Evaluation of Green Clover Leaves as Green and Economic Sorbent for Removal of High Levels of Iron from Different Water Sources

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Submission: December 12, 2016; Published: January 05, 2017

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Abstract

Green clover powdered leaves and their modified forms with lactic acid and tri sodium citrate have been used as low cost and eco-friendly adsorbents for the removal of iron from aqueous media. Samples were collected from different water supplies (surface, tap and ground water). The different factors affecting the adsorption procedure such as: adsorbent dose, stirring time and pH have been optimized for the sake of realizing maximum removal efficiency. The removal efficiency of the unmodified green clover was increased with the increase of the pH value until reaching its maximum uptake in the range 4-7. Both the sodium citrate and lactic acid modified green clover powders showed maximum uptake in the pH range 5-6. The removal process was slow in the first 35 min. then the uptake% was gradually increased till equilibrium after 50 min in case of unmodified green clover; the tri sodium citrate modified form showed equilibrium after 40 min. and the lactic acid modified one reached equilibrium after 50 min. Desorption processes proved the possibility of regeneration and reuse of the adsorbent.

Modified forms displayed better adsorption capacity and capability comparable with that of the crude leaves. The removal process was applied on some samples of wastewater successfully.

Keywords: Water sources; Heavy metals; Fe; Green clover leaves; Economic sorbent; Adsorption

Introduction

Air, food, soil and water were narrated to be the media where heavy metals such as copper, cadmium, nickel, lead, and zinc are introduced into the environment [1-4]. Heavy metals cause serious health disease, including reduced growth and development, cancer, organ and nervous system damage. In severe cases, it leads to death [5]. These heavy metals are reported to be hazardous resulting in damage to ecosystems as well as human health [6,7] especially if their concentration is more than the accepted limit [8]. Their higher sources include contaminant water discharged from hospitals [9], several industries such as Cd-Ni battery, metal plating and alloy manufacturing [10-13]. Chemical precipitation, ion exchange, electrodialysis, solvent extraction, coagulation, evaporation and adsorption are among the most known techniques for the removal of metal ions from aqueous solutions [14-17].

Iron is one of the earth’s most spreading resources making up about 5% of the earth crust. It is one of the major heavy metal impurities that are commonly present in many water sources which cause several problems for the human health [18]. There are many methods for removal of iron from ground water, viz., oxidation with chlorine and potassium permanganate, treatment with limestone, liquid-liquid extraction, ion exchange, chemical precipitation, bioremediation, activated carbon and other filtering materials [19-23]. Many of these methods became not economically feasible for the removal processes.

In recent years, the need for safe and economical methods has necessitated the use of low cost agricultural by-products such as sugarcane bagasse [24-26], rice husk [27,28], sawdust [29,30], coconut husk [31], oil palm shell [32], black gram husk [33], neem bark [34], tea waste, turkish coffee and walnut shell. Some more adsorbents like papaya wood [35], maize leaf [36], teakleaf powder [37], coraindrumsativum [38], lalang (Imperata cylindrica) leaf powder [39], peanut hull pellets [40], sago waste [41], saltbush (Atriplex canescens) leaves [42,43], tree fern [44-45], grape stalk wastes [46], etc. Sorption methods are
considered flexible and easy to operate with much less sludge disposal problems and economically feasible [47,48].

However, the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be termed a low cost one if it requires little processing, abundant in nature, an agricultural waste or is a by-product or a waste material from an industry. On the other hand, plant wastes can be used in their crude form, or in most cases, require to be modified or treated for being applied for the cleansing of heavy metals. Thus, the present study was forwarded towards the use of green clover powdered leaves as economic sorbent in both crude and modified forms with trisodium citrate and lactic acid for removal of iron from different water sources. The different factors affecting the adsorption procedure such as: adsorbent dose, stirring time and pH have been optimized to achieve maximum removal efficiency.

**Experimental**

**Materials and Methods**

**a) Chemicals**

Ferrous ammonium sulphate (Aldrich), Hydrochloric acid (BDH), 1, 10 Phenanthroline (Aldrich) Tri sodium citrate (Aldrich) and Hydroxylamine hydrochloride (Aldrich).

**b) Reagents**

i. **Standard Iron (II) solution**

(1000 ppm) Fe (II) stock solution was prepared by dissolving 0.7016 g of ammonium ferrous sulphate (NH4)2SO4·FeSO4·6H2O, (Aldrich, USA) in DDW containing 5 mL conc. H2SO4 and accurately diluted with water to volume in 100 mL volumetric flask.

ii. **1, 10 Phenanthroline (0.2%)**

Phenanthroline hydrochloride or hydrate (phen), in 100 mL vol. flask 0.2 gm of phenanthroline were dissolved in doubly distilled water (DDW) and diluted to the mark with in 0.1 M HCl.

iii. **Tri sodium citrate (10 %) solution**

in 100 mL vol. flask, 10 g of tri sodium citrate were dissolved in doubly distilled water (DDW) and diluted to the mark.

iv. **Hydroxylamine hydrochloride (10 %)**

10g of hydroxylamine-HCl were dissolved in DDW and diluted to 100mL.

**c) Preparation of the green leaves clover powder and its modified forms:**

**i. Preparation of the green clover leaves powder**

Green clover leaves are collected from the agricultural Egyptian fields. The leaves are 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 green clover leaves powder for the removal of iron from water samples according to the proposed procedure.

**ii. Lactic Acid Modified Green Clover leaves powder**

100 g of the crude green clover powder are refluxed with 500 mL of 0.5 M lactic acid solution over a boiling water bath for 6 h. The produced precipitate was separated, repeatedly washed with DDW till free from acid then dried in an oven at 60ºC for 2 hrs. After cooling in a desiccator to room temperature, it is finely grinded once again.

**iii. Tri Sodium Citrate Modified Green Clover leaves powder:**

100 g of the crude green clover powder are, similarly, refluxed with 500 mL of 0.5 M trisodium citrate solution over a boiling water bath for 6 h. The produced precipitate was separated, repeatedly washed with DDW till free from both the sodium and citrate ions, then dried and grinded.

**Instruments**

UV/Vis. Spectrophotometer (Shimadzu UV/Vis. Perkin Elemer Lambada 3B Spectrophotometer using 1 cm Quartz cell" was used for the determination of residual iron in the effluents after the adsorption processes); Flame Atomic Absorption Spectrophotometer AA 240FS, Agilent Technologies, used for rapid and confirmational determination of iron; pH meter (The pH measurements were carried out using the microprocessor pH meter BT 500 BOECO, Germany, which was calibrated against two standard buffer solutions at pH4 and 9 and Mechanical Shaker (with up to 200 rpm with speed control was used).

The morphologies of the prepared samples and composites were investigated using Scanning Electron Microscopy (SEM), X-Ray diffractometer was used to investigate the phase structure of the investigated samples under the following conditions which were kept constant in all the analysis processes Cu: X-ray tube, scan speed = 8/min, current = 30 mA, voltage = 40 kV and preset time = 10s.

**Procedure**

**Spectrophotometric Method for Determination of iron**

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

**Flame Atomic Absorption procedure**

The concentration of residual iron in the solution after the adsorption process is directly measured by using a mixture of Acetelyne – Nitrous Oxide flame.
Optimization of the factors affecting the extraction of iron from standard solutions

i. Optimization of the pH

To investigate the effect of pH on the uptake % (adsorption) of iron from aqueous media by the crude green clover leaves 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 of each flask to a value ranging from 2-10, respectively using 0.1M NaOH and HCl solutions and stir for 1hr. Centrifuge the contents of each flask and determine the residual iron content in the supernatant solution. The sorption percentage of the metal ion by the green clover leaves powder is calculated from the relation:

\[
\text{Uptake} \% = \frac{[C_o - C]}{C_o} \times 100
\]

Where \(C_o\) and \(C\) are the initial and final concentrations of metal ion respectively. The optimum pH was found to be in the range 4-7.

When the same procedure was parallely repeated using the sodium citrate and lactic acid modified powder instead, the optimum pH was in the range 5-6.

ii. Sorbent Dose

Aliquots of 25 mL solution containing 20 ppm iron are transferred to a group of 100 mL conical flasks. Adjust the pH of each flask to the optimum value. Varying amounts of the crude green clover leaves powder in the range 0.05 - 0.35 g are added to each flask, respectively. The mixtures were stirred for 1hr. The residual iron content in the supernatant solution separated by centrifugation is determined spectrophotometrically.

iii. Contact Time

A group of 100 mL conical flasks, each of which is charged with 0.2 g of the crude green clover leaves powder and aliquots of 25 mL solution containing 20 ppm of iron at the optimum pH and the shaking time is changed for different intervals of time (10-80 min.) for each flask in its role, respectively.

iv. Metal Ion Concentration range

Applying the optimum conditions of the weight of green clover leaves powder, pH and stirring time in a group of flasks. Aliquots of 25 ml solution containing varying concentrations of iron in the range 10-100 ppm are added to the flasks, respectively. The same procedure is applied and the residual iron content is determined from which the uptake percent is calculated.

v. Optimum Sample Volume

Different volumes of iron samples in the range from 10-100 mL were used.

Results and Discussion

Cellulosic materials and their derivatives have shown quite good metal ion adsorptive capacity. Among all the heavy metal removal techniques reported so far, adsorption technique using cellulose-based agricultural waste products appears to be most attractive since it is an effective and relatively simple method for removal of heavy metal ions. However, the leaves and pseudostem are usually discarded as waste products of the food and herbalism industries.

The use of plant's leaves is reported in literature for the removal of various heavy metals from wastewater e.g., adsorption of thallium(I) ions using eucalyptus leaves powder [10], the adsorption of lead by maize leaf [36], Cu(II) by teak leaves powder [37], Pb by Lalang (Imperata cylindrica) leaf powder [39], Zn(II) by leaves of saltbush (Atriplex canescens) [42-43], by cypress and cinchona leaves [49], Cr(VI) by black tea leaves [50] and biosorption of Cu(II), Pb(II), and and Cu(II) ions in aqueous solutions using Mangifera indica (Mango) leaf powder [51].

Hence, the thinking of trying green clover leaves fine powder as a low cost adsorbent for the treatment of a real local problem viz., the flourishing 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.

Different factors that affect the adsorption process have been extensively studied to improve the uptake % of iron from the aqueous solutions.

Optimum pH

The pH of the aqueous solution plays the most important role in the adsorption process. It not only influences the speciation of metal ions but also the charges on the sorption sites. 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 rather than metal ions [52,53]. The removal efficiency of the sorbent is increased by increasing the pH value until reaches its maximum uptake at the range 4-7 by the unmodified green clover. The sodium citrate and lactic acid modified green clover powders showed maximum uptake at pH range 5-6 (Figure 1). Heavy metal biosorption onto specific and non specific biosorbents is pH dependent; other researchers [54] found that an increase in adsorption is a result of increasing the pH of the solution (Figure 1).

Stirring Time

The amount of removed metal ions by adsorption depends on the time after which equilibrium is reached, this is expressed as the equilibrium time. The results indicate that removal was slow.
in the first 35 min then the uptake % was gradually increased till equilibrium at 50 min for the unmodified powder. While the powder modified with tri sodium citrate shows equilibrium after 40 min and the lactic acid form reached equilibrium after 50 min. The rate of biosorption seems to occur in two steps, the first one is very rapid surface biosorption, while the second is slow intracellular diffusion (Figure 2).

Figure 2: Effect of stirring time on the adsorption of iron on the crude and modified green clover leaves powders.

Sorbent Dose

The biosorbent dose is considered the most important parameter affecting the removal efficiency. For the unmodified powder, a dose of 0.35 g sorbent has achieved an uptake of 91% of iron at optimum pH conditions. While for the tri sodium citrate modified form, a dose of 0.25 g achieved an uptake % of iron of 97.5%. Correspondingly, 0.25 g of the lactic acid modified one achieved iron removal of 93.5% (Figure 3).

Figure 3: Effect of sorbent dose on the adsorption of Fe (II) on the crude and modified green clover leaves powders.

Initial Metal ion Concentration

At lower concentrations the adsorption sites utilized the available metal ion more rapidly when compared to higher concentrations where the metal ions need to diffuse to the sorbent surface by intra particle diffusion. The maximum metal uptake was 92 % in the case of the unmodified green clover, 94% for lactic acid modified powder and 97% in the case of tri sodium citrate modified form at metal ion concentration of 10 ppm (Figure 4).

Figure 4: Effect of metal ion concentration on the adsorption of iron on the crude and modified green leaves powders.

Sample volume

At optimum conditions the volume of 25 mL achieved the best adsorption percentage with all tested green clover leaves powders. It is clear from the figure that iron removal decreases with the increase of volume (Figure 5).

Figure 5: Effect of sample volume on the adsorption of iron on the crude and modified green clover leave powders.

The morphologies of the prepared adsorbents and composites

Structures and morphologies of the crude green clover powder, its loaded composites with lactic acid and trisodium citrate ones are studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Figure 6). Anchor scan parameters, graphics and the peak list for every xrd scan. These scans assure the successful loading (modifying) of the crude green clover leaves powder with the two modifiers viz., lactic acid and trisodium citrate. Modification succeeded in increasing the removal percentage, but hasn’t had any improvement effect on selectivity.

Figure 6: Structures and morphologies of the crude green clover powder.

XRD scans assures the successful loading of the crude powder with the two modifiers used.

Selectivity of the adsorbent

Adsorption studies applying the three adsorbents, under study, proved that they are nonselective towards heavy metals that may be present in wastewaters as pollutants. The spiking of the iron authentic samples with different concentrations of other metal ions e.g., Fe(III), Mn(II), Ni(II) and Cu (II) resulted in additive concentrations of the collection of metal ions present in a solution without any discrimination among them.

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.
Desorption studies

The adsorbed iron ions on the adsorbent surface 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 was measured using the recommended spectrophotometric method and the percentage desorption ($R_d$) was calculated according to the relation:

$$R_d = \frac{C_t - C_f}{C_t} \times 100$$

where $C_t$ is the experimental concentration in the solution at time t (ppm), $C_f$ is the adsorbed concentration of sorbate onto the adsorbent.

i. Effect of pH on desorption of iron: In strong acidic media at pH range (1.4-2.2) the three forms of the green clover leaves powder showed high desorption percentages, on increasing the pH values desorption percentage decreases (Figure 7).

![Figure 7: Effect of pH on desorption of iron on the crude and modified green clover leaves powders.](image1)

ii. Stirring Time: The desorption percentages % were gradually increased till equilibrium at 35 min for the unmodified and lactic acid modified powders, while the powder modified with trisodium citrate shows equilibrium after 40 min. A value of 89% has been recorded for the unmodified green powder, 93% for the trisodium citrate modified form and 91% for lactic acid one (Figure 8).

![Figure 8: Effect of Stirring Time on desorption of iron on the crude and modified green clover leaves powders.](image2)

Table 1: Summary of the optimum conditions for the adsorption of Iron on the green clover leaves powders.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unmodified Green Clover Leaves powder</th>
<th>Tri sodium citrate modified green clover powder</th>
<th>Lactic acid modified green clover powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.7</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Optimum shaking time</td>
<td>50 min</td>
<td>40 min</td>
<td>50 min</td>
</tr>
</tbody>
</table>

iii. Real samples: Water samples collected from tap water, Bahr Youssef water, ground water and Ibrahimia water, samples were subjected to the adsorption procedure as illustrated previously and the residual iron is analyzed by two methods of finish viz., colorimetry and AAS (Table 2).

Table 2: Determination of iron in real water samples.

<table>
<thead>
<tr>
<th>Sample volume</th>
<th>Colorimetry</th>
<th>AAS</th>
<th>Water samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mL</td>
<td>0.615 ppm</td>
<td>0.448 ppm</td>
<td>Bahr yousef water</td>
</tr>
<tr>
<td>25 mL</td>
<td>1.426 ppm</td>
<td>1.124 ppm</td>
<td>Ground water</td>
</tr>
<tr>
<td>25 mL</td>
<td>0.978 ppm</td>
<td>0.777 ppm</td>
<td>Ibrahimia water</td>
</tr>
<tr>
<td>25 mL</td>
<td>0.355 ppm</td>
<td>0.291 ppm</td>
<td>Drinking water</td>
</tr>
</tbody>
</table>

Conclusion

Green clover leaves powders proved to be potential biosorbents for the removal of iron from aqueous solutions being available low cost material. Results of desorption study also confirmed that there is a possibility to regenerate and reuse the biosorbent again.

Acknowledgement

The authors are thankful to the Publishers of the International Journal of Environmental Sciences & Natural Resources (IJESNR) for the publication gift provided.

References


