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RESEARCH ARTICLE

Green purification of different natural water samples in Fayoum governorate by using a novel and safe modified rice husk.

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Abstract

A study on the modification of rice husk by sodium carbonate showed that sodium carbonate modified rice husk (NaCMRH) has a high capacity for extraction of some metal ions like Cd(II), Cu(II), Pb(II) and Zn(II). For this task, several techniques such as spectroscopy and thermogravimetry were used for the elucidation of the possible functional groups responsible for the extraction of the studied metal ions; the morphological characteristics of this material were evaluated as well. Batch adsorption studies were conducted for all the studied metal ions in the concentration range 10–100 mg/L. The adsorption was favoured with maximum adsorption at pH 6, whereas the adsorption starts at pH 4 for all metal ions. The effects of contact time, initial concentration of metal ions and adsorbent dosage have been reported. Natural water samples were obtained from different locations over Fayoum governorate, Egypt. The high efficient, low cost and rapid uptake of metals (Al^{3+} , Cd^{+2} , Co^{+2} , Cr^{+3} , Cu^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Pb^{+2} , Ti^{+3} , V^{+5} , Zn^{+2}) in different matrices indicated that the new modified sorbent, NaCMRH, could be an excellent alternative for the extraction and purification of some natural waters.

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Introduction

Water pollution due to toxic heavy metals is a major cause of concern. Industrial and domestic wastewater are responsible for causing damage to the environment and adversely affecting the health of the people. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chains (Kumar and Bandyopadhyay, 2006). Even, their minor content can bio-accumulate and enter the food chains causing mental retardation, reduction in hemoglobin production and interference with normal cellular metabolism and, consequently, may damage the nervous system. Exposure to heavy metals may cause gastric pain, nausea, severe diarrhea and even cancer in the digestive tract and lungs (Klaassen, 2001; Mohanty et al., 2005). Heavy-metal pollution occurs in many industrial wastewaters such as those produced by metal plating facilities, mining operations, battery manufacturing process, the production of paints and pigments, the glass production industry, refinery and petrochemicals, leather goods manufacturing, fertilizer and pesticides industry, etc. (Srivastava et al., 2006a; Wang et al., 2011). Many of these metal ions are reported to be toxic, carcinogenic and tend to bioaccumulate in aquatic organisms (Wang et al., 2011).

Many analytical techniques have been used for the determination of toxic metal ions. These include: inductively coupled plasma atomic emission spectrometry (ICP-AES) (Thakkar and Chudasama, 2009), X-ray fluorescence spectrometry (XRF) (Mages et al., 2008), flame atomic absorption spectrometric (FAAS) (Burham, 2009), graphite furnace atomic absorption spectrometric (GFAAS) (Tuzen et al., 2007), and inductively coupled plasma mass spectrometry (ICP-MS) (Curdova et al., 2004). However, GFAAS is difficult to determine multi-elements simultaneously, while the sensitivity of XRF is lower than that of ICP-AES. ICP-MS has been acknowledged as one

of the most powerful techniques for the ions determination, but the equipment is still too expensive for many institutions especially in a country in the developing area like Egypt. However, the direct determination of heavy metal ions at trace levels is limited due to their low concentrations and matrix effects. This limitation can be overcome by the use of a separation and a preconcentration step (Burham et al., 2006). Several treatment technologies have been developed for the determination, separation and preconcentration of heavy metals from solution such as solid phase extraction (SPE) (Simpson, 2000; Valerie, 2003; Starvin and Rao, 2004; Tu et al., 2009), ion-exchange (Zhang et al., 2009), adsorption (Gao et al., 2010) and coprecipitation (Karatepe et al., 2010) etc. Among these techniques, SPE is the most common approach because it reduces the disposal costs and time for sample preparation. SPE has been preferably applied using organic supports, modified inorganic sorbents, synthetic and natural sorbents. Many sorbents have been applied as solid-phase extractors, such as activated carbon (Chand et al., 2009), and biosorbents (Tasdelen et al., 2009).

The removal of heavy metals from contaminated water has become a major research topic due to the toxicological problems (Zhengang and Zhang, 2009). Gupta et al developed novel carbon (RTAC) by physical activation from waste tire rubber, as an adsorbent for assessing its removal capacity of lead and nickel ions from aqueous solutions. Approximately 96% and 87% lead and nickel removal was achieved by RTAC from simulated electroplating industry waste water (Gupta et al., 2012). The main techniques used to remove heavy metal ions from aqueous systems include ion-exchange, reverse-osmosis, chemical precipitation, and adsorption. However, applications of such methods are sometimes restricted because of technical or economic constraints. Among these processes, adsorption is a very effective separation technique and now it is considered as an economic and efficient method for the removal of metal ions present at low concentrations from wastewater (Naiya et al., 2009). Suksabye and Thiravetyan studied the chemical modification of coir pith by grafting with acrylic acid. The acrylic acid-grafted coir pith demonstrated a better adsorption capacity for Cr (VI) compared to the original. The results of this study showed that the acrylic acid-grafted coir pith was suitable for the development of efficient adsorbent for the removal of Cr (VI) in contaminated wastewater (Suksabye and Thiravetyan, 2012). Among the different adsorbents, activated carbon is the most widely used in a variety of applications (Cooney, 1998). The use of commercially available activated carbon as a sorbent is limited, especially in developing countries, because of its relatively high cost and the difficulties associated with its regeneration. As a result, several non-conventional adsorbents have been used by a number of investigators (Feng et al., 2004). Biosorbents are considered attractive, and low-cost materials for pollution treatment. Ramana et al. used pigeon hulls powder as eco-friendly green adsorbent for the removal of Pb(II) and Ni(II) ions from aqueous solutions (Ramana et al., 2012). Pollutants including metal ions (Mcafee et al., 2001; Mata and Gavrilesco, 2004; Torres et al., 2009), pesticides (Boucher et al., 2007) and dyes (Khattri and Singh, 2000) were treated using different biosorbents derived from agricultural and industrial biomass, the quest for an alternative adsorbent which is affordable and environment friendly is inevitable (Roskill, 2009). Undoubtedly, agricultural waste biomass is presently one of the most challenging topics, which is gaining stern considerations during the past several decades (Andrew et al., 2003).

Rice is one of the major crops grown throughout the world. After the separation of the rice from the paddy, one-third of the mass remains as a waste material. Many workers have tried to use this agricultural waste to produce useful materials such as activated carbon, silica or silicon carbide (FAO, 2002). Globally, approximately 600 million tons of rice is produced each year, giving an average of 20% of the rice as husk, i.e. an annual total production of about 120 million tons per annum. In Egypt, the annual rice production is about 5,700,000 tons, which produces 1,000,000 tons of rice husk (FAO, 2002). In the majority of rice producing countries, the husk produced from the processing of rice is either burnt or dumped as waste (FAO, 2002). In recent years, rice husk can be used to generate electric power, but that will release a large amounts of greenhouse gases, and the emission of rice husk ash into the ecosystem has attracted huge criticisms and complaints, mainly associated with its persistent, carcinogenic and bio-accumulative effects, resulting in silicosis syndrome, fatigue, shortness of breath, loss of appetite (Foo and Hameed, 2009). Numerous researchers have studied the utilization of rice husk. Dilute sulfuric acid solution has been used as the pre-treatment chemical to prepare D-xylose (Zhang et al., 2010). Biomass was impregnated with KOH and NaOH at activation temperature of 650–800 °C, resulted in activated carbons with high surface areas (Ahmedna et al., 2004; Guo et al., 2003). Rice husk contains lots of silica, cellulose, hemicellulose, lignin and some functional groups such as carboxyl, hydroxyl and amidogen (Nakbanpote et al., 2007), which make the adsorption processes possible. Rice husk has been successfully used to remove the metal ions from water (Srivastava et al., 2006b, 2009; Naiya et al., 2009). It was reported to be good sorbent for a variety of metals cation and basic dyes (Suemitsu et al., 1986; Low and Lee, 1997). Various modifications on rice husk have been reported in order to enhance sorption capacities for metal ions and other pollutants (Krishnani et al., 2008; Ngah and Hanafiah, 2008).

This work deals with a simple, cheap and very safe modification of rice husk by sodium carbonate. The treated and raw husk were tested to extract Cd(II), Cu(II), Pb(II) and Zn(II) from aqueous solution. It was found that the

carbonate modified rice husk has higher adsorption capacities than the unmodified husk in short equilibrium time which can be attributed to the surface structural changes of the sorbent. Application of this study in natural water showed satisfactory results and common interfering ions present in natural water did not effect on the adsorption of the studied metals.

2. Materials and Methods

2.1. Instruments and Apparatus

The Cd (II), Cu (II), Pb (II) and Zn (II) concentrations were determined by using inductively coupled plasma optical emission spectrometer (ICP OES), an Optima 5300 DV (Perkin Elmer, USA, 2008), equipped with Ultrasonic nebulizer (C-tac U5000+). Graphite furnace atomic absorption (GFAA), an AAnalyst 600 (Perkin Elmer, singbora, 2008) equipped with zeeman background correction was also used for measuring some metals in water samples. The pH measurements were carried out using the microprocessor pH meter (Denver UB, USA, 2008) which was calibrated against two standard buffer solutions at pH 4 and 10. A mechanical shaker with up to 200 rpm (3018 GFL, Germany, 1995) was used to study the required shaking time.

2.2 Reagents and Samples

Rice husk was obtained from Etsa, Fayoum, Egypt. All reagents were of analytical grade. Deionized water DW was obtained from a Milli-Q element purification system (Millipore, Molsheim, France, 2008). The Cd (II), Cu (II), Pb (II) and Zn (II) solutions used in the adsorption studies were obtained in concentration $1000 \mu\text{g/ml} \pm 5\mu\text{g/ml}$ from (BDH, England). Ultra-pure HNO_3 for digestion of the samples from (Merck, Germany).

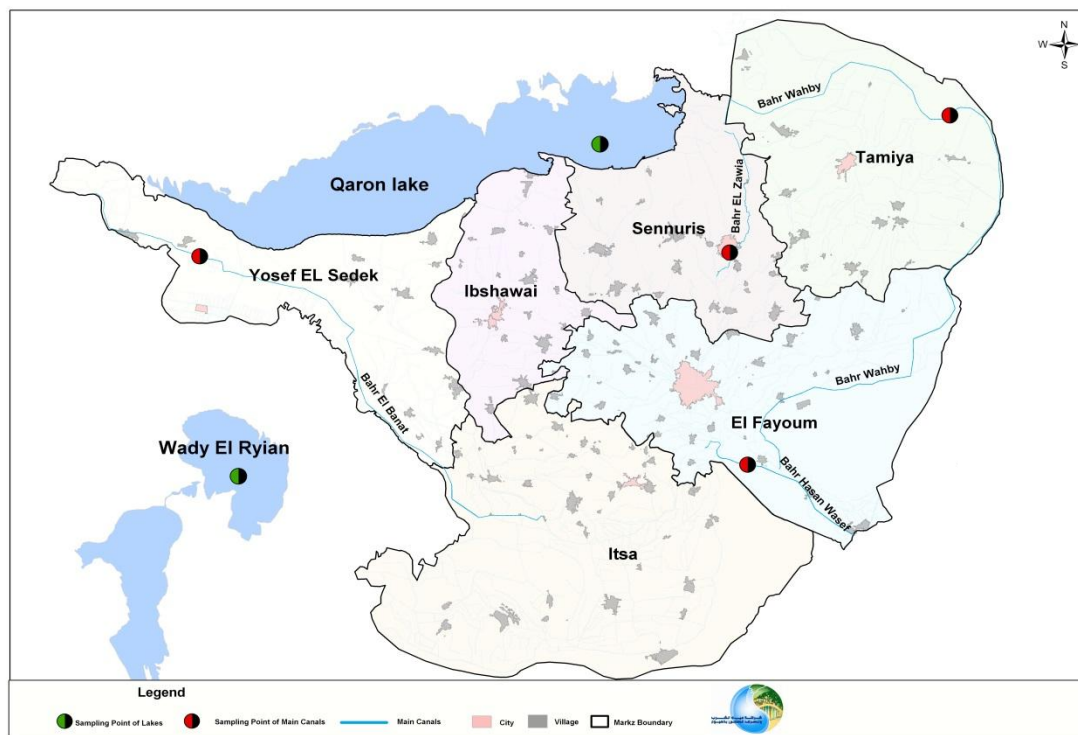


Fig.1. Fayoum governorate map showing the sampling points

The water samples were collected from different locations of Fayoum governorate Fig. (1). They were taken from the main canals, Baher Hassan Wasef, Baher Elbanat, Baher Wahby and Bahr Elzawia, these canals are the intakes for drinking water treatment plants and also main sources used in the irrigation. Other samples were collected from Qaron Lake (brackish water) and Wadi Elryan lakes protected area (fresh water). Global positioning system (GPS) was used to determine the sampling points with insignificant deviation and locate them on the map.

2.3 Preparation of the solid adsorbents

Initially, the rice husk was washed thoroughly with running tap water followed by washing with deionized water to remove dust and particulate matters from the rice husk surface. The husk material was dried at 60°C in an oven to a constant weight. Drying at 60 °C was chosen because high drying temperature might cause a decrease in the number of cellulose based OH groups on the rice husk. The rice husk was crushed and sieved to the particle size \approx 500 μ m by an electrical sieve shaker. Then the dried husk was soaked and shake in 0.1 M sodium carbonate for 12 hours, then washed by deionized water until the filtrate become neutral. The treated material was dried at 60°C to a constant weight and stored in a sealed polyethylene bottle for its further usage.

2.4 Sodium Carbonate Rice husk characterization

For elemental analysis of the rice husk samples a Perkin-Elmer PE 2400 elemental analyzer was used. A Perkin-Elmer FT-IR Spectrum 100 infrared spectrometer was used to elucidate the functional groups present in the modified rice husk. The experiments were made using KBr discs technique and the spectral range varied from 4000 to 400 cm^{-1} . The thermal behaviour of rice husk was obtained by using a TGA 7 Perkin Elmer gravimetric analyzer. About 11.1 mg of rice husk was heated up to 800 °C in an oxidant atmosphere at a 20 °Cmin⁻¹ temperature rate. A JEOL JSM-6390LA scanning electron microscope (SEM) was additionally used to examine the morphological characteristics of this sorbent.

2.5 Batch Experiments

The adsorption study was conducted in the batch experiments to determine the optimum conditions necessary to reach equilibrium. Effect of pH was studied by varying the initial pH in the range of 2-7 at room temperature (\approx 25 °C). 0.2 gram of the adsorbent was contacted with 25 ml of 5.0 mg/L of cadmium nitrate, copper nitrate, lead nitrate, and zinc nitrate in 125 ml poly-ethylene bottles sealed with caps and agitated at 100 rpm for 1 hour on a shaker. The samples were analyzed for metal ion concentrations using inductively coupled plasma optical emission spectrometer (ICP OES). Similar experiments were carried out to study the effect of adsorbent mass (0.05-0.3 g) and shaking time (10-100 min). The equilibrium study was undertaken to investigate the effect of initial concentrations (15-100 ppm).

2.6 Procedure to remove heavy metals from water samples

A glass column (25 x 2.5 cm) coupled to a vacuum pump and glass wool was inserted in the column in the bottom to prevent loss of sorbent. The column was packed with 1 g of NaCMRH with the particle size \approx 500 μ m. The water samples, containing several pollutants were adjusted to the optimum pH. Initially, the concentrations of the metal ions were determined then 100 mL of the solution was passed through the column. By using the pump, the flow rate was adjusted to the desired value. The metal concentrations before and after treatment were compared.

3. RESULTS AND DISCUSSION

3.1 Sorbent characterization

3.1.1 Elemental analysis

The data obtained from elemental analyses indicates that rice husk composed of a higher content of carbon, followed by hydrogen as shown in table (1). These results are in agreement to those obtained for other vegetable biomass, which are basically composed of cellulose, hemicellulose and lignin (Juliano, 1985).

Table 1 Elemental analysis of the unmodified and modified rice husk

Sorbent	C%	H%	N%
RH	37.72	3.53	Not detected
NaCMRH	38.74	3.66	Not detected

3.1.2 Fourier Transformer Infrared (FT-IR)

It is an important technique to identify some characteristic functional groups, which are capable to extract metal ions from polluted solutions. According to Fig.(2), a broad band between 3000 – 3809 cm^{-1} indicates the presence of OH groups on the surface of the rice husk (Kamath and Proctor, 1998), this stretching of the OH groups is due to both the silanol groups (Si-OH) and adsorbed water on the husk surface. The band at 2922 cm^{-1} is assigned to symmetric vibration of CH_2 , especially alkenes. These groups are common in the lignin structure (Pasquali and Herrera, 1997). The peak at 1638 cm^{-1} is an indication of COO, C=O and can also indicate the bending vibration of adsorbed water. These groups can be conjugated or non- conjugated to aromatic ring according to the modified rice husk spectra, the peak related to non-conjugated carbonyl groups is verified, which indicate the hydrolysis of carboxylate groups during the treatment with sodium carbonate solution. The peaks associated with the stretching of the aromatic rings were verified at 1551 cm^{-1} , while siloxane bands appear around 1080 cm^{-1} , due to Si-O-Si formation. FTIR spectrum shows that the rice husk mainly composed of polymeric OH groups, CH_2 and COOH groups and OH of poly saccharides, these groups have affinities of Cd, Cu, Pb and Zn ions extraction. This interpretation is in a good agreement with other work (Tarley et al., 2004)

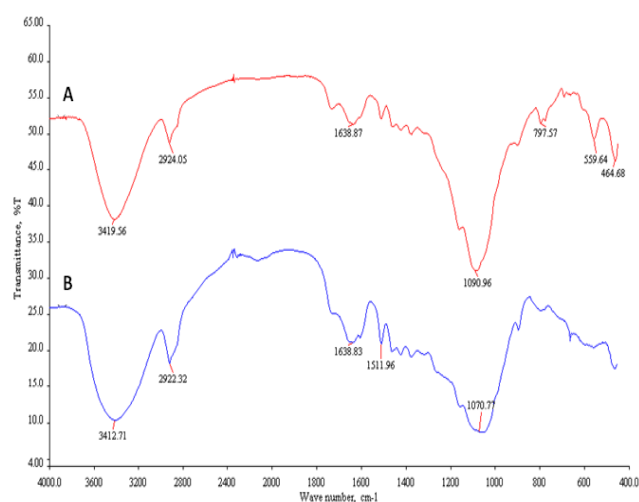


Fig.2. FT-IR spectra of (A) unmodified and (B) modified rice husk

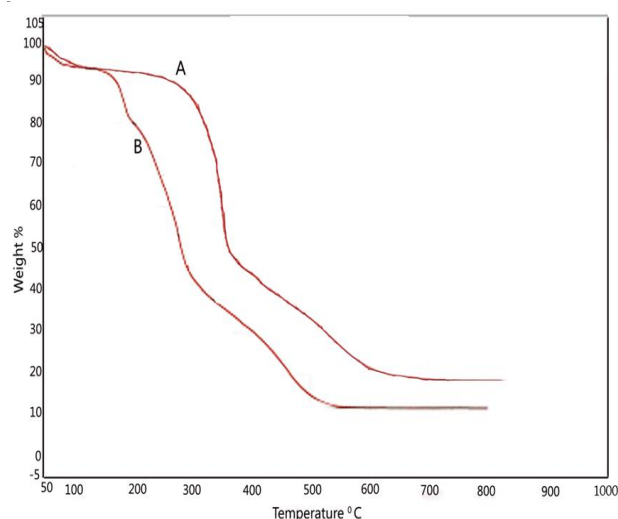


Fig.3. Thermogravimetric curve of (A) unmodified and (B) modified rice husk

3.1.3 Thermogravimetric analysis (TGA)

This analysis indicates the mass loss related to moisture elimination, cellulose, hemicellulose and lignin decomposition Fig. (3). Thus, the moisture loss of 18.5 % by heating the husk sample up to 210 °C. The second step is pyrolysis corresponding to temperature from 210 – 340. This step provides higher mass loss of 42.4 % and 47.7 % for modified and unmodified RH respectively. The pyrolysis curve in this temperature range indicates that cellulose and hemicellulose decomposition, as well as the loss of remaining adsorped water (Teng and Wei, 1998). Lignin was decomposed in temperature range 340- 580 C, due to the higher stability of lignin composed to cellulose and hemicellulose, the mass loss in this step was 25.8%. Finally, no mass loss was observed when the temperature was increased up to 800 °C. Residual masses of 13.25 % and 15.4 % where observed for the modified and unmodified rice husk. This indicating the presence of sable oxides based on silicon, which are stable at higher temperatures (Tarley et al., 2004).

3.1.4 Scanning electron microscope (SEM)

The SEM was additionally used to examine the surface of the modified and unmodified rice husk Fig.4. It is clear that some imperfections on the surface of the RH wall verified after treatment with sodium carbonate solution. Thus, it can be concluded that the modified RH presents an adequate morphological profile to retain the studied analyte ions (Tarley and Arruda, 2004). Hence, the SEM photographs show good progressive changes in the surface of the modified RH due to the effect of the alkaline sodium carbonate.

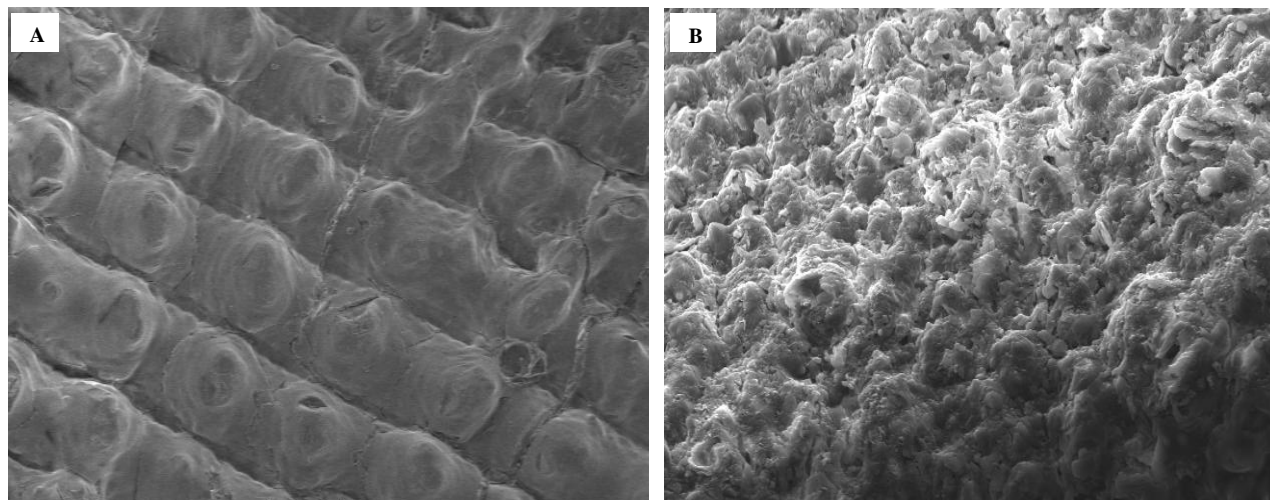


Fig.4. Scanning electron micrographs of rice husks: (A) unmodified and (B) modified rice husks

3.2. Effect of pH

The pH of the solution is one of the most important parameters affecting metal ion uptake. This is because the hydrogen ions compete with the positively charged metal ions on the active sites of the NaCMRH. As shown in Fig. 5B, it can be found that removal efficiency increased with increasing of pH. Although a maximum extraction was noted at a pH 4.5, 6, 5.5 and 6.5 for Cd(II), Cu(II), Pb(II) and Zn(II) respectively. Therefore, the optimum pH for Cd(II), Cu(II), Pb(II) and Zn(II) are 4.5, 6, 5.5 and 6.5 respectively. On pH value higher than 6.5 a slight decrease of the uptake for Cd, Cu and Pb ions was observed. Based on that behaviour of these metal ions on NaCMRH, it is speculated that the hydrogen bonding and ion exchange may be the principle mechanism for the metal ions extraction (Ajmal et al., 1998). At $\text{pH} \leq 3$ the extraction efficiency is found to be low. This is due to the competitive sorption of the hydronium ions and the tested metal ions on the same active site. As the pH increased more than 3, the active sites become less positive, therefore electrostatic attraction between the active sites and the studied metal ions is increased.

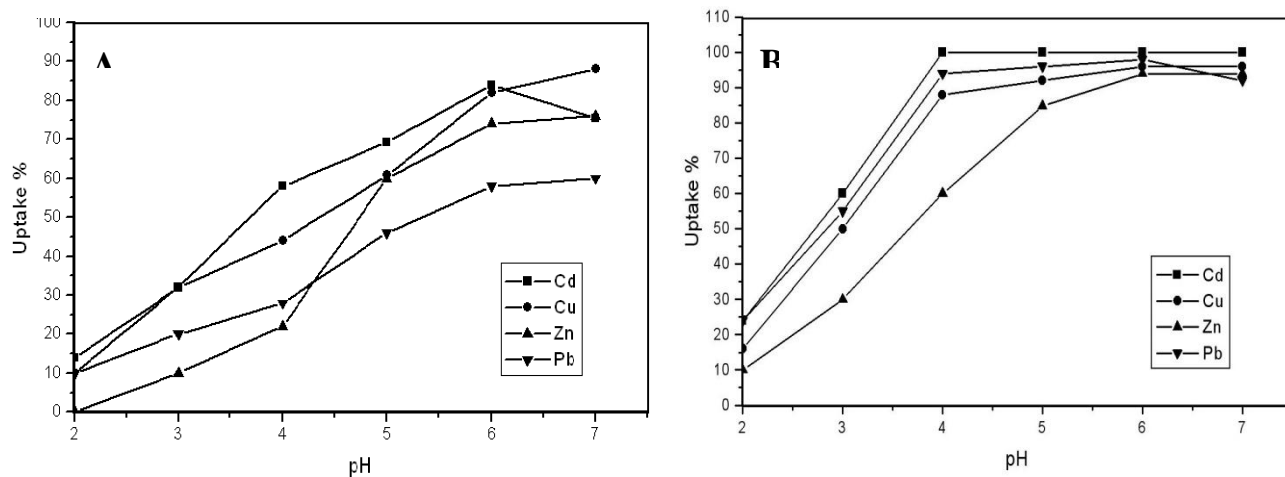


Fig.5. Effect of pH on the extraction of Cd (II), Cu (II), Pb (II), Zn (II) by (A) unmodified and (B) modified rice husk.

3.3 Effect of sorbent weight

The adsorption studies of Cd(II), Cu(II), Pb(II) and Zn(II) ions on NaCMRH were conducted at room temperature $\sim 25^\circ\text{C}$ by varying the weight from 0.05 to 0.3 g, while keeping the volume of the metal solution and other parameters constant. The influence of sorbent dosage on the extraction percent of the tested ions is shown in Fig. 6. The results showed the uptake % increases with increasing of the sorbent dose from 0.1g to 0.2g which is due to the opportunities

available for the metal ions to attack the active sites, whereas there is no more adsorption with increasing of the sorbent dose above 0.2 g.

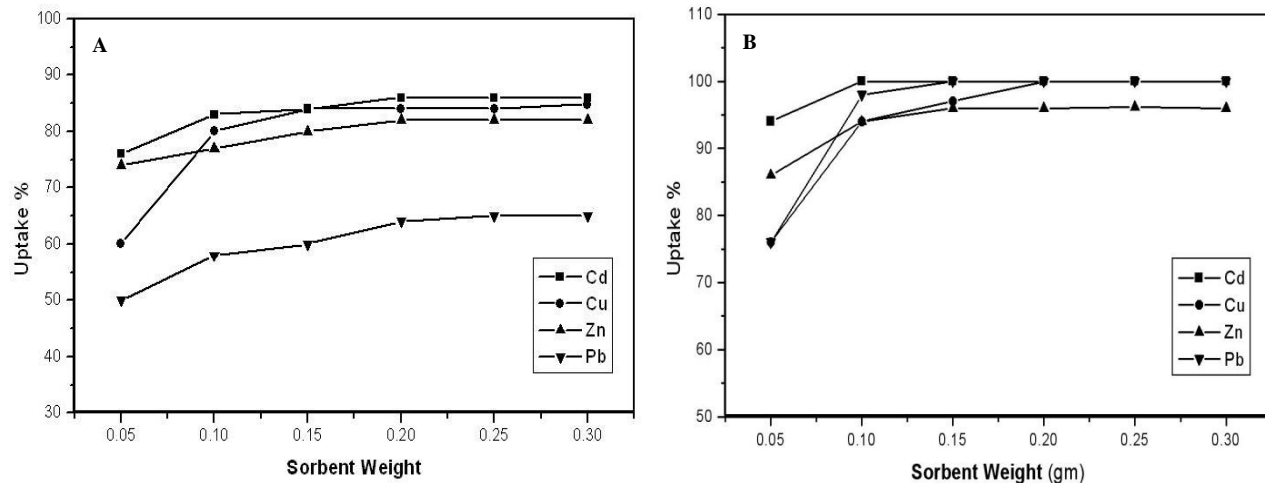


Fig.6. Effect of sorbent weight on the extraction of Cd (II), Cu (II), Pb (II), Zn (II) by (A) unmodified and (B) modified rice husk.

3.4 Effect of shaking time

The extraction profiles of the studied ions on both rice husks at different shaking time values are shown in Fig. 7. The results mentioned that 60 min. is enough for the quantitative extraction of the metal ions on the modified RH and the loading half time ($t_{1/2}$) needed to reach 50% extraction of the total loading capacity has been found to be less than 20 min. for Cu(II) and Zn(II), while reached 10 min only for Cd(II) and Pb(II) ions. The kinetics of the modified RH-metals interaction is sufficiently rapid for the tested analytes at the optimum pH value. In all subsequent works, 60 min was selected as a shaking time.

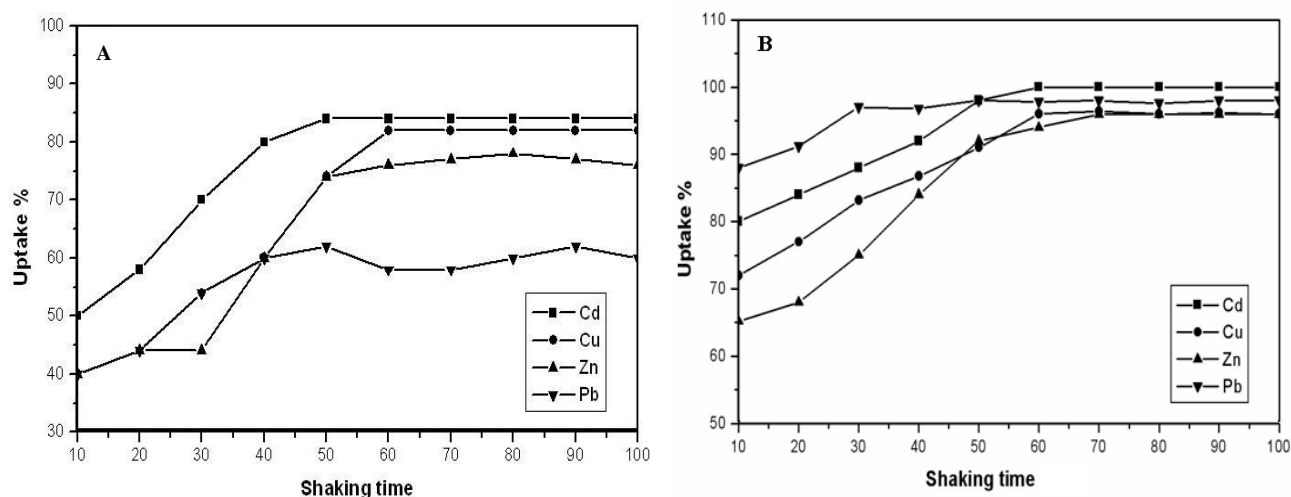


Fig.7. Effect of shaking time on the extraction of Cd (II), Cu (II), Pb (II), Zn (II) by (A) unmodified and (B) modified rice husk.

3.5 Effect of initial concentration

In the batch adsorption processes, the initial metal ion concentration of the solution plays a key role as a driving force to overcome the mass transfer resistance of metal ions between the aqueous and the solid phases. Therefore, the amount of metal ions adsorbed was expected to be higher with a higher initial concentration of the metal ions. The effect of the initial concentration of Cd(II), Cu(II), Pb(II) and Zn(II) ions on the adsorption process is shown in Fig.8. The percent adsorption increased with the increase of the initial metal ion concentration. The amount of all metal ions

adsorbed at equilibrium appeared to follow the same increasing trend with the initial metal ion concentration. As a result of the above observations, it was indicated that the adsorption process of different heavy metal ions on NaCMRH was to be dependent on the concentration of adsorbate up to some extent. Furthermore, uptake of the metal ions by the modified RH is higher than the unmodified one.

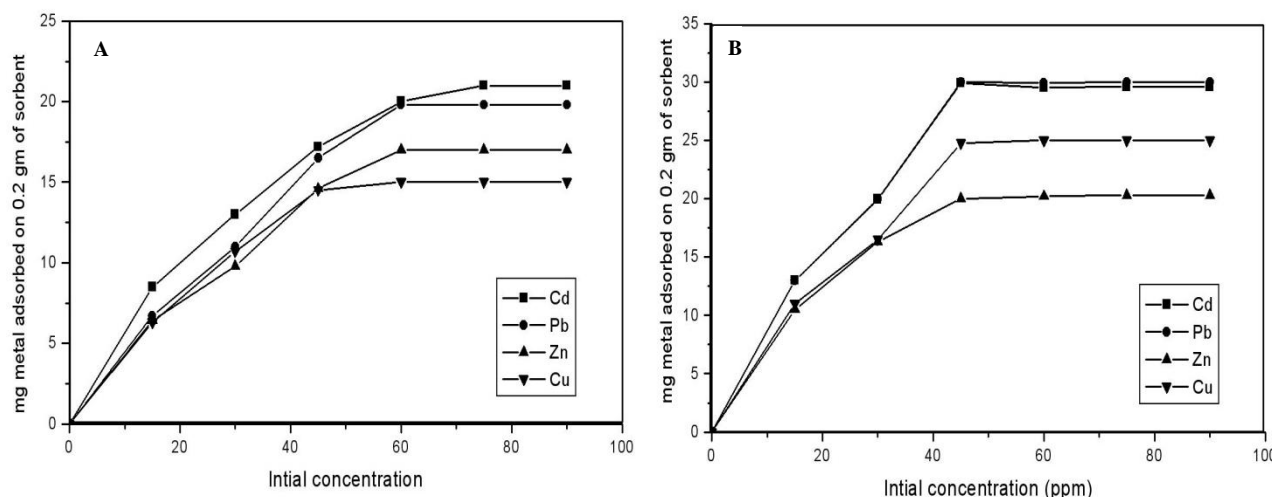


Fig.8. Effect of initial concentration on the extraction of Cd (II), Cu (II), Pb (II), Zn (II) by (A) unmodified and (B) modified rice husk

3.6 Effect of flow rate

Another important parameter in the adsorption is the flow rate of the sample solution which influences the adsorption of metal ions to the sorbent surface and the time of complete process. Therefore, the effect of the flow rate of the sample solution was examined under the optimum conditions by passing 100mL of sample solution through the column with a vacuum pump. The flow rates were adjusted in the range of 2.0–8.0mLmin⁻¹. It was found that quantitative removal (>95%) of Cd ((II), Cu (II), Pb (II) and Zn ((II) was obtained in flow rate of 2.0 – 4.0 mLmin⁻¹, a flow rate <2.0 mLmin⁻¹ was not employed to avoid the long extraction time. Whilst over 4.0 mLmin⁻¹, the removal of the metal ions decreases probably because the metal ions do not equilibrate sufficiently with the sorbent. Thus, a flow rate of 4.0 mLmin⁻¹ is selected in this work.

3.7 Column Desorption

Since the studied metal uptake occurred at neutral or weakly acidic conditions, consequently, the desorption of Cd ((II), Cu (II), Pb (II) and Zn (II) is possible by controlling the pH. Really, the extraction of the tested ions on NaCMRH in batch or mini-coloumn is nearly negligible under strong acidic conditions (pH < 2). Therefore, elution studies were performed with hydrochloric acid solution in concentrations (0.05 – 1.0 mol/L). Complete desorption was achieved at HCl concentration ≥ 0.5 mol/L for all the metal ions.

Table 2. Specifications of the real water samples before treatment with NaCMRH

Parameter	Unit	Bahr Hassen Wasef	Bahr Elbanat	Bahr Wahby	Bahr Elzawia	Wadi Elrayan	Qaron Lake
Temperature	(°C)	25	26.8	25.1	27.9	22.6	23.4
Electrical Conductivity (EC)	(µmh)	425	712	870	517	558	39200.0
Total Solids (TS)	(mg/l)	280	556	644	366	372	42594.0
Total Dissolved Solids (TDS)	(mg/l)	250	427	522	310	279	3339.0
Total Suspend Solids (TSS)	(mg/l)	24	66	100	66	93	12255.0
pH		7.7	7.6	7.9	7.9	7.5	8.3
Dissolved Oxygen (DO)	(mg/l)	7.1	6.1	6.3	6.3	6.8	7.04
Biological Oxygen Demand (BOD)	(mg/l)	4	2	13	5	11	22.0
Chemical Oxygen Demand (COD)	(mg/l)	12	22	21	27	40	790.0
Bicarbonate (HCO ₃ ⁻)	(mg/l)	140	178	139.2	162	170	5300.0
Sulfate (SO ₄ ²⁻)	(mg/l)	70	80.2	110	71	65	3373.0
Chloride (Cl ⁻)	(mg/l)	60	73.6	136.3	43	48	11060.0
Fluoride (F ⁻)	(mg/l)	0.3	0.34	0.37	0.32	0.5	12.25
Nitrite (NO ₂ ⁻)	(mg/l)	0.001	0.002	0.002	0.002	0.1	0.015
Nitrate (NO ₃ ⁻)	(mg/l)	0.8	1.17	1.87	1.0	1.7	2.20
Ammonia (NH ₄ ⁺)	(mg/l)	0.2	4	1.0	0.4	1.0	2.0
Silicate (SiO ₂ ²⁻)	(mg/l)	6.1	8.8	7.5	6.2	5.9	8.59
Phosphate (PO ₄ ³⁻)	(µg/l)	40	110	150	130	200	500

Table 3. Measurements of the metal ions during year 2008 – 2009. Before treatment with NaCMRH

Parameter	Unit	Baher Hassen Wasef	Bahr Elbanat	Bahr Wahby	Bahr Elzawia	Wadi Elrayan (protected area)	Qaron Lake
Ca ²⁺	(mg/l)	40±3.6	88.4±7.9	51.2±4.6	40.8±3.6	55.48± 4.99	147.80 ± 13.30
Mg ²⁺	(mg/l)	13±1.5	9.6±1.1	17.2±2.0	15.3±1.7	42.75 ± 4.70	7.90 ± 0.87
Na ⁺	(mg/l)	50±6.0	95.9±11	133.8±16	61.6±7.4	200 ± 24	7950.0 ± 954
K ⁺	(mg/l)	6.0±0.5	6.8±0.54	8.4±0.67	6.2±0.49	10 ± 0.8	225.0 ± 18.00
Al ³⁺	(mg/l)	0.1±0.001	9.2±0.13	3.5±0.05	2.7±0.037	0.51± 0.01	5.11 ± 0.05
^a As ³⁺	(µg /l)	ND	2.5±3.7	1.4±0.21	1.5±0.22	0.10± 0.01	0.35 ± 0.03
B ³⁺	(µg /l)	20±0.6	100±3.0	90±2.7	200±6.0	230 ± 7.0	300 ± 9.0
Ba ²⁺	(µg /l)	10±0.4	100±4.0	700±28.0	100±4.0	25.50± 1.02	38.0 ± 1.52
^a Cd ²⁺	(µg /l)	ND	0.4±0.03	ND	0.8±0.056	0.90 ± 0.08	1.22 ± 0.11
Co ²⁺	(µg /l)	ND	0.6±0.05	2.02±0.16	2.4±0.19	0.14 ± 0.01	0.80 ± 0.07
Cr ³⁺	(µg /l)	ND	5.8±0.29	13.5±0.67	12.5±0.62	1.14 ± 0.10	3.90 ± 0.35
^a Cu ²⁺	(µg /l)	2.0±0.24	5.1±0.61	10.0±1.2	103±12.4	57.30 ± 5.16	37.10 ± 3.34
Fe ²⁺	(mg/l)	0.3±0.004	8.4±0.11	4.3±0.05	1.6±0.02	0.65 ± 0.06	3.60 ± 0.32
Mn ²⁺	(µg /l)	9.0±0.54	48.0±2.88	51.5±3.1	10.0±0.6	11.0 ± 0.66	156.80 ± 9.41
Ni ²⁺	(µg /l)	ND	7.4±0.6	9.92±0.8	9.6±0.76	0.70 ± 0.06	4.0 ± 0.36
^a Pb ²⁺	(µg /l)	ND	14.0±1.0	5.00±0.35	11.0±0.77	3.76 ± 0.34	2.90 ± 0.26
Sr ⁺	(µg /l)	ND	800±24	650±19.5	500±15	1860 ± 52.08	2600 ± 72.80
Ti ²⁺	(µg /l)	ND	305±33.5	50.0±5.5	246±27.1	11.31 ± 1.02	162.4 ± 14.62
V ⁵⁺	(µg /l)	ND	22.0±2.0	10.0±0.9	18.5±1.66	ND	12.38 ± 1.36
Zn ²⁺	(µg /l)	5.0±0.7	20.0±2.8	20.0±2.8	30.0±4.2	6.02 ± 0.54	28.20 ± 2.54

^a These metals were measured by GFAA and the others by ICP-OES

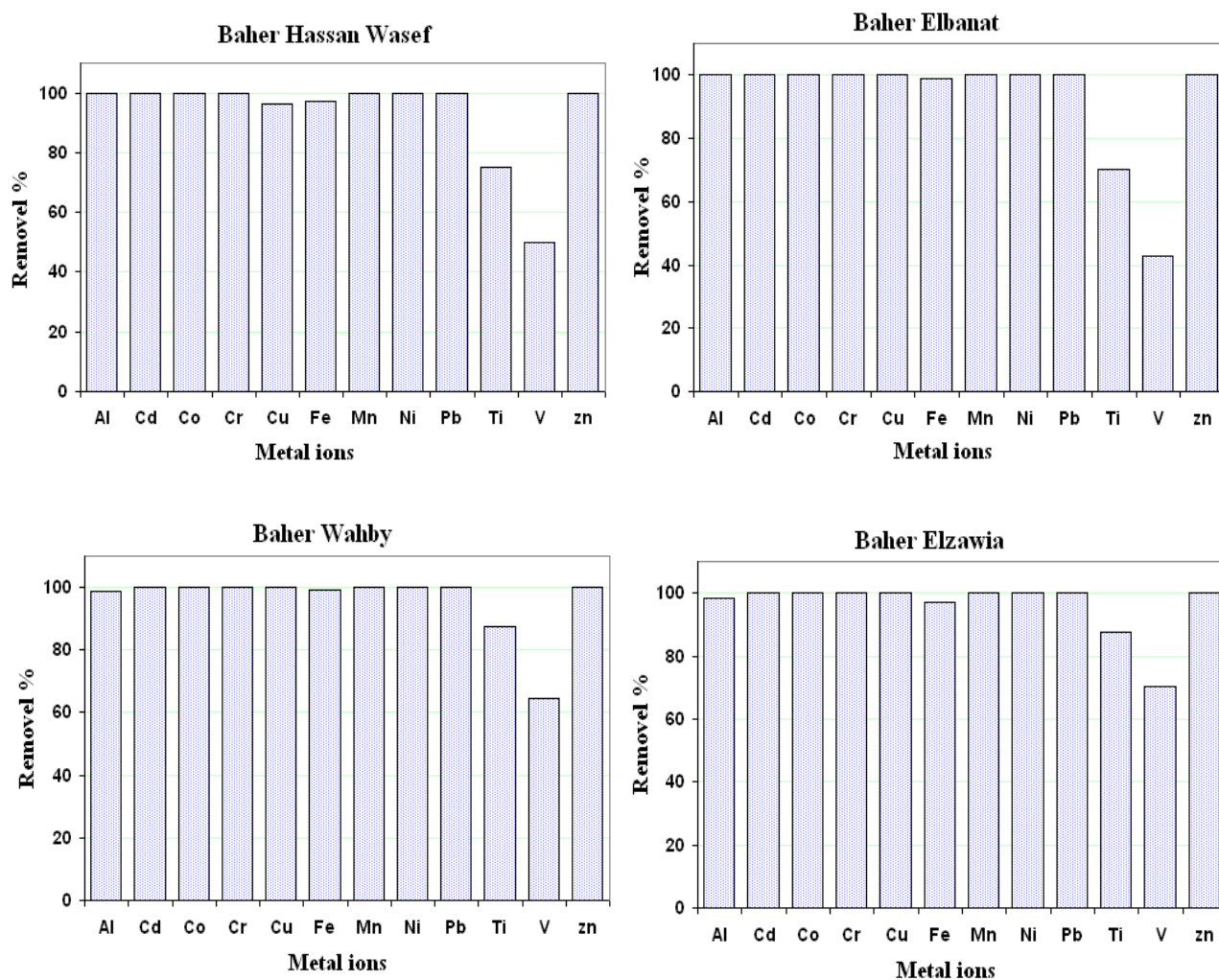
ND: Not detected

4. APPLICATION

In order to assess the applicability of the method to real water samples, with different matrices containing varying amounts of different interfering ions, water samples were obtained from four canals, river water, in fayoum (Baher Hassen Wasef, Baher Elbanat, Baher wahby, Baher Elzawia), Wadi Elrayan protected area and Qaron lake. These samples represent the different contamination degrees of water bodies in Fayoum governorate. The water samples were transferred to our laboratory in closed poly ethylene bottles, the physico-chemical parameters were measured as shown in table (2) and the metal ions were determined by using ICP-OES and GFAAS in table (3).

The metal ions concentration of these natural waters is in the range of permissible level according to Egyptian Environmental Affairs Agency law # 4, 1995. However, decreasing of the ions concentration could improve the quality of water. Sodium Carbonate modified rice husk removed many ions. For example quantitative extraction, more than 95 %, for Al^{3+} , Cd^{+2} , Co^{+2} , Cr^{+3} , Cu^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , and Zn^{+2} from Bahr Hassan Wasef, Bahr Elbanat, Bahr Wahby, Baher Elzawia, Wadi Elrayan protected area and Qaron lake was achieved as shown in Figures 9. Application of this sorbent can help to a complete refinement of these natural waters. In Wadi Elrayan protected area, application of this modified sorbent can help to a complete refinement of Al^{3+} , Cd^{+2} , Co^{+2} , Cr^{+3} , Cu^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Pb^{+2} , Ti^{+3} , V^{+5} , Zn^{+2} .

In general, the proposed procedure in this work presents the advantage of being rather inexpensive since the analyte ions are determined in complex matrix samples using common techniques and inexpensive chemicals. Moreover matrix interferences are easily eliminated. Furthermore, the modification is very simple and the reagents used in this work are environmentally safe.



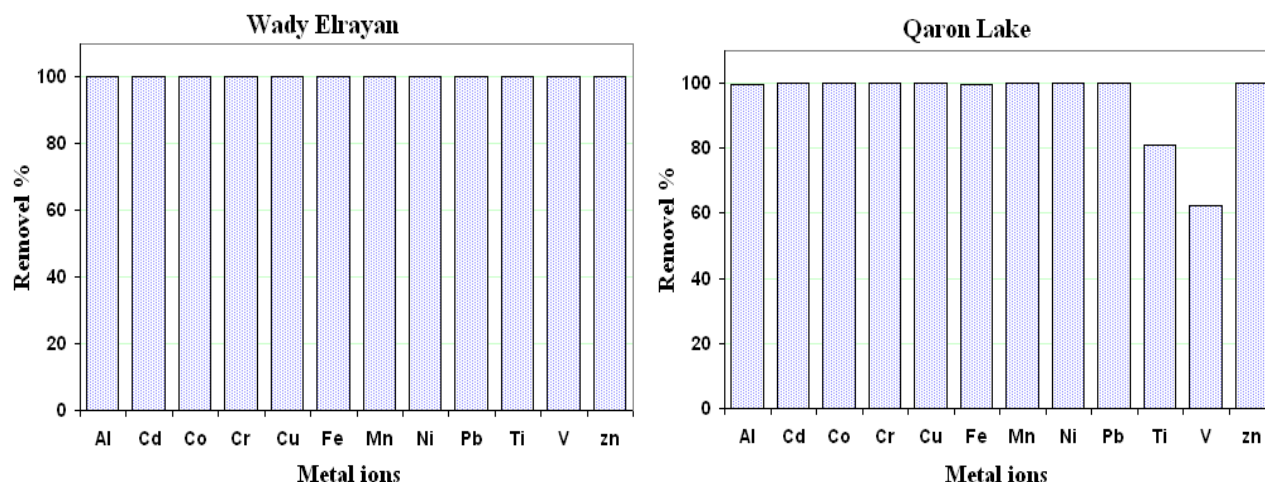


Fig.9. Removal percentage of some metal ions of different water sources in Fayoum governorate after treatment by NaCMRH

5. CONCLUSION

Agricultural by-product materials especially modified natural polymers appears as cheap and effective biosorbents for the extraction of metal ions from aqueous solutions. Moreover, these materials could be used for the purification of natural water. The extraction of metal ions from effluents or natural water is important to countries over the entire world both environmentally and for water reuse. Sodium carbonate MRH is not only a low cost biomass with high adsorption capacity, but also the sorbed ions could be easily eluted with low concentration HCl solution. Furthermore, Modified rice husk is found to be a suitable adsorbent for the adsorption of Cadmium, Copper, Lead and Zinc ions from the real water samples. Adsorption rate of sodium carbonate rice husk is fast and effective at nearly neutral pH. Nevertheless, this work proposes an analytical method for Cd (II), Cu (II), Pb (II) and Zn (II) extraction and determination based on off line coupling of a mini-column packed with only one gram of modified RH to an analytical technique as an alternative strategy for enhancing the detectability. Therefore, the new proposed method is very simple, low cost, effective, and ecofriendly alternative methodology to determine and extract metal ions from real water samples.

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