

Evaluation of Water Melon Peels as Economic Adsorbents for Removal of High Levels of Iron from Different Water Sources



Hassouna MEM^{1*}, Marzouk MA², Elbably MA³ and El Maghrabi AH¹

¹Department of Chemistry, Beni-Suef University, Egypt

²Department of Botany & Microbiology, Beni-Suef University, Egypt

³Department of Hygiene, Management & Zoonoses, Beni-Suef University, Egypt

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***Corresponding author:** Hassouna MEM, Department of Chemistry, Faculty of Science, Beni-Suef University, Egypt

Abstract

Optimum conditions for the adsorption of iron onto crude and modified (with lactic acid and tri sodium citrate) water melons peels (WMP) from aqueous solution are investigated as inexpensive and eco-friendly available adsorbents. Water samples are gathered from different sources (surface, tap and ground). The three WMP forms are characterized by FT-IR and SEM. Adsorption variables such as: adsorbent dose, stirring time and pH have been optimized. The removal efficiency of the unmodified WMP reaches its maximum uptake in the pH range 4-6, the other modified WMP powders in the range 5-7. The removal process is slow in the first 10min. then it is gradually increased till equilibrium after 20min in case of unmodified WMP, the two modified forms reach equilibrium after 15min. Kinetic studies indicated that adsorption follows the Langmuir and Freundlich adsorption isotherms. Desorption processes assured the possibility to regenerate and reuse the adsorbents. .

Keywords: Heavy metals; Fe; Water melon peels; Economic sorbent; Water sources; Adsorption

Introduction

Heavy metals have become a question of global concern considering their hard consequences which requires ongoing evaluation and revision of water resource policy at all standard international levels down to individual aquifers and wells [1,2]. Their main sources include wastewater discharged from health facilities [3], other industries, metal plating and alloy manufacturing [4,5]. The technological advancement in electronic industry is posing a new environmental challenge in the form of electronic waste, the electronic devices after their disposal into the soil are not processed properly which result in the accumulation of the toxic metals in the soil [6]. Heavy metals present in the wastewater are persistent and non-degradable in nature [7]. Presence of these metals in waste stream and ground water is one of the most environmental concerns since these metal ions are toxic to various life forms especially if their concentration is more than the accepted limit [8,9]. For the elimination of dissolved heavy metal ions, literature [10] is full of techniques that have been performed such as solvent extraction, ion exchange, membrane process, electro dialysis, precipitation, phytoextraction, ultra-filtration, reverse osmosis and adsorption. These methods, generally, are of

high cost with troubles such as incomplete metal removal, high reagent consumption, energy requirements and generation of toxic sludge or other waste products that need further disposal or treatment [11]. Iron is commonly found in rocks and soil. Under suitable conditions, iron will leach into water resources. Iron concentration greater than 0.3mg/L causes water staining that negatively affects plumbing fixtures dishware and clothes and produce a yellow to reddish color in water appearance. These levels may also change the taste and odor of drinking water. This led many investigators to search for inexpensive substitutes such as zeolites, silica gel, chitosan, clay materials and agricultural wastes [12,13]. The adsorption technique remains the more favorable method because of its high capacity and low cost. During the past few years, several research articles were published reporting the successful use of different kinds of agricultural wastes for the removal of metal ions from aqueous solutions [14-17]. Such as *Acacia leucocephala* bark powder [18], *Moringa oleifera* bark (MOB) [19], cork waste biomass [20,21] rice straw [22], sugarcane bagasse waste [23,24], garden grass (GG) [25], castor leaf powder [26], green bean husk (GBH) [27], *ficus carcia* leaves [28], *Avenafatua* biomass [29]. Fruit peels have been extensively used [30-34] for the

same purpose including banana (*Musa paradisiaca*), lemon (*Citrus limonum*) and orange (*Citrus sinensis*) peels [35]. The present study has been carried out to investigate the possibility of the use of peels of water melons (*Citrullus vulgaris*) (WMP) powder as an effective and efficient agricultural solid waste byproduct for the removal of iron ions from aqueous solutions.

Materials and Methods

Chemicals

Ferrous ammonium sulphate (Aldrich), Hydrochloric acid (BDH), 1, 10 Phenanthroline (Aldrich) (0.2%) solution of phenanthroline hydrochloride or hydrate (phen.) in 0.1M HCl, Tri sodium citrate (Aldrich) and Hydroxylamine hydrochloride (Aldrich).

Reagents

- Standard Iron (II) solution (1000 ppm) Fe (II) stock solution was prepared by dissolving 0.7016g of ammonium ferrous sulphate ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, (Aldrich, USA) in DDW containing 5mL conc. H_2SO_4 and accurately dilute to volume in 100mL volumetric flask.
- 1, 10 Phenanthroline (0.2%) Phenanthroline hydrochloride or hydrate (phen), in 100mL volumetric flask 0.2gm of phenanthroline are dissolved in doubly distilled water (DDW) and diluted to the mark with 0.1M HCl.
- Tri sodium citrate (10 %) solution in 100mL volumetric flask, 10g of tri sodium citrate are dissolved in doubly distilled water (DDW) and dilute to the mark.
- Hydroxylamine hydrochloride (10 %): 10g of hydroxylamine-HCl are dissolved in DDW and diluted to 100mL.

Preparation of the WMP powder and its modified forms

Preparation of the WMP powder

Water melon peels (WMP) are collected from the agricultural Egyptian fields. The white part of peels is cut, washed, air dried and then are finely powdered in a mixer till being near the nano size. The final product is applied as the crude peels powder for the removal of iron from water samples according to the proposed procedure.

Lactic Acid Modified (WMP) powder

100g of the crude (WMP) powder are refluxed with 500mL of 0.5M lactic acid solution over a boiling water bath for 6h. The produced precipitate is separated, repeatedly washed with DDW till free from acid then dried in an oven at 60°C for two hrs. After cooling in a desiccator to room temperature, it is finely grinded once again.

Tri sodium citrate Modified WMP powder

100g of the crude (WMP) are, similarly, refluxed with 500mL of 0.5M tri sodium citrate solution over a boiling water bath for 6h. The produced precipitate is, similarly, separated, washed, dried and grinded.

Instruments

UV/Vis. Spectrophotometer (Shimadzu UV/Vis. Perkin Elmer Lambda 3B Spectrophotometer using 1cm Quartz cell is applied to determine the concentration of the residual iron ions in the effluents after the application of the adsorption processes); Flame Atomic Absorption Spectrophotometer AA 240FS, Agilent Technologies, applied for the rapid and confirmation determination of the concentration of iron ions; pH meter (The pH measurements are carried by using the microprocessor pH meter BT 500 BOECO, Germany, which is calibrated versus two standard buffer solutions at pH4 & 9 and Mechanical Shaker (with up to 200rpm with speed control was used). The morphologies of the prepared samples and composites are examined using Scanning Electron Microscopy (SEM), FTIR spectroscopy Fourier transform infrared spectra of crude and chemically modified (WMP) powder forms are recorded with a Shimadzu FTIR spectrometer (resolution 4cm^{-1}), equipped with highly sensitive pyroelectric detector (DLATGS). The IR shows the structure morphology, nature of surface hydroxyl groups, and adsorbed H_2O .

Procedure

Spectrophotometric Determination of Iron

The remaining iron in the solution is determined spectrophotometrically after reduction to the Fe (II). In a 25mL volumetric flask, add 0.5mL of the 10% hydroxylamine solution, 2mL 10% tri sodium citrate solution and 5mL of the standard Fe (II) solution. The pH is adjusted in the range 3-4. Add 2.5mL of 0.2% 1, 10 phenanthroline solution, dilute to the mark with DDW and mix thoroughly. After 5min the absorbance of the solution is measured at 512nm against a blank.

FAA spectrometric method: Flame Atomic Absorption Spectrophotometer is used for the rapid and confirmation determination of the residual concentrations of iron ions after carrying out both the adsorption or the desorption procedures after making appropriate dilutions. The solution is directly measured at λ_{max} equals 372.0nm with detection limit of 50 $\mu\text{g/L}$ using a mixture of Acetylene - Nitrous Oxide flame.

Optimization of the Factors Affecting the Adsorption of Iron from Standard Solutions

Optimization of the pH

To investigate the effect of pH on the uptake % (adsorption) of iron from aqueous media by the crude (WMP) powder, aliquots of 25 mL containing 20 ppm of the metal ion are transferred to a group of 100 mL conical flasks each containing 0.1 g of the crude adsorbent. Adjust the pH for each flask in the order ranging from 2-10, respectively by using 0.1M NaOH and HCl solutions and stir for 1hr. Centrifuge the contents of each flask and determine the remaining iron content in the supernatant solution. The sorption percentage of the metal ion by the WMP powder is calculated by equation (1):

$$\text{Uptake (\%)} = [(C_i - C_f) / C_f] \times 100$$

Where C_i and C_f are the initial and final concentrations of metal ion respectively. Biosorption capacity q (mg/g) is calculated by equation (2):

$$q = \frac{C_i - C_f}{W_t} * V$$

Where C_i and C_f are the initial and final concentrations of iron (ppm), W_t is the dose of sorbents (g) and V is the volume of solution (mL). The optimum pH is adjusted to be in the range 4-7. When the same procedure is parallel repeated using the sodium citrate and lactic acid modified powders, the optimum pH is in the range 5-6 in both cases.

Effect of temperature

The effect of temperature on the removal of iron ions by the three modified (WMP) powdered forms are studied at different temperatures between 30 and 70°C.

Sorbent dose

Aliquots of 25mL solution containing 20ppm iron are transferred to a group of 100mL conical flasks. Adjust the pH for each flask to the optimum value. Varying amounts of the crude (WLP) powder in the range 50-350mg are added to each flask, respectively. The mixtures are stirred for 1h. The remaining iron content in supernatant soln. separated by centrifugation is determined spectrophotometrically. The procedure is repeated with the other two (WLP) modified powders.

Contact time

A set of 100mL conical flasks, each of which is uploaded with 0.2g of the three (WMP) powder forms and aliquots of 25mL solution containing 20ppm of iron at the optimum pH and the shaking time is varied for different intervals of time (10-80min) for each flask in its turn, respectively.

Metal ion concentration range

Applying the optimum conditions of the weight of (WMP) powder, pH and stirring time in a group of flasks. Aliquots of 25mL solution containing varying concentrations of iron ions in the range 10-100ppm are added to each flask, respectively. The same procedure is applied, and the remaining iron content is determined from which the uptake percent is calculated.

Optimum sample volume

Different volumes of iron sample in the range from 10-100mL are tested.

Results and Discussion

Bio sorbent production may be an added value to the agro-wastes and eventually reduces the agro-wastes management problems over the world. Agro-materials usually have their composition of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which include al-

cohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups can bind to some extent heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [36]. During the past few years, several research articles were published reporting the successful use of different kinds of agricultural wastes in the removal of metal ions from aqueous solutions. The use of plant's peels is reported in literature e.g., Ni (II) and Cd (II) removal from aqueous solution on modified plantain peels [8], biosorption of cadmium and nickel by grapefruit peels [34], biosorption of heavy metals present on polluted water by using different waste fruit cortex, banana (*Musa paradisiaca*), lemon (*Citrus limonum*) and orange (*Citrus sinensis*) peel [35], biosorption of aquatic cadmium (II) on unmodified rice straw [21], biosorption on peanut shell [22], equilibrium and kinetics of biosorption of cadmium(II), copper(II) ions by wheat straw [37] and iron by green clover leaves [38]. Watermelon's botanical name, *Citrullus vulgaris*, comes from the diminutive form of citrus, referring to the color and shape of the fruit, and vulgaris meaning common or ordinary fruit [39]. Our thinking was forwarded towards trying (WMP) fine powder as a low cost adsorbent for the treatment of a real local problem viz., the existence of iron (and manganese) in the ground water of some wells at El-Wasta, a town which lies 35 Km to the north of Beni-Suef Governorate, Egypt.

Factors that affect the Adsorption Process have been Studied in Details to Improve the Uptake % of Iron from the Aqueous Solutions

Optimum pH

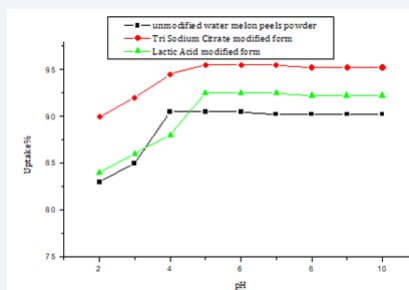


Figure 1: Effect of pH on the adsorption of Fe ions on the crude and modified water melon peels powder.

The pH is directly related to the competition ability of hydrogen ions with metal ions to active sites on the bio sorbent surface. The results indicated low sorption efficiency at low pH values (pH=2-3), this was attributed to the high concentration and high mobility of H^+ , which are preferentially adsorbed instead of metal ions. The removal efficiency of the sorbent is increased by increasing the pH value until reaches its maximum uptake in the range 4-6 by the unmodified (WMP). The sodium citrate and lactic acid modified (WMP) powders showed maximum adsorption at the pH range 5-7. Heavy metal biosorption on the specific and nonspecific bio sorbents is pH dependent; other researchers found that an increase in adsorption is a result of increasing the pH of the solution (Figure 1, Table 1).

Table 1: Effect of pH on the adsorption of Fe ions on crude and modified water melon peels powders.

pH	Crude Form		Lactic Acid Form		Trisodium Citrate Form	
	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
2.00	0.1000	83.10 ± 0.0577	0.1527	84.16 ± 0.0882	0.2000	90.20 ± 0.1155
3.00	0.2082	85.23 ± 0.1202	0.2000	86.20 ± 0.1155	0.1527	92.13 ± 0.0882
4.00	0.1527	90.53 ± 0.0882	0.1527	88.13 ± 0.0882	0.1527	94.46 ± 0.0882
5.00	0.1000	90.60 ± 0.0577	0.1527	92.46 ± 0.0882	0.1527	95.53 ± 0.0882
6.00	0.1527	90.33 ± 0.0882	0.2000	92.30 ± 0.1155	0.2082	95.43 ± 0.1202
7.00	0.0153	90.23 ± 0.0088	0.2311	93.93 ± 0.7705	0.1527	95.46 ± 0.0882
8.00	0.0100	90.25 ± 0.0058	0.0200	92.25 ± 0.0115	0.0200	95.25 ± 0.0115
9.00	0.0153	90.25 ± 0.0088	0.0321	92.26 ± 0.0186	0.0289	95.26 ± 0.0167
10.00	0.0153	90.25 ± 0.0088	0.0100	92.24 ± 0.0058	0.0252	95.25 ± 0.0145

Effect of temperature

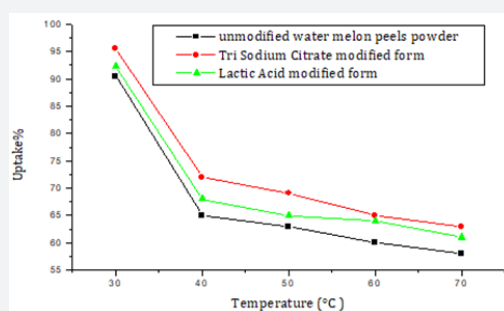


Figure 2: Effect of temperature on the adsorption of Fe ions on the water melon peels powder forms.

Maximum adsorption recovery is obtained at 30 °C for the three adsorbent forms. The uptake percentage decreased with the increase in temperature suggesting that the adsorption process is exothermic [40]. As observed in (Figure 2, Table 2), tri sodium ci-

trate modified form gave better adsorption performance than the crude and lactic acid forms. These results also proved that during the adsorption process, no permanent chemical bonds are formed [41].

Table 2: Effect of temperature on the adsorption of Fe ions on the crude and modified water melon peels powders.

Temperature °C	Crude Form		Lactic Acid Form		Trisodium Citrate Form	
	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
30.00	0.1000	90.60 ± 0.0577	0.0153	92.25 ± 0.0088	0.1000	95.60 ± 0.0577
40.00	0.1527	65.16 ± 0.0882	0.1732	68.20 ± 0.1000	0.1527	72.13 ± 0.0882
50.00	0.0577	63.06 ± 0.0333	0.1000	65.10 ± 0.0577	0.1527	69.16 ± 0.0882
60.00	0.1527	60.16 ± 0.0882	0.2082	64.23 ± 0.1202	0.1000	65.10 ± 0.0577
70.00	0.1527	58.16 ± 0.0882	0.1000	61.10 ± 0.0577	0.1155	63.13 ± 0.0667

Stirring time

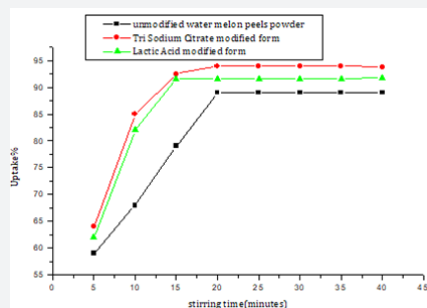


Figure 3: Effect of stirring time on the adsorption of Fe ions on the crude and modified water melon peels powder.

Equilibrium time is one of the important parameters for selecting a wastewater treatment system [37]. The results show that removal is slow in the first 10 min, then the adsorption % is gradually increased till equilibrium is reached after 20 min for the unmodified powder. While both the tri sodium citrate and the lactic

acid modified forms attained equilibrium after 15 min. The rate of biosorption seems to pass through two steps, the first one is very rapid surface biosorption, while the second is slow intracellular diffusion (Figure 3, Table 3).

Table 3: Effect of stirring time on the adsorption of Fe ions on the water melon peels powder forms.

Stirring time, min.	Crude Form		Lactic Acid Form		Trisodium Citrate Form	
	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
5.00	0.1527	59.16 ± 0.0882	0.1527	62.13 ± 0.0882	0.1000	64.10 ± 0.0577
10.00	0.1527	68.13 ± 0.0882	0.0321	82.02 ± 0.0186	0.0513	85.05 ± 0.0296
15.00	0.1000	79.10 ± 0.0577	0.1000	91.60 ± 0.0577	0.0379	92.54 ± 0.0219
20.00	0.0100	89.01 ± 0.0058	0.0321	91.54 ± 0.0186	0.0100	94.01 ± 0.0058
25.00	0.0100	89.04 ± 0.0058	0.0208	91.55 ± 0.0120	0.0252	94.05 ± 0.0145
30.00	0.0153	89.07 ± 0.0088	0.0100	91.52 ± 0.0058	0.0265	94.04 ± 0.0153
35.00	0.0208	89.03 ± 0.0120	0.0100	91.54 ± 0.0058	0.0493	94.03 ± 0.0285
40.00	0.0153	89.04 ± 0.0088	0.0265	91.53 ± 0.0153	0.0100	94.02 ± 0.0058
45.00	0.0321	89.03 ± 0.0186	0.0231	91.52 ± 0.0133	0.0208	94.03 ± 0.0120

Sorbent dose

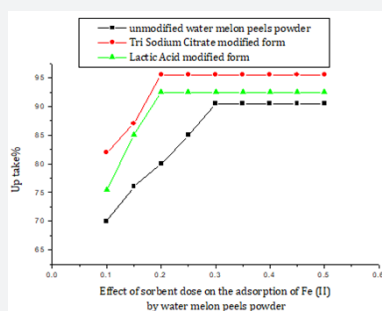


Figure 4: Effect of sorbent dose on the adsorption of Fe ions on the crude and modified water melon peels powder.

For a specific metal initial concentration, increasing the adsorbent dose provides greater surface area and availability of more active sites, thus leading to the enhancement of metal ion uptake till reach equilibrium [42]. For the unmodified powder, a dose of 0.3 g sorbent can achieve an uptake of 90.5% of iron at

optimum pH conditions. While for the tri sodium citrate modified form, a dose of 0.2 g achieved better uptake % of iron of 95.5%. Correspondingly, 0.2 g of the lactic acid modified one achieved an intermediate iron removal % of 92. (Figure 4, Table 4).

Table 4: Effect of sorbent dose on the adsorption of Fe ions on crude and modified water melon peels powders.

Dose g.	Crude Form		Lactic Acid Form		Trisodium Citrate Form	
	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
0.10	0.1000	70.10 ± 0.0577	0.1000	75.50 ± 0.0577	0.1527	82.16 ± 0.0882
0.15	0.2082	76.16 ± 0.1202	0.1527	85.13 ± 0.0882	0.1527	87.13 ± 0.0882
0.20	0.1000	80.10 ± 0.0577	0.1242	91.73 ± 0.7172	0.1000	95.40 ± 0.0577
0.25	0.1527	85.16 ± 0.0882	0.1155	92.43 ± 0.0667	0.1527	95.33 ± 0.0882
0.30	0.1000	90.60 ± 0.0577	0.1000	92.60 ± 0.0577	0.2000	95.30 ± 0.1154
0.35	0.1732	90.60 ± 0.1000	0.1732	92.60 ± 0.1000	0.2646	95.30 ± 0.1527
0.40	0.1000	90.50 ± 0.0577	0.1527	92.53 ± 0.0882	0.1000	95.40 ± 0.0577
0.45	0.1000	90.60 ± 0.0577	0.1000	92.40 ± 0.0577	0.1000	95.60 ± 0.0577
0.50	0.1155	90.43 ± 0.0667	0.1527	92.46 ± 0.0882	0.0577	95.53 ± 0.0333

Initial metal ion concentration

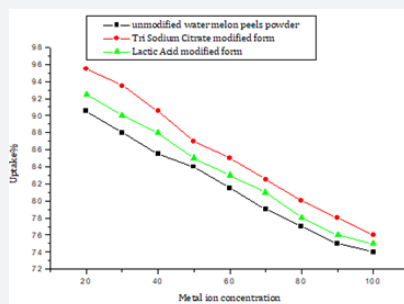


Figure 5: Effect of metal ion concentration on the adsorption of Fe ions on the crude and modified water melon peels powders.

The initial metal ion concentration does a substantial force to overcome all mass transfer resistances of the metal ions between aqueous and solid phase [43]. At lower concentrations the adsorption sites utilize the available metal ion more rapidly in comparison to higher concentrations where the metal ions need

to diffuse to the sorbent surface by intra particle diffusion. The maximum metal uptake was 90.5 % in the case of the unmodified (WMP) powder, 92.5% for lactic acid modified one and 95.5% in the case of tri sodium citrate form at metal ion concentration of 20 ppm, (Figure 5, Table 5).

Table 5: Effect of metal ion concentration on the adsorption of Fe ions on crude and modified water melon peels powders.

Metal Conc. ppm	Crude Form		Lactic Acid Form		Trisodium Citrate Form	
	Std. deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
20.00	0.1000	90.60 ± 0.0577	0.1000	92.40 ± 0.0577	0.1000	95.50 ± 0.0577
30.00	0.1527	88.13 ± 0.0882	0.1000	90.10 ± 0.0577	0.1000	93.50 ± 0.0577
40.00	0.1000	85.40 ± 0.0577	0.1527	88.13 ± 0.0882	0.1000	90.60 ± 0.0577
50.00	0.1000	84.10 ± 0.0577	0.1527	85.16 ± 0.0882	0.1000	87.10 ± 0.0577
60.00	0.1527	81.33 ± 0.0882	0.2000	83.20 ± 0.0509	0.1527	85.16 ± 0.0882
70.00	0.2517	79.03 ± 0.1453	0.1000	81.00 ± 0.0577	0.1000	82.60 ± 0.0577
80.00	0.1527	77.16 ± 0.0882	0.1000	78.10 ± 0.0577	0.1000	80.10 ± 0.0577
90.00	0.1527	75.16 ± 0.0882	0.1527	76.13 ± 0.0882	0.1527	78.16 ± 0.0882
100.00	0.1000	90.60 ± 0.0577	0.1527	75.16 ± 0.0882	0.2082	76.23 ± 0.1202

Sample volume

Table 6: Effect of sample volume on the adsorption of Fe ions on the crude and modified water melon peels powders.

Sample Vol. mL	Crude Form		Lactic Acid Form		Trisodium Citrate Form	
	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
25.00	0.1000	90.60 ± 0.0577	0.1000	92.60 ± 0.0577	0.1000	95.60 ± 0.0577
50.00	0.1000	89.60 ± 0.0577	0.1000	92.10 ± 0.0577	0.1000	94.60 ± 0.0577
75.00	0.1000	88.60 ± 0.0577	0.1154	91.56 ± 0.0667	0.1527	93.53 ± 0.0882
100.00	0.1527	88.13 ± 0.0882	0.2081	91.23 ± 0.1202	0.1000	92.50 ± 0.0577
125.00	0.2081	88.23 ± 0.1202	0.1000	90.60 ± 0.0577	0.1000	92.10 ± 0.0577
150.00	0.1000	88.10 ± 0.0577	0.1732	90.60 ± 0.1000	0.2309	92.13 ± 0.1333
175.00	0.1527	88.16 ± 0.0882	0.1000	90.50 ± 0.0577	0.1527	92.13 ± 0.0882
200.00	0.2081	88.16 ± 0.1202	0.1732	90.60 ± 0.1000	0.2886	92.17 ± 0.1667
225.00	0.1527	88.16 ± 0.0882	0.1000	90.60 ± 0.0577	0.1000	92.10 ± 0.0577
250.00	0.1000	88.10 ± 0.0577	0.0577	90.53 ± 0.0333	0.0577	92.03 ± 0.0333

At optimum conditions the volume of 25 mL achieved the best adsorption percentage with all tested (WMP) powders. It is clear

from the Table 6, it is clear that iron removal percentage decreases with the increase of the volume.

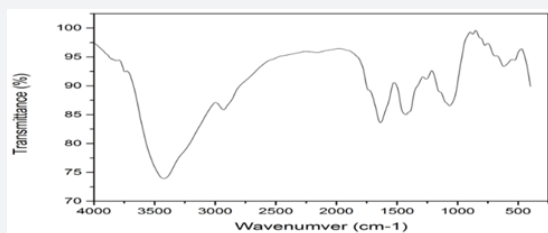


Figure 6: FTIR Spectrum of crude water melons peels powder in the Range 500 -4000cm⁻¹.

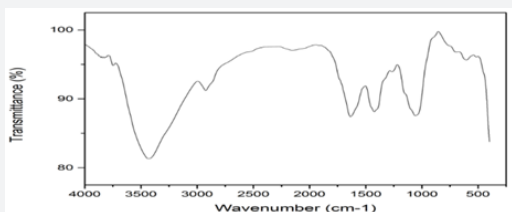


Figure 7: FTIR Spectrum of adsorbent tri sodium citrate water melons peels powder form in the Range 500 - 4000cm⁻¹.

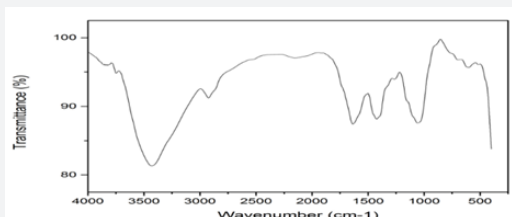


Figure 8: FTIR Spectrum of Adsorbent lactic acid water melons peels powder form in the Range 500 -4000cm⁻¹.

Characterization of used adsorbents

The composition and topography of the studied adsorbents have been characterized by FT-IR and SEM.

Infra-red spectroscopy: Figure 9 & 10 depicts the FT-IR spectrum of the unmodified (WMP) powder form. The broad band in the region around 3425cm⁻¹ is specific to the surface hydroxyl groups of bonded carboxylic acid. The O-H stretching vibrations occurred within a broad range of frequencies indicating the presence of free hydroxyl groups and bonded O-H bands of carboxylic acid, the -OH carbonyl and carboxylic groups have been reported as very important sorption sites for metal ions. The asymmetric C-H stretching of surface methyl groups usually present on the lignin structure is observed at 2900cm⁻¹. The characteristic peaks because of the C-O group in carboxylic and alcoholic groups are present at 1053cm⁻¹ [44]. The ionization of both the carboxylic acid and hydroxyl functional groups present in the structure of the adsorbent can be achieved by deprotonation that allowing it to interact with metals more easily and therefore provides the major biosorption sites for the removal of iron ions from solutions [44]. A broadening peak at around 1650cm⁻¹ due to carbonyl group peak is observed. This indicates the involvement of both the hydroxyl and carbonyl groups in the adsorption of iron. Figure 7 the presence of COO⁻ of the carboxylate can be

attributed to the peak positions at 1452.30cm⁻¹ and 1400.22cm⁻¹. Alkyl chains around are observed at 2920-2850cm⁻¹. The peaks in range 1000-1200cm⁻¹ symbolize C-C and C-O stretching.

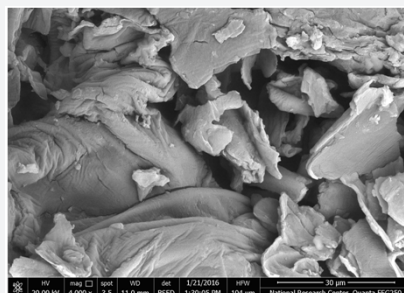


Figure 9: SEM of crude water melon peels powder.

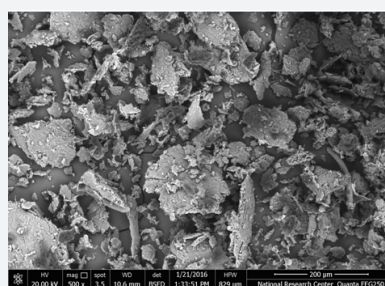


Figure 10: SEM of lactic acid water melon peels powder.

The Morphologies of the prepared adsorbents

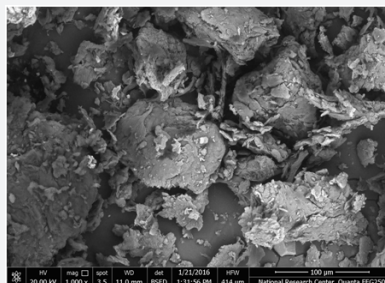


Figure 11: SEM of tri sodium citrate water melon peels powder.

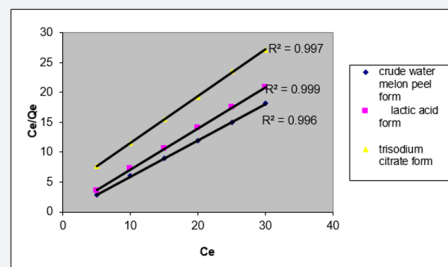


Figure 12: Langmuir isotherm plots for the adsorption of iron ions by water melon peels powders.

This study revealed the micro porous structure of the adsorbent. The SEM micrographs of (WMP) are as shown in Figures 9-11. The micrographs showed that the bio sorbent has

a smoothening and irregular surface (Figure 9). A significant change in the bio sorbent surface is observed after the modification (Figure 11&12). A rough effect is perceived in (Figure 12) It is observed as providing a large area for ion-surface interaction. Different surface shapes of the bio sorbent may be due to its modification with lactic acid and tri sodium citrate.

Selectivity of the adsorbent

Adsorption studies applying the three adsorbents under investigation, proved that they are nonselective towards different heavy metals that may be present in wastewaters as pollutants. However, the non-selectivity of such types of adsorbents is frequent in the literature; their tolerance is attributed to being low cost and available. Current work in our laboratory is devoted for the development and applications of selective and low-cost adsorbent.

Adsorption isotherm studies

For solid-liquid adsorption system, the adsorption behavior can well be described as adsorption isotherm model, the adsorption isotherm meaning the distribution of adsorbate molecules among the solid phase and the liquid phase at equilibrium. Equilibrium is said to be reached when the concentration of adsorbate in bulk solution is in dynamic balance with that on the liquid adsorbate interface. It is significant to study the adsorption behavior in order to describe adsorption process using appropriate adsorption isotherm model.

Langmuir adsorption isotherm

The Langmuir isotherm model assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between the sorbet species [45]. The equilibrium adsorption data for the concentrations of iron ions is fitted into the linear

form of Langmuir’s isotherm equation, to determine the distribution of iron ions between the adsorbent and solution according to equation (3):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

Where C_e is the concentration of the iron ions in solution (mg L⁻¹), Q_e is the equilibrium concentration of iron ions on (WMP) adsorbent (mg g⁻¹), Q_m and K_L are Langmuir constants related to sorption capacity and the rate of adsorption respectively. Maximum adsorption capacity (Q_m) is the monolayer capacity of the adsorbent (mg g⁻¹) and K_L is the Langmuir adsorption constant. A plot of C_e/Q_e against C_e over the entire concentration range is a straight line with a slope of $1/Q_m$ and the intercept of $1/Q_m K_L$. The correlation coefficient (R_2) values reported are very close to 1 indicating that the adsorption follows the Langmuir adsorption isotherm. The quality of Langmuir isotherm can be determined by the magnitude of a dimensionless constant R_L known as the separation factor expressed in equation (4):

$$R_L = \frac{1}{1 + C_0 R_L} \quad (4)$$

where C_0 is the initial concentration of the iron ions in mg L⁻¹ and K_L is the Langmuir constant described earlier. The adsorption process is favorable within the range $0 < R_L < 1$, unfavorable when $R_L > 1$, becomes linear when $R_L = 1$, and the process is irreversible when $R_L = 0$. The value of RL for crude WMP is 0.0475 and for forms modified with tri sodium citrate and lactic acid equal to 0.0408 and 0.0460 respectively; hence the adsorption process is favorable (Figure 13, Table 7).

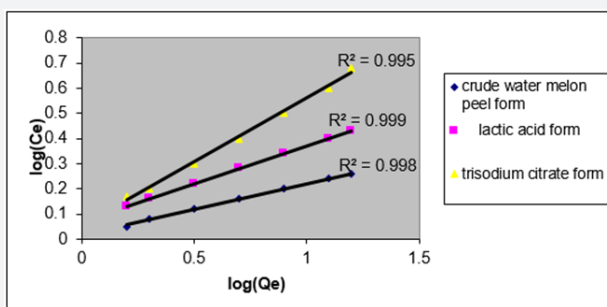


Figure 13: Freundlich isotherm plots for the adsorption of iron ions by water melon peels powder.

Table 7: Langmuir and Freundlich adsorption isotherm Parameters.

Langmuir and Freundlich Adsorption Isotherm Parameters of Iron Ions by Water Melon Peel Forms							
S./No	Langmuir Isotherm Parameters	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters		
		Unmodified water melon peels powder	Tri sodium citrate modified form	Lactic acid modified form	Unmodified water melon peels powder	Tri sodium citrate modified form	Lactic acid modified form
1	Q_{max} (mg/g)	90	97	93	0.471	0.288	0.311

2	K_L	1.002	1.174	1.035	0.796	0.958	0.899
3	R_2	0.996	0.997	0.999	0.998	0.995	0.999
4	R_L	0.047	0.041	0.046			

Freundlich adsorption isotherm

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules, and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent [28]. The linear form of the Freundlich adsorption Model equation (5):

$$\log Q_e = \log_e K_F + \frac{1}{n} \log_e C_e \quad (5)$$

Where Q_e is the amount of iron ions adsorbed at equilibrium per gram of the adsorbent (mg g^{-1}), C_e is the equilibrium concentration of the iron ions in the solution (mg L^{-1}), and K_f and n are the Freundlich adsorption model constants related to the adsorption capacity and adsorption intensity respectively. $\log_e Q_e$ is plotted against $\log_e C_e$ and a straight line obtained gave the intercept of $\log K_f$ and the slope of $1/n$. The numerical value of $1/n$ reported is less than 1, (Figure 13, Table 7).

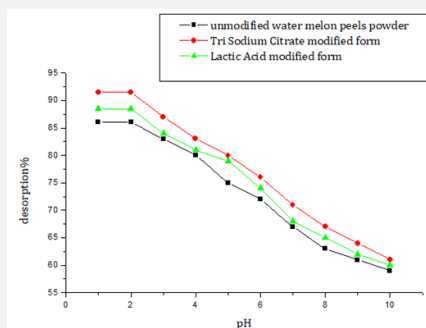


Figure 14: Effect of pH on desorption of Fe ions on the crude and modified water melon peels Powder.

Analysis of real samples

Water samples are collected from tap water, Bahr Youssef water, ground water and Ibrahimia (stream) water; samples are

subjected to the adsorption procedure as explained previously and the residual iron is analyzed by two methods of finish viz., colorimetry and AAS (Table 8).

Table 8: Concentration of Fe (II) in real water samples.

Collected samples	AAS	Colorimetry	Crude		Lactic acid form		Trisodium citrate form	
	Found iron concentration	Found iron concentration	Recovery %	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
Drinking water	3.56ppm	3.571ppm	89.62 ± 0.0219	89.62 ± 0.0219	0.03215	92.02 ± 0.0185	0.0252	94.05 ± 0.0145
Bahr youssef water	3.20ppm	3.211ppm	85.01 ± 0.0088	85.01 ± 0.0088	0.02082	90.01 ± 0.0120	0.0265	92.51 ± 0.0153
Ground water	4.79ppm	4.882ppm	86.13 ± 0.0120	86.13 ± 0.0120	0.01	90.58 ± 0.0058	0.0493	92.11 ± 0.0285
Ibrahimia water	1.12ppm	1.123ppm	87.77 ± 0.0088	87.77 ± 0.0088	0.05132	91.32 ± 0.0296	0.01	93.53 ± 0.0058

Desorption studies

Reusability of the adsorbent is tested by regenerating the spent adsorbent following a modified literature procedure [46]. The adsorbed iron ions onto the three WMP surfaces are treated with 25 mL 0.1M HCl and stirred for 1h. The amount of iron ions remained in the solution after filtration or centrifugation is measured using the mentioned spectrophotometric and/ the FAAS

methods and the percentage desorption (R_b) was calculated relatively to the equation (6):

$$= \frac{C_t}{C_a} \times 100(6) R_b$$

Where C_t is the experimental concentration in the solution at time t (ppm), C_a is the adsorbed concentration of sorbate onto the adsorbent surface.

The Parameters Affecting the Desorption Process are Studied as Illustrated Below

Effect of pH on desorption of iron

Table 9: Effect of stirring time on desorption of Fe ions from the crude and modified water melon peels powders.

Stirring time, min.	Crude form		Lactic acid form		Trisodium citrate form	
	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %	Std. Deviation*	Recovery %
5.00	0.1000	68.10 ± 0.0577	0.1527	72.16 ± 0.0882	0.1527	75.17 ± 0.0882
10.00	0.1527	71.17 ± 0.0882	0.1050	74.60 ± 0.0606	0.2248	78.25 ± 0.1202
15.00	0.1000	75.10 ± 0.0577	0.1000	79.10 ± 0.0577	0.2081	82.23 ± 0.1202
20.00	0.2081	82.07 ± 0.1202	0.1527	82.13 ± 0.0882	0.1527	85.13 ± 0.0882
25.00	0.2773	85.50 ± 1.6010	0.2203	85.21 ± 0.1272	0.1527	89.13 ± 0.0882
30.00	0.0577	87.07 ± 0.0333	0.1000	89.10 ± 0.0577	0.1000	92.10 ± 0.0577
35.00	0.1000	87.10 ± 0.0577	0.1527	89.16 ± 0.0882	0.2082	92.23 ± 0.1202
40.00	0.1527	87.13 ± 0.0882	0.1155	89.13 ± 0.0667	0.1527	92.13 ± 0.0882
45.00	0.1154	87.13 ± 0.0667	0.1527	89.17 ± 0.0882	0.1527	92.13 ± 0.0882
50.00	0.0577	87.07 ± 0.0333	0.1527	89.13 ± 0.0882	0.2000	92.20 ± 0.1155
55.00	0.7505	87.43 ± 0.4333	0.2000	89.20 ± 0.1155	0.1527	92.16 ± 0.0882
60.00	0.0252	86.75 ± 0.0145	0.0153	88.74 ± 0.0088	0.0115	91.74 ± 0.0067

In strong acidic media at pH range (1.2-1.9) the three forms of the WMP powder showed high desorption percentages, on increasing the pH values desorption percentage decreases (Figure 11, Table 9).

Stirring Time

Table 10: Summary of the optimum conditions for the adsorption of Fe on the crude and modified water melon peels powders.

Parameter	Crude Form			Lactic Acid Form			Trisodium Citrate Form		
	Optimum Values	Colorimetry Recovery %	AAS Recovery%	Optimum Values	Colorimetry Recovery %	AAS Recovery%	Optimum Values	Colorimetry Recovery %	AAS Recovery%
pH	4-6	90.60 ± 0.0577	90.53 ± 0.0882	5-7	92.46 ± 0.0882	92.30 ± 0.1155	5-7	95.53 ± 0.0882	95.47 ± 0.0882
Shaking time, min	20min	89.01 ± 0.0058	89.03 ± 0.0120	15min	91.60 ± 0.0577	91.54 ± 0.0058	20min	94.01 ± 0.0058	94.02 ± 0.0058
Metal concentration	20ppm	90.60 ± 0.0577	90.40 ± 0.0366	20ppm	92.40 ± 0.0577	92.50 ± 0.0666	20ppm	95.50 ± 0.0577	95.46 ± 0.0033
Sorbent dose	0.3g	90.60 ± 0.0577	90.50 ± 0.0333	0.2g	92.73 ± 0.7172	92.43 ± 0.5563	0.2g	95.40 ± 0.0577	95.51 ± 0.0677
Sample volume	25mL	90.60 ± 0.0537	90.71 ± 0.0577	25mL	92.60 ± 0.0577	92.50 ± 0.0577	25mL	95.60 ± 0.0577	95.56 ± 0.0577
Temperature	Exothermic 30°C	90.60 ± 0.0577	90.60 ± 0.0447	Exothermic 30°C	92.25 ± 0.0088	92.26 ± 0.0077	Exothermic 30°C	95.60 ± 0.0577	95.39 ± 0.0577

The desorption percentages are gradually increased till equilibrium is reached after 25 min in case of the crude WMP powder, while the powders modified with lactic acid and tri sodium citrate show equilibrium after 30min. A desorption value of 87% has been recorded for the unmodified WMP powder, 92.5% for the tri sodium citrate modified form and 89% for lactic acid one (Figure 14, Table 9).

Conclusion

Water melon peels powder (WMP) and its modified forms proved to be potential bio sorbents for the removal of iron and

other co present heavy metals from aqueous solutions, being available low-cost material. The proposed adsorbents were applied on real water samples. The adsorption process is best described by the Langmuir and Freundlich isotherm models. Results of desorption investigations also, assured the possibility to regenerate and reuse the bio sorbents once again.

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