Removal of Fe(II) and Cu(II) from Aqueous Solutions using Activated Carbon Derived from Wooden Parts of Mangifera Indica by Chemical Activation with ZnCl₂

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Abstract— The purpose of this study was to investigate the use of activated carbon derived from wooden Parts of Mangifera Indica by chemical activation with ZnCl₂, named (MI-ZnCl₂), in the removal of Fe(II) and Cu(II) ions from aqueous solutions. Batch experiments were conducted to determine the effect of varying adsorption parameters on their removal. The adsorption of Fe(II) ions was found to be maximum (82%±2.21), at pH 6 using adsorbent mass of 1.00 g. While the optimum adsorption of Cu(II) ions was found to be (61%±1.74), at pH 5 using adsorbent mass of 1.80 g. The Langmuir level of conformity for Cu(II) is high compared to Fe(II) ions, according to the correlation coefficients (R²) of 0.9942 and 0.9753, respectively. The adsorption capacity, Q₀, (mg g⁻¹) of Cu(II) is higher than that of Fe(II) ions, they were found to be 7.08 and 3.59 respectively. The affinity of the two metals for the adsorbent surface in terms of b is higher for Cu(II). The values of b (L/mg) were high, which implies high surface energy in the process and consequently high bonding between metal ions and the (MI-ZnCl₂). Freundlich level of conformity for Fe(II) is to a high extent compared to the Langmuir adsorption isotherms as indicated by higher correlation coefficient value of 0.9929. On the other hand, the level of conformity for Cu(II) is low compared to the Langmuir adsorption isotherms as indicated by the lower correlation coefficient value of 0.9729. The values of n (2.56 and 2.43) for Fe(II) and Cu(II) ions respectively, confirm that the (MI-ZnCl₂) have a heterogeneous surface since the values satisfy the heterogeneity condition where n, must be in the range 1 < n < 10. (MI-ZnCl₂) can be used as a cost effective adsorbent for the removal of Fe(II) and Cu(II) ions from aqueous solutions in the treatment of industrial effluent.

Keywords— Mangifera Indica (MI- ZnCl₂), Activated carbons; Adsorption; Heavy metals; Langmuir and Freundlich isotherms.

I. INTRODUCTION

Increased industrialization use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence pose environmental-disposal problems. The industries mainly responsible for the discharge of waste water containing metals are mining and mineral processing, pigment manufacture, painting and photographic industry, metal working and finishing processes [1]. Fe(II) is needed in plant metabolism, but when it presents in excess, it can become extremely toxic. The presence of high concentrations of iron and copper in water causes economic and technological problems. Since several decades along with the growth of industrial activities, contamination of the environment with wastewaters including heavy metals has become a major problem [2]. Iron ion as an important corrosive product is one of the substances that is commonly found in fluids of many industries. Conventional techniques aimed at removing heavy metals usually include chemical precipitation, ion exchange, membrane process, crystallization, and electro-chemical treatment [3]. Although many investigations have been conducted so far about the ability of some materials to remove Fe(III) [4], different heavy metals and dyes[5-12]. Only a few investigators have studied Fe(II) adsorption using pods of acacia nilotica var astringens (Sunt tree) [11], crab shell [13], bark of a tree [14], waste coir fiber [15], wooden charcoal [16], and pine bark [17].

Adsorption of heavy metals on activated carbons (ACs) and modified ACs proved to be the most efficient technique in this application. It is recommended to use low cost precursors that are available in large amount, renewable and contain high carbon content and low inorganic content. These requirements are found in many agricultural wastes [11, 14, 16]. The aim of this research was to investigate the use of (MI-ZnCl₂) to remove Fe(II) and Cu (II) ions from aqueous solutions has been assessed in a batch process. The study involved the examination of experimental conditions such as pH of the solution, contact time and adsorbent loading on the removal of Fe (II) and Cu (II) from aqueous solutions. The Freundlich and Langmuir adsorption isotherms were used to investigate the adsorption process.

II. MATERIALS AND METHODS

2.1 Materials:

2.1.1 Preparation of the adsorbate solutions:

All chemicals used, were of analytical grade (Merck, Germany). Two stock solutions of the metal ions, each containing 1000 mg/L of (NH₄)₂Fe(SO₄)₆·6H₂O and Cu(NO₃)₂·6H₂O, were prepared by dissolving the calculated amounts in double distilled water.
The experimental solutions were prepared by diluting the metal ion stock solution in accurate proportions to different initial concentrations from 10-100 mg/L, and each of them was stored in 100-ml reagent bottles, respectively. The supernatant was carefully decanted into cleaned polyethylene containers and analyzed using a Flame Atomic Absorption Spectrometer (FAAS) Pin AAcle 500 Spectrometer, unit size 1/EA.

2.1.2 Preparation of the Modified Adsorbent (MI-ZnCl₂):

The adsorbent used in this study was powdered, activated carbon obtained from wooden parts of Mangifera Indica (Mango tree), collected from Elzaidab Agricultural Project in the River Nile State, (Northern Sudan) and authenticated by the department of Botany, University of Khartoum; the carbonization was done at high temperature (525°C). (MI-ZnCl₂) activated carbon, was obtained with 10% ZnCl₂ solution and residence time of 48hrs, and pretreated according to the method reported in the literature [12, 18, 19].

The sample was screened and washed with de-ionized water to remove dirt impurities, then dried in the oven at 110°C for 3 hours. The modification was done by chemical treatment of 50 g of the sample with ZnCl₂ as described above. The modified sample was washed again with de-ionized water until the pH being in the range of (6.9 - 7.2), the pH was determined using a pH meter (model ATRP-6), then dried in the oven at about 95°C to remove moisture. The dried sample was ground and sieved in the mesh to collect the fraction of (90-125 μm) which preserved in a desiccators for use.

2.2 Methods:

2.2.1 Batch Equilibrium Experiments:

The adsorption experiments were conducted in an experimental apparatus in an appropriate condition. A rotary shaker at 150 rpm using 250 ml shaking flasks containing 100 ml of the metal ions solutions at different concentrations, and initial pH values. The corresponding amounts of the adsorbent were added to each flask, and then the flasks were sealed to insure no volume change during the experiments. The samples were shaken for predetermined time intervals, and then withdrawn, and the metal ions solutions separated from the adsorbent by centrifugation and filtration respectively. The pH values for the separated metal ions solutions were again measured.

The data obtained in the batch modes were used to calculate the equilibrium metal ions adsorptive amounts (mg/g) were calculated using the following expressions [11,13]:

\[ q_e = \left(\frac{V}{w}\right) \left(C_o - C_e\right) \]  
\[ \%\text{ removal} = 100 \left(\frac{C_o - C_e}{C_o}\right) \]

Where \( q_e \) is the amount of the heavy metal ion adsorbed by the (MI-ZnCl₂) sample in (mg/g), \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of the metal ion respectively in (mg/L), \( V \) is the volume of the solution treated (L) and \( w \) is the adsorbent mass of (MI-ZnCl₂) in (g). All experiments were duplicated and the mean values are reported. The maximum deviation was observed to be 2.3 and 1.9% for Fe(II) and Cu(II) ions respectively.

Effect of each parameter, (pH, initial metal concentration, adsorbent mass and contact time) were studied in experiments by varying the parameter under consideration, while all the other parameters were maintained as constant. The negative control (with no adsorbent) was used to ensure that the adsorption is only due to (MI-ZnCl₂) sample and not to the reaction vessels. The data were fitted into Langmuir and Freundlich isotherms models [11, 13]. All batch experiments were carried out at constant temperature (30±0.2 °C).

FTIR analysis was done using IPReSteige-21, FTIR-8400S, SHIMADZU Corporation (Kyoto, Japan). 0.1 g sample of (MI-ZnCl₂) was mixed with 1 g of KBr, spectroscopy grade (Merck, Darmstadt, Germany), in a mortar. Part of mixture was transferred to the FTIR analyzer and the corresponding spectrogram was obtained showing wave lengths of the different functional groups in the sample which were identified by comparing these values with those in the library [21].

III. RESULTS AND DISCUSSION

3.1 Sample Characterizations:

The physico-chemical parameters of (MI-ZnCl₂) sample are shown in (Table 1). The FT-IR spectrum showed the absorption bands at these regions (2880-3460cm⁻¹), (1315-1770cm⁻¹), (1100-1260cm⁻¹), and (475-750cm⁻¹).

The sample showed a broad band with two maxima at 2890cm⁻¹ which is attributed to C-H interaction with the surface of the carbon and at 3435cm⁻¹is due to an O-H stretching mode. Furthermore, the indicated bands in the range of 3320-3670 cm⁻¹ have also been attributed to the hydrogen-bonded OH group of alcohols and phenols. However, the band at 1480 cm⁻¹ may be attributed to the aromatic carbon–carbon stretching vibration. The two peaks at 1110-1150 cm⁻¹ showed the fingerprint of this carbon. The sharp absorption band at 1120 cm⁻¹ is ascribed to either Si-O or C=O stretching in alcohol, ether or hydroxyl groups. [21, 22].
The band at 1150 cm\(^{-1}\) can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring) [21]. This band could also be attributed to the anti-symmetrical Si-O-Si stretching mode as a result of existing silica within the samples [22].

3.2 Equilibrium adsorption studies:

3.2.1 Effect of pH:

The effect of pH on metals ions adsorption were monitored over a pH range of 2 to 9. 100 ml of separate solutions, 35 mg/L Fe(II) and 15 mg/L Cu(II) ions, were transferred into 250 ml conical flasks agitated at 150 rpm for 100 min with 1.00 and 1.80g (MI-ZnCl\(_2\)) for Fe(II) and Cu(II) ions respectively. The mixtures were filtered and the filtrate analyzed for residual metal ions.

Fig. 1, represents the effect of pH on the adsorption of Fe(II) and Cu(II) ions. The equilibrium adsorption capacity of metals removal from aqueous solutions are influenced by the pH [11, 23]. On the other hand, the state of chemically active sites is changed by the solution pH [11, 12, 24]. The optimum adsorption of Fe(II) and Cu(II) ions were achieved at pH 6 and 5 respectively. At pH values higher than 7.2, both metals ions were precipitated. Therefore the removal of metal ions at higher pH values is due to the formation of precipitates rather than adsorption [25]. The adsorption capacity (q\(_e\)) increased with increases in pH up to pH 6 for Fe(II) ions and pH 5 for Cu(II) ions. The increase in metal adsorption with increase in pH is due to a decrease in competition between hydrogen ions and metal ions for the surface sites and also due to decrease in positive surface charge.

As the pH increases, more negatively charged surface becomes available thus facilitating greater metal adsorption. At low pH, higher concentration and mobility of H\(^+\) ions favour H\(^+\) adsorption compared to metal ions. Metal ions are more soluble in solution at lower pH values and this reduces their adsorption [26]. At lower pH, the surface of the adsorbent is surrounded by hydronium ions (H\(^+\)) thereby blocking metal ions from binding sites on adsorbents.

3.2.2 Effect of contact time:

The investigation was done to determine the optimum time for adsorption of both metals Fe(II) and Cu(II) ions using (MI-ZnCl\(_2\)). 1.0 and 1.80 g samples were contacted with 100 ml separate solutions of 35 mg/L Fe(II) and 15 mg/L Cu(II) ions adjusted to pH 6 and 5 respectively. The solutions were agitated at 150 rpm for different contact times (15-100 min). The mixtures were filtered and residual metal ions in filtrate were analyzed.

The influence of contact time on the adsorption of Fe(II) and Cu(II) ions is shown in Fig. 2. The amount adsorbed increases with increasing time up to (50 min for Fe(II) and 75min for Cu(II)). The constant adsorption at equilibration is due to the saturation of adsorption sites of (MI-ZnCl\(_2\)). Rapid adsorption of metal ions during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on (MI-ZnCl\(_2\) surface. The adsorption capacity for Fe(II) ions was higher than for Cu(II) ions.

3.2.3 Effect of adsorbent mass:

The effect of (MI-ZnCl\(_2\)) mass was investigated by equilibrating separate 100 ml solutions of 35 mg/L Fe(II) and 15 mg/L Cu(II) ions, adjusted to pH 6 and 5 respectively, with different masses of the adsorbent (0.25-2.50g) agitated at 150 rpm for 100 min. The mixtures were filtered and the residual metal ions in their filtrate were analyzed.

Fig. 3 represents the effect of adsorbent mass on the adsorption capacity of Fe(II) and Cu(II). An increase in adsorption capacity with increasing adsorbent mass up to a maximum of 1.00 g for Fe and 1.80 g for Cu giving the corresponding optimum percentage removal of 82\% \pm 2.21 and 61\%\pm1.74 respectively. The initial increase in adsorption capacity with increasing adsorbent mass is explained by the increase in the number of exchangeable sites for metal ion adsorption [26]. The decline in adsorption beyond certain adsorbent masses could be due to the aggregation/agglomeration of adsorbent particles at higher dosages which would lead to a decrease in the total surface area of the adsorbent particles available to the metal ions. As a result the adsorption capacity of the adsorbent is not fully utilized [27].

3.2.4 Effect of initial metal concentration:

Separate 100 ml solutions of Fe(II) and Cu(II) ions with different initial concentrations (10-100 mg/L) were contacted with optimized adsorbent mass (1.00 g for iron at pH 6 and 1.8 g for copper at pH 5). The mixtures were agitated at 150 rpm for 100 min. The mixtures were filtered and filtrate analyzed for residual metal ions.

The effect of initial concentrations of Fe(II) and Cu(II) ions are shown in Fig. 4. For both metal ions, an increase in initial concentration resulted in increase in the adsorption capacity. This can also be explained in terms of increase in adsorption sites coverage as the metal ion concentration is increased [13]. High metal concentration saturates the adsorbent sites more quickly thereby decreasing the overall percentage metal removal [11].
3.3 Adsorption Isotherms:

The Langmuir and Freundlich isotherms models were applied to the equilibrium studies to test the data conformity. The linear forms of the isotherms are represented by the equations (Eq. 3 and 4) respectively.

\[ \frac{Q}{q_e} = \left( \frac{1}{Q_s} \right) + \frac{1}{Q_s} b \]

\[ \ln(q_e) = \ln(K_f) + \frac{1}{n} \ln C_e \]

Where \( Q_o \) (mg g\(^{-1}\)) is the monolayer adsorption saturation capacity; \( b \) (L mg\(^{-1}\)) Langmuir constant relating to adsorption energy; \( q_e \) (mg g\(^{-1}\)) the amount of metal ion bound to per gram of the adsorbent at equilibrium; and \( C_e \), the residual (equilibrium) metal ion concentration left in the solution after binding. The \( Q_o \) and \( b \) can be determined from \( C_e/q_e \) versus the \( C_e \) plot which gives a straight line of slope \( (1/Q_o) \) and intercept of \((1/bQ_o)\). \( K_f \) and \( n \) are the Freundlich constants characteristic of the activated carbon system.

It was observed that, the Langmuir adsorption isotherm satisfactorily describes the adsorption of Cu(II) and Fe(II) ions from aqueous solutions using (MI-ZnCl\(_2\)), but the level of conformity for Cu(II) is high compared to Fe(II) ions, according to the correlation coefficients\( (R^2) \) of 0.9942 and 0.9753, respectively (Fig. 5). The applicability of the Langmuir isotherm indicates good monolayer coverage of Cu(II) more than Fe(II) ions on the surface of (MI-ZnCl\(_2\)) which consequently suggests the formation of a mono layer on the adsorbent surface in the given concentration range [28]. The fact that the Langmuir isotherm fits the experimental data very well for Cu(II) may be due to the homogenous distribution of active sites on the adsorbent since the Langmuir equation assumes that the surface is homogenous. Thus the applicability of the Langmuir isotherm in the present system indicates the monolayer coverage of Cu(II) to a high extend more than Fe(II) ions on the outer surfaces of the adsorbent [29]. The calculated model parameters with correlation coefficients are shown in Table 2. The adsorption capacity, \( Q_o \) (mg g\(^{-1}\)) of Cu(II) is higher than that of Fe(II) ions. The affinity of the two metals for the adsorbent surface in terms of b(L/mg) is higher for Cu(II),0.35 compared to that of 0.31 for Fe(II). The values implies high surface energy in the process and consequently high bonding between metal ions and the (MI-ZnCl\(_2\)).

The Freundlich isotherms for Fe(II) and Cu(II) ions adsorption are shown in Fig. 6. It was observed that the Freundlich adsorption isotherm also conforms to the adsorption of Fe(II) and Cu(II) ions from aqueous solutions using (MI-ZnCl\(_2\)). However, the level of conformity for Fe(II) is to a high extent compared to the Langmuir adsorption isotherms as indicated by higher correlation coefficient values of 0.9929. On the other hand, the level of conformity for Cu(II) is low compared to the Langmuir adsorption isotherms as indicated by the lower correlation coefficients values of 0.9729. The values of \( n \) (2.56 and 2.43) for Fe(II) and Cu(II) ions respectively, confirm that the (MI-ZnCl\(_2\)) have a heterogeneous surface since the values satisfy the heterogeneity condition where \( n \) must be in the range \( 1 < n < 10 \) [11,29]. The values of 1/\( n \) ranging from 0 to 1 are a measure of adsorption intensity or surface homogeneity as the values approach zero. Values for 1/\( n \) less than 1 indicate normal Langmuir adsorption isotherm while those values above 1 are indicative of cooperative adsorption [21, 30]. The values of \( K_f \) for Fe(II) ions (1.12) and Cu(II) ions (2.22) imply that there was low uptake of the metal ions onto the adsorbent surface.

IV. CONCLUSION

This study has demonstrated that (MI-ZnCl\(_2\)) has favourable properties for the adsorption of Fe(II) and Cu(II) ions from aqueous solutions and the adsorbent properties are modified by ZnCl\(_2\) treatment. The adsorption of Fe(II) and Cu(II) ions were highly dependent on experimental parameters such as contact time, initial metal concentration, pH and adsorbent mass. The adsorption of Fe(II) was found to be optimum at pH 6, adsorbent dose of 1.0 g, metal ion concentration of 35 mg/L and contact time of 50 min. The adsorption of Cu(II) was found to be optimum at pH 5, adsorbent mass of 1.8 g, metal ion concentration of 15 mg/L and contact time of 75 min.

REFERENCES


Table 1: Physico-chemical parameters of (MI-ZnCl₂) sample.

<table>
<thead>
<tr>
<th>Physical Aspect</th>
<th>Crystallinity (XRD)</th>
<th>Energy Dispersive X-ray Analyses</th>
<th>FTIR Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder activated carbon</td>
<td>Amorphous</td>
<td>C(82%);O(11%);Si(2%);Cl(3%);Zn(2%)</td>
<td>-C₆H₅-,CH₂-,CH₃-,CO-,CH₂-OH</td>
</tr>
</tbody>
</table>

Table (2): Langmuir and Freundlich Isotherm parameters for the removal of Fe(II) and Cu(II) by (MI-ZnCl₂) sample.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q₀ (mg/g)</td>
<td>b, (L/mg)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>3.59</td>
<td>0.31</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>7.08</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Figure 1. Effect of pH on Fe(II) and Cu(II) removal by MI-ZnCl₂; initial concentrations=35, 15 mg/L, time=50, 75 min., adsorbent masses=1.00, 1.80 g respectively.
Figure 2. Effect of contact time on Fe(II) and Cu(II) removal by MI-ZnCl₂: pH= 6.5; initial concentrations=35, 15 mg/L; adsorbent masses =1.00, 1.80 g respectively.

Figure 3. Effect of adsorbent mass on Fe(II) and Cu(II) removal by MI-ZnCl₂: pH= 6.5; initial concentrations=35, 15 mg/L; time=50, 75 min respectively.
Figure 4. Effect of Fe(II) and Cu(II) initial concentrations on their removal by MI-ZnCl₂: pH= 6, 5 ; time=50, 75 min.; adsorbent dose =1.00, 1.80 g respectively.

Figure 5. Langmuir adsorption isotherm for Fe(II) and Cu(II) by (MI-ZnCl₂)
Figure 6. Freundlich adsorption isotherm for Fe(II) and Cu(II) by (M1-ZnCl2)