) are desorbed for 1.5 gram sodium acetate, sodium carbonate or sodium chloride modified shrimp shells respectively, under the optimum conditions. It was found that, The volume of HCl acid necessary for the quantitative extraction of the tested ions from sodium acetate,sodium carbonate or sodium chloride modified shrimp shells was 10 ml for all tested ions. The investigated volumes are applied in the enrichment procedures of the studied ions for larger volume samples.

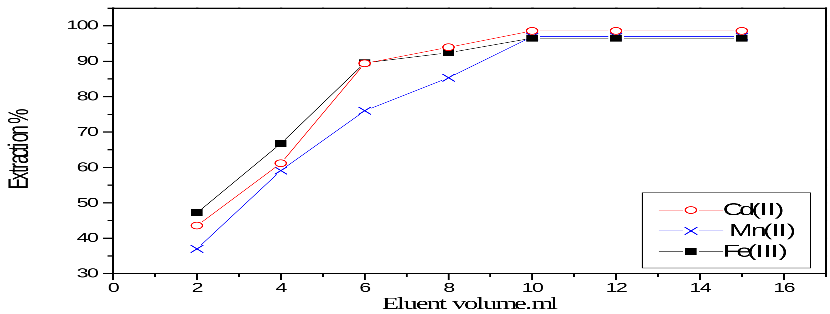

Figure 18:Effect of eluent volume HCl on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shells modified with sod.chlorid

Figure 18

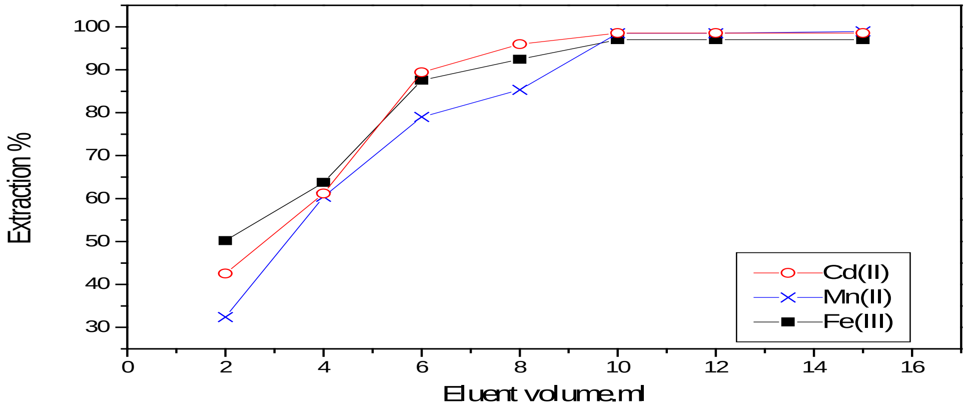

Figure 19:Effect of eluent volum HCl on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shells modified with sod acetat

Figure 19

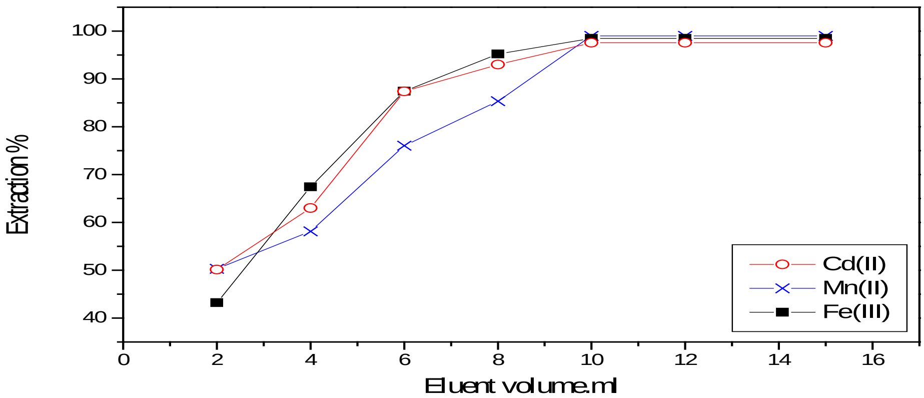

Figure 20:Effect of eluent volum HCl on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shells with modified sod.carbonate

Figure 20

3.6.4. Eluent concentration

The maximum desorption % is found at acids solution, because the bonding between the modified shrimp shells and extracted cations are strongly reduced at acidic conditions so, the cohesion between hydrogen ions and the removed cations increased. The desorption of bounded metal ions to the different modified shrimp shells sorbents is expected to be achieved by proton exchange from acidic solutions. After extraction of analyte ions on the solid phase t the optimum conditions follow by washing the column with double distilled water. The elution process is performed by passing 10 ml HCl acid solution at different concentrations. The obtained results are showen in Fig [21-23]. Quantitative extraction for Mn (II), Cd (II) and Fe (III) is achieved with HCl acid between 0.1 and 1.5 mole. Thus 1 mole of HCl acid concentration is chosen as a good stripping solution for all the studied meal ions.

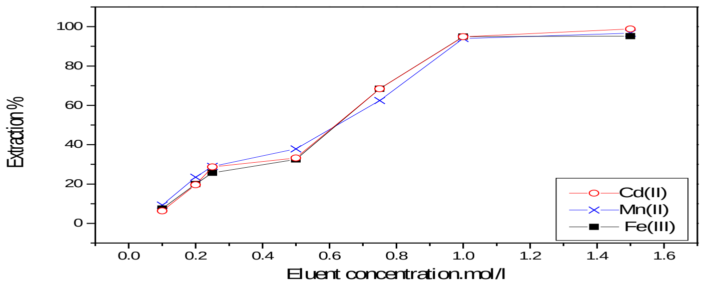

Figure 21:Effect of elluent concentration on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shell modified with sod. chlorid

Figure 21

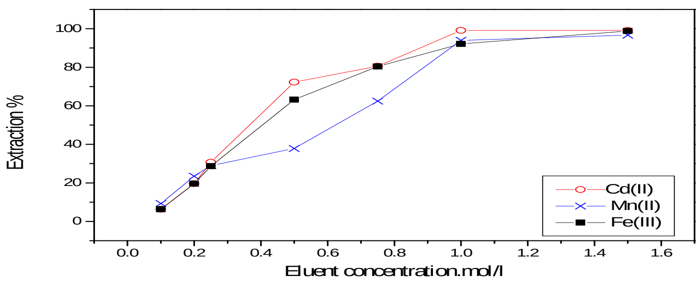

Figure 22:Effect of elluent concentration on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shell modified with sod.acetate

Figure 22

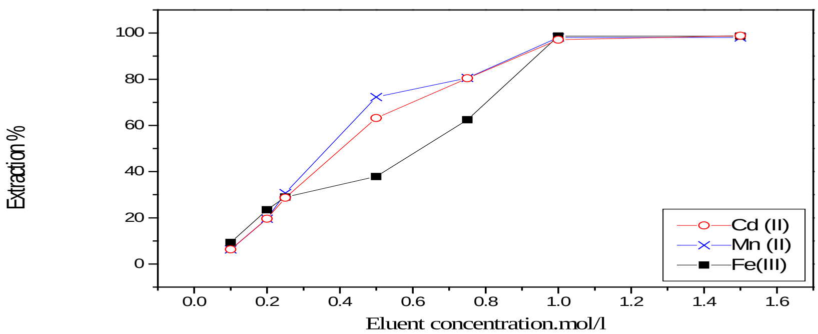

Figure 23:Effect of elluent concentration on the extraction of Mn(II),Cd(II)&Fe(III) by shrimp shell modified with sod.carbonate

Figure 23

3.6.5. Preconcentration

The ability of the three modified shrimp shells are tested to preconcentrate the analyte ions under investigation by column technique. In these experiments, the volume of the sample is increased while keeping the added mount of the studied ions fixed at 20µg.

The solutions are adjusted to the optimized extraction conditions and passed completely through the modified shrimp shells columns.

The loaded metal ions are eluted and the elute is analyzed for each metal ions by the recommended method table [5-7]

Table 5: Prconcentration for Fe (III), Cd (II) and Mn(II) by shrimp shell modified with Sod.carbonate

V(ml)	Mn (II)	Cd(II)	Fe(III)
50	100	100	100
100	100	100	100
250	100	100	100
500	100	98.1	100
1000	100	97.3	98
1500	95.2	91.23	95.8
2000	89	77.68	76.36

Table 6: Prconcentration for Fe (III), Cd (II) and Mn (II) by shrimp shell modified with Sod.acetate

V(ml)	Mn (II)	Cd(II)	Fe(III)
50	100	100	100
100	100	100	100
250	100	100	100
500	100	100	98.2
1000	97.87	100	98.1
1500	93.6	98.7	90
2000	89	90.2	76.36

Table 7: Prconcentration for Fe (III), Cd (II) and Mn (II) by shrimp shell modified with Sod.chloride

V(ml)	Mn (II)	Cd(II)	Fe(III)
50	100	100	100
100	100	100	100
250	100	100	100
500	100	98.2	100
1000	100	97.6	98.4
1500	97.2	89	92.52
2000	91	76.53	81

3.6.6. Prconcentration factor

In order to explore the possibility of extraction low concentration of the studied ions from large sample volumes, the influence of sample volume on the uptake % is examined. The amount of Mn (II),Cd(II), or Fe (III) taken 20 μg in model solution is kept fixed while increasing the sample volume at the optimized conditions. The volume is investigated in the range 50-1500ml.The maximum analyte volume taken into consideration is that which gives the lower limit of extraction .The feed volumes for loading and the prconcentration factors are given in tables [8-10].The extraction % in the range 97-100 %for the three modified shrimp shells .The shrimp shells has prconcentration factor 100 for all analyte ions .

3.6.7. Analytical Applications

In order to evaluate the applicability of the studied modified shrimp shells. The prconcentration step for real sample aimed to achieve sample concentration and matrix extraction prior to the analyte ions determination. The extraction data indicated that the uptake is quantitave for Mn (II), Cd (II) and Fe (III) ions with all the modified shrimp shells. Finally, satisfactory results are obtained for the studied ions, which confirm the selectivity and validity of the proposed method or the determination of the analyte ions and the prconcentration in different real water sample stables [11-12].

comparison between the three modified shrimp shells sorbents exhibit approximately similar working pH range 5-6 for Mn (II), 6-8 for Cd (II) and 4-6 for Fe(III)by using sodium acetate modified shrimp shells ,sodium carbonate modified shrimp shells or sodium chloride modified shrimp shells. The pH range light varied slightly in going for one biomass to another or with varying the metal ions but still in the overall optimized pH rang.

Table 8: Prconcentration Factor for Fe (III), Cd (II) and Mn(II) by shrimp shell modified with Sod.carbonate

Metal ion	**Initial volume (ml)**	**Eluent volume (ml)**	**% R**	**CF**
Fe(III)	1000	10	98	100
Mn (II)	1000	10	100	100
Cd(II)	1000	10	97.3	100

Table 9: Prconcentration Factor for Fe (III), Cd (II) and Mn (II) by shrimp shell modified with Sod.acetate

Metal ion	**Initial volume (ml)**	**Eluent volume (ml)**	**% R**	**CF**
Fe(III)	1000	10	98.1	100
Mn (II)	1000	10	97.87	100
Cd(II)	1000	10	100	100

Table 10: Prconcentration Factor for Fe (III), Cd (II) and Mn(II) by shrimp shell modified with Sod.chloride

Metal ion	**Initial volume (ml)**	**Eluent volume (ml)**	**% R**	**CF**
Fe(III)	1000	10	98.4	100
Mn (II)	1000	10	100	100
Cd(II)	1000	10	97.6	100

The extraction time to reach equilibrium is the shorter with Sod.acetate shrimp shells 50min for Mn (II), 80 min for Fe (III) and 60 min for Cd (II), with sod. Chloride shrimp shells. Its reaches after 100,100 and 90 min for Mn (II), Cd (II) and Fe (III) respectively ,with sod.carbonate, the equilibrium time reaches after 120, 110 and 110 min Mn (II),

Cd (II) and Fe (III), respectively for modified shrimp shells. The difference in appropriate flow rate is insignificant in going for one sorbent to another. The 3 ml /min is suitable for the three modified biomass. Finally, quantitave extraction of the element to the sodium acetate, sodium carbonate or sodium chloride modified shrimp shells extractors are achieved for Mn (II) up to:(50 to 1500),((50 to 1000) and (50 to 1500) respectively ,(50 to 100),(50 to 1500) and (50 to 1000) for Cd (II) respectively and (50 to 150),(50 to 1000) and(50 to 1000) for Fe (III) respectively. The new modified biomass shows good prconcentration ability by the column procedure, which confirms better extraction ability or the for the examined metal ions for large volume samples.

Table 11: The Recovery % for spiked tap water samples for modified shrimp shells

Sorbent	Metal ion	Added (μg/ml)	Found (μg/ml± SD*)	% R
sod.Carbonate	Fe(III)	0.2	0.0862 ±0.1827	94.1
	Mn (II)	0.2	0.07612 ±0.1501	98.7
	Cd(II)	0.2	0.0483 ±0. 0.1332	97.34
sod. Acetate	Fe(III)	0.2	0.0931 ±0.3249	97.04
	Mn (II)	0.2	0.0548 ±0.2411	92.76
	Cd(II)	0.2	0.0460 ±0.30159	96.014
sod. Chloride	Fe(III)	0.2	0.0547 ±0.1391	91.31
	Mn (II)	0.2	0.0618 ±0.1607	93.76
	Cd(II)	0.2	0.0358 ±0.1054	94.07

Table 12: he Recovery % for spiked Qaroun Lake water samples for modified shrimp shells

Sorbent	**Metal ion**	**Added (µg/ml)**	**Found (µg/ml± SD*)**	**% R**
sod.Carbonate	Fe(III)	0.2	0.0370±0.0875	102.6
	Mn (II)	0.2	0.0227±0.0985	105.11
	Cd(II)	0.2	0.0338±0.0784	97.06
Sod. Acetate	Fe(III)	0.2	0.095±0.21	107.12
	Mn (II)	0.2	0.0669 ±0.47	113.01
	Cd(II)	0.2	0.0825±0.3925	117.9
Sod. Chloride	Fe(III)	0.2	0.0431±0.0168	98.07
	Mn (II)	0.2	0.0448±0.0295	92.44
	Cd(II)	0.2	0.0629±0.0794	103.66

SD*: Standard deviation Based on three replicate measurements in the same loaded column.

4. Conclusion

This study has shown the novel modified shrimp shells can be good alternative for the extraction of Cd (II), Mn (II) and Fe (III) from real water due to both excellent and attractive properties such as high capacity, good reusability and high prconcentration factor. The extraction capacity of modified shrimp shells is superior. This study shows that the modified shrimp shells can be good alternative for the extraction of the toxic ions from natural sources due to their excellent and attractive features such as Low cost, high extraction capacity and good chemical reusability.

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