A New Comparison between Ag-Nano Adsorbent and Walnut Shell Adsorbent

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Abstract

Silver nanoparticles were synthesised and used as a nano-adsorbent. Silver nanoparticles were added to adsorption system contain (walnut husks – Manganese ions). The concept of this addition is to enhance the adsorption system due to high surface area to volume ratio of silver nanoparticles. Characterization of walnut husks was done by Fourier transformation infrared (FTIR). Characterization of silver nanoparticles was done also using many techniques, dynamic light scattering (DLS) and field emission scanning electron microscopy (FE-SEM) were used for determination of size and the potential of silver nanoparticles and also to identify the size and the shape of silver nanoparticles. The image showed an average particle diameter in the range (10-85 nm). Energy dispersive X-ray spectra (EDS) was used to examine the quantity of prepared silver nanoparticles. The optimum parameters were studied for this adsorption system such as contact time, weight of adsorpant, effect of pH, manganese concentration and the effect of addition of silver nanoparticles on the (walnut husks– Mn (II) ions) adsorption system. All the experiment parameters were fixed then silver nanoparticles were added to the system contain (walnut husks - Mn (II) ions). The results showed enhancement in the percentage of releasing by 2.2%. The data of the experiment has been investigated through Langmuir, Ferndelsch and Temkin. By evaluating the results, it can be concluded that the adsorption isotherm is most distinct through Freundlich.

Keywords: Silver Nanoparticles, (walnut husks–Mn (II)) Adsorption System, Nano Adsorbents, Isotherms

Introduction

Nanotechnology is the partition of science which deals with nano scale. It provides various important facts to the varied fields of science like medicine and bio-engineering [1]. Nanomaterials have different properties compared to non-nanomaterials materials of the same components due to their size difference and high surface area and the quantum effects [2, 3]. Recently, many methods are performed for the synthesis of metal nanoparticles using the plant extract [4, 5]. These methods have developed impressively due to its properties including; cost effective, easiness and eco-friendly [6]. Specific physicochemical properties are related to nanomaterials, these properties cause them to be chiefly attractive for many application [7-12]. Wastewater purification

Metal nanoparticles were used in eliminating pollution from the environment [13], one of these pollutants are heavy metals [14]. Though, these nanoparticles be able to agglomerate which may minimize its usage. Nanomaterials such nanocomposite can be used as an alternative instead of nanoparticles with great sanitizing capability [15-20]. Via the agricultural wastes metal adsorption and biosorption wastes is considered a complicated process affected by multiple factors [21]. Mechanisms include ion exchange, chemisorption, adsorption-complexation on surface and pores, heavy metal hydroxide strengthening onto the biosurface, and microprecipitation [22].

Manganese is a heavy metal in drinking water, which can cause many problems. Manganese is a very toxic element which is obviously occurring in the environment, also presented as a contaminants from industrial pollution and industrial discarded [23]. Removal of Manganese is done through biological, chemical, and physical processes or by a combination of these procedures[24]. Regardless of the presence and study of physical and chemical removal processes for periods, knowledge gaps are still found. Manganese levels lower than 0.02 mg/L are normally detected in water [25]. Most recent publications from the Water Research Foundation...
and the American Water Works Association provide beneficial guidance [26].

Various mechanisms of methods include (oxidative-reductive) degradation, coagulation, separation of membrane and adsorption have been established for the cleansing of water and waste water. Concerning them adsorption is the most important methods for water refining [26]. Scientists refer to one of the best options for removal of Manganese using multiwall carbon nanotubes which adsorb Manganese by adsorption system, multiwall carbon nanotubes are used because they have greater metal-ion absorption capacity (3–4 times) more than the rough and powder of activated carbon. The obtainable conventional adsorbent are much less competent in comparison with nano-adsorbsents this is because nano-adsorbent have short intraparticle diffusion distance, high surface area and tunable pore size which result in higher success for adsorption. The high surface area and aspect ratio of the nanomaterial makes them one of the new nano adsorbent with superior action [26]. Because of their precise surface characteristics and unique structure. These materials have the ability to remove noxious metal ions even at trace concentration [12]. As well as with a very high adsorption capacity and selectivity[27]. In this study the concept of using silver nanoparticles is to enhance the adsorption of walnut husks. Because of to an excessive surface area to volume ratio of silver nanoparticles. In this study efficient low-cost sorbents based on walnut shells were used as an adsorbent material [28]. Walnut husks [29] was used in this study because their availability and their cheap [28].

In this study, the aim is to use nanoscale silver prepared by adsorption of polluting elements in the water by introducing the nanomaterial into an adsorption system based on the use of materials that are from plant residues such as walnut shells, which are pollutants of the environment, and the use of nut shells to clean the environment from other pollutants such as manganese and others. Adsorption has been studied using many adsorbents, but the use of nanomaterials for this purpose is very little, as well as adding nanomaterials to other adsorption systems and comparative adsorption efficiency is our new study in this field.

Experimental

2.1 Instruments

All chemicals and solvents were purchased from Sigma-Aldrich. The UV-Vis spectrophotometer was accomplished by using UV-160v, Shimadzu spectrophotometer at the regions (400-700 nm). Field emission -Scanning electron microscopy (FE-SEM) images were taken by a Zeiss instrument with an accelerating voltage of 200kv (Iraq/Basrah). Zeta sizer and zeta potential from Malvern. Atomic absorption spectroscopy was used for determination of Mn before and after the adsorption.

2.2 Preparation of Adsorbents

Walnut husks were collected from local restaurants. The powdered materials were sieved to obtain particles of size 150 micrometre. The sieved materials were tested for their adsorbent qualities without further chemical or physical treatment. Different conditions were tested such as the effect of contact time, the effect of adsorbent weight, the effect of PH, the effect of Mn (II) ions concentration and the effect of addition of silver nanoparticles. The experiments of adsorption of single component system of Mn (II) ions have been carried out at 70°C and the speed of shaker 185 rpm to establish the optimal working parameters: pH, the concentration, contact time, adsorbent dose and particles diameter. Experiments were appropriate at the power of hydrogen value ranging from 2 to 10; the initial concentration of heavy metal Mn (II) ions in the range (5 – 100) µg/ml, the contact time was studied at (10–120) minutes, adsorbent dose (0.4–2) gram and particles diameter at (150 µm). After equilibrium, the established samples (25 ml) were reserved from the flask. These samples were filtered by filter paper types (Whatman 40 mm) and the concentration of Mn was determined by flame atomic absorption spectroscopy (FAAS). Moreover, the removal efficiency (% of Adsorption) was also measured.

In a series of conical flasks with size of (100 ml) walnut husks with particle size of (150 µm) were added to (0.5gm) of (100 ug/ml) from Mn (II) ions solution. The experiments were carried out at room temperature and shaking was done for the desired time at (250) rpm. The mixture was then centrifuged and the concentration of Mn (II) ions in the solution was determined using (FAAS). The removal efficiency and the equilibrium up take of Mn (II) ions were calculated according to following equations:

\[
\text{% Removal} = \frac{(C_o - C_e)}{C_o} \times 100
\]

\[
Q_e = \frac{V_{sol}(C_o - C_e)}{m}
\]

Where \(C_o\) is concentration of Mn (II) ions before the adsorption (mg/L) \(b\), \(C_e\) is the equilibrium concentration (mg/L), adsorbent weight is mass in (gm) and \(V\) is the volume of the solution in liter, \(Q_e\)
is the equilibrium adsorption capacity measured in (mg/g).

2.3 Formation of Silver Nanoparticles

The mixture of glucose sugar, silver nitrate solution and the capping agent of trisodium citrate were prepared at a concentration of (1000µg/ml). Preparation was done by using 0.1 g in 100 ml of each material in deionized water. After, the mixture was placed in a beaker and placed on a hot plate stirrer at 80°C. Observations showed visual change in colour from colorless to light brown after 5 minutes. This can be considered as an indication for the creation of silver nanoparticles. [30, 31].

3. Results and Discussion
3.1 Characterization of Walnut Husks

In order to elucidate the particle properties depend on the activated groups, walnut husks were examined by the Fourier transform infrared analysis using FTIR type shiatsu using KBr pellet method. The spectra Fig. 1 were retrieved in the wave number ranging from 400 to 4000cm⁻¹. Walnut husks is contain functional groups such tannin groups, carbonyl and hydroxyl which can bind heavy metals. [32- 34]. Table 1, contain these functional groups.

![Fig. (1) IR spectra of walnut husks](image)

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Structural and Functional groups</th>
<th>Wavelength(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon oxygen group</td>
<td>C-O</td>
<td>1051.20-1300</td>
</tr>
<tr>
<td>Hydroxyl group</td>
<td>O-H</td>
<td>3421.72-3650</td>
</tr>
<tr>
<td>Carbonyl groups (ester of tannin)</td>
<td>O=C-O</td>
<td>1750-1730</td>
</tr>
<tr>
<td>Carbonyl groups(ketone )</td>
<td>C=O</td>
<td>1700-1725</td>
</tr>
<tr>
<td>Alkene group</td>
<td>C=H</td>
<td>1680-1600</td>
</tr>
<tr>
<td>Aromatic group</td>
<td>C=C</td>
<td>1600-1475</td>
</tr>
<tr>
<td>Carbon hydrogen group</td>
<td>C-H</td>
<td>2933-3150</td>
</tr>
<tr>
<td>Halogen carbon group(iodin)</td>
<td>C-X</td>
<td>702.09-500</td>
</tr>
</tbody>
</table>

3.2 Characterization of silver nanoparticles
3.2.1 Field Emission Scanning Electron Microscope (FE-SEM)

The surface morphology was imaged by Field Emission Scanning Electron Microscope (FE-SEM) [34, 35]. The shape and size of silver nanoparticles were investigated under scanning electron microscope as shown in Fig. 2. The size of the particle was between (10) nm to (85) nm. From the Fig. 2 silver nanoparticles can be recognized as spherical in shape. The image demonstrates a clear separation between the different particles. Examination of the percentage of elements within the sample was done by Energy dispersive x-ray. Fig. 2 and table 2 illustrate that the percentage of silver is 57.23% which demonstrates the greatest percentage of all elements in the prepared sample. Furthermore, the percentage of other elements were registered as displayed in table2.

Dynamic light scattering (dls) is a system can be used to define the size distribution of small particles in suspension. Zeta sizer and zeta potential were used to scan the size and the potential of solution respectively. Fig.3 shows the distribution of silver ion. It is clear that the size of Ag nanoparticles was almost in the nano range. From Fig.4 the zeta
potential distribution of silver nanoparticles was a negative value (-9.7) Millivolts confirming the presence of stable silver nanoparticles.

Fig. (2) FE-SEM images of created Ag nanoparticles, show the average diameter ranged from (10-85 nm) and the spherical shape of Ag nanoparticles.

Table (2) EDS-FESEM analysis demonstration the percentage of silver nanoparticles equal (57.23) %

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass [%]</th>
<th>Atom. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>18.89</td>
<td>55.03</td>
</tr>
<tr>
<td>Silicon</td>
<td>12.10</td>
<td>20.07</td>
</tr>
<tr>
<td>Iron</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Bromine</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Silver</td>
<td>57.23</td>
<td>24.73</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Sum</td>
<td>88.55</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. (3) Displays zeta size distribution of Ag nanoparticles by number and volume.
A NEW COMPARISON BETWEEN AG-NANO ADSORBENT

Fig. (4) Zeta potential distribution of Ag nanoparticles in a negative value (-9.7) Millivolts

Zeta potential is a measure of the effective electric charge on the nanoparticle surface. The magnitude of the zeta potential delivers information about particle stability, with particles with higher magnitude zeta potentials showing increased stability due to a larger electrostatic attraction between particles. Instruments in the Zetasizer family are used to measure the particle size of distributed systems from sub-nanometer to several micrometers in diameter, using the performance of dynamic light scattering (dls). Zeta sizer and zeta potential were measured in order to scan the size of nanoparticles in the resulted solution. The distribution of silver ion (Fig. 3). It was noted that the particle size of nanoparticles was less than 10 nm. Zeta sizer provides a good agreement with SEM results and the best results with regard to a small size of the nanoparticles can be achieved by Zeta sizer due to the measurement of colloidal is basic in the particles with free distribution and migration. Moreover, zeta potential distribution of silver nanoparticles was a negative value (-27 mV) because the presence of silver ions (Fig.4). Zeta potential can be calculated by tracking the colloidal particles through a microscope as they transfer in a voltage field. Hence the positive ions collect on the voltage as a negative value.

3.3 Study the optimum condition of the equilibrium

3.3.1 Effect of Contact Time

The elimination of Mn(II) ions by adsorption on walnut husks powder was calculated as a function of contact time at different time periods (0-120 min) at (25°C). The percentage removal plotted against time. (Fig. 5) clarifies the adsorption rate of Mn(II) ions onto walnut husks powder which is quick at the start and reaches plateau after (40 min). However, 60 min was fixed for removal in order to cover all the adsorption process. The removal percentage of Mn(II) ions on the walnut husks powder was found to be (89.712)%.

Fig. (5) The percentage removal plotted against time.

3.3.2 Effect of Adsorbent Weight

The influence of different weight of walnut husks powder on Mn(II) ions percentage removal at contact time (60 min) was inspected by using powder weights ranging from (0.4-2g) in (100) mg/l Mn(II) ions solution. Fig. 6 shows an elevation in the percentage of removal of Mn(II) ions with increasing of walnut husks weight, this is due to an increased surface area which implies greater number of adsorbent sites achieved by increase the weight of powder. 2g from the walnut husks powder gives release percentage 91.4%.

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3.3.3 Effect of pH

Potential of hydrogen (pH) of the solution of Mn (II) ions shows an important role in the adsorption capacity where it affects both the degree ionization of the Mn (II) ions as well as the surface properties of the adsorbent. The effect of pH on adsorption of the solution was studied within pH range (2-10). At pH=10 the release percentage 91.4%. Fig 7 shows this result.

The removal percentage of heavy metal from solution increases with increasing pH due to electrostatic interactions, precipitation and formation of mineral complexes due to ionic or covalent bonding. Moreover, the competition of manganese metal ions for the active sites in the surface of Ag-nanoparticles is greatly affected by the charge that the manganese has in the solution from which it is. The fact that in the acidic environment, the ions (H+) will compete with the Mn (II) ions for the negative sites, and with the increase of pH, the largest ions will be (OH-) therefore, the competition for manganese ions decreases in favour of adsorption in the neutral and basic medium.

3.3.4 Effect of Mn(II) Ions Concentration

The influence of initial concentration of Mn(II) ions was studied by varying initial concentration from (10-100 µg/ml) at 25ºC. The result show that the percentage adsorption of Mn (II) ions was decrease with increases in initial concentration. The obtainable of free adsorption sites reduced by increasing the initial concentration of the metal as a result the removal percentage decreasing as presented in Fig.8
3.3.5 Study the Effect of Nanomaterials Addition

The synthesized nanoparticles were applied to study their ability to improve the (walnut husks – Mn (II) ions) adsorption system as illustrated in fig. 9. Typically, the nanoparticles which are used in studies function as self-adsorbing particles. From our knowledge this is the first time that silver nanoparticles were added for enhancement of the adsorption system, from Fig. 9 our study illustrates that the adsorption percentage becomes (91.974%) compared with the original percentage without addition of silver nanoparticles (89.712 %); it is evident that there is an increase by 2.2% when nanoparticles were added as shown in fig.9. The addition of nano silver plays two major roles firstly, nano silver can adsorb Mn(II) ions spontaneously, secondly it also assist the main adsorption system (walnut husks) indirectly by increasing its surface area.

It’s believed that the mechanism of the adsorption is through two mechanism of adsorption could be attributed to a two-step mechanism. The first one relating with electrostatic interactions and the second due to H-bonding between the adsorbent and adsorbate [36].

Fig. (9) Graph shows the processes for the removal of Mn (II) ions using two adsorbents.

Fig. (10) The removal percentage of Mn(II) ions in (walnut husks - Mn(II) ions) adsorption system without silver nanoparticles and after addition of silver nanoparticles.

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3.3.6 Study of Adsorption Isotherms

The adsorption of Mn(II) ions were studied using the surface of walnut husk powder according to Langmuir, Ferndelsch and Temkin equation. The graphs of the isotherm were draw and the equations were described, the constants as shown in table (3) were obtained. It has been observed that the adsorption isotherm of this experiment matches Freundlich equation for adsorption, because the value of $R^2$ is the largest among the values of the Langmuir and Temkin isotherm and was able to be equal to (0.9131). Thus, Freundlich isotherm is more identical to the explanation of this type of adsorption as illustrated in Fig.11.

Where $Qe$ and $Qmax$ are the balance and most extreme sorption limits (mg/g biosorbent) ,$Ce$ is harmony focus (mg/l arrangement), $b$ is the balance steady, $Kf$ and $n$ are Freundlich constants normal for the framework.

Table (3) Study of isotherm

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Constant 1</th>
<th>Constant 2</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$\frac{Qe}{Ce} = \frac{1}{Kl} + a \frac{Kl}{Ce}$</td>
<td>$Kl$</td>
<td>A</td>
<td>0.0345</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\log qe = \log Kf + \frac{1}{n} \log Ce$</td>
<td>$Kf$</td>
<td>N</td>
<td>0.9131</td>
</tr>
<tr>
<td>Temkin</td>
<td>$Qe = BlnKt + BioCe$ Where: $B$ = $RT/b$</td>
<td>$Kt$</td>
<td>B</td>
<td>0.8253</td>
</tr>
</tbody>
</table>

Conclusions

Walnut husks permit achieving the removal of pollutants from wastewater and at same time to contribute to the waste minimization, recovery and reuse. Moreover, walnut husks is suitable adsorbent because of its availability and low cost. The present study emphasize that the Walnut husks was active an adsorbent for the removal of Mn (II) ions from aqueous solution. The maximum percentage removal of (89.712 %) occurred at optimum condition. It can be concluded that Walnut husks prepared is a promising low cost and high efficiency adsorbent for Mn(II) ions removal from waste water and can be applied in a water treatment technology.

The concept of this study is improve of the adsorption percentage by adding silver nanoparticles which is also nano-adsorbent. Silver nanoparticles were synthesized and the average particle size of silver nanoparticles in the range (10-85 nm). The addition of silver nanoparticles to the (Walnut husks - Mn (II) ions) adsorption system was enhance the percentage of releasing to (91.974%). Silver nanoparticles have high surface area to volume ratio therefore they have the capability to adsorb materials as well as having the capability to increase the surface area to another adsorption system. The measurements of the experiment have been investigated through Temkin, Langmuir and Freundlich. Equilibrium data followed Freundlich isotherm modal.

Fig. (11) Isotherms of adsorption

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مقارة جديدة بين نانو الفضة الماز وممتر قشرة الجوذ

المنغنيز يتم استخدامه في تشكيك نظام امتزاز جديد. في هذه الدراسة تم إضافة حجم جسيمات الفضة النانوية للنظام (نظام امتزاز - أيون المنغنيز الثنائي) ليكون نظام امتزاز جديد يتم على مادتين مازتين لإزالة أيونات المنغنيز الثنائي مثل متغير هذه الإضافة في تعزز نظام امتزاز نظرًا لكبر مساحة السطح إلى نسبة الحجم لجسيمات الفضة النانوية المضافة. تم تشخيص قشرة الجوذ عن طريق تحويل فورييه للأنماط تحت الحمراء (DLS) (FTIR) ثم أيضًا يتم تحليل الجسيمات النانوية للنظام (نظام امتزاز) باستخدام العديد من التقنات، حيث تم استخدام تشتت الضوء البصريي (المسح الإلكتروني لمسح الأنبوب الجهاز الفوتوغرافي (EDS) فور مطهرة البيئة (عنف الطاقة) لقياس كمية جسيمات الفضة النانوية المحضر. تم دراسة الأداء المظلي لنظام الامتزاز مثل زمن التلامس وزن مادته المذنب وتأثير الرماد الهيدروجيني ومزج المنغنيز، وهو تأثير إضافة جزيئات الفضة النانوية على نظام الامتزاز (نظام امتزاز - أيون المنغنيز الثنائي). في الظروف المثلى، أدت إضافة جسيمات الفضة النانوية إلى زيادة نسبة الامتزاز إلى 2.2%. تم التحقق من بيانات التجربة من خلال تقدير النتائج، يمكن استنتاج أن الامتزاز هو الأكثر تميزًا من خلال فرين تش.