Adsorption of Pb (II) and Cu (II) from Aqueous Solution onto Activated Carbon Prepared from Dates Stones

Jamal A. Abudaia, Mohamed O. Sulyman, Khalad Y. Elazaby, and Salah M. Ben-Ali

Abstract—Potentially toxic trace elements such as Lead Pb(II) and Copper Cu (II), with high levels in water are very serious problem in many places around the world, sometimes in relation to natural sources and in other cases to anthropogenic ones. Adsorption process is among the most effective techniques for removing of many heavy metal (HM) ions from different types of water. In this study, an attempt has been made to investigate the efficiency of granular activated carbon (GAC) and powder activated carbon (PAC) obtained from easy available agricultural by-products dates stones (DS) in removing of Pb (II), Cu (II) from their aqueous solutions using batch mode technique. During the removal process, the effects of solution pH, HM concentrations and contact time, and adsorbent concentration, on adsorption efficiency by both GAC & PAC were studied. Under the experimental conditions, the removal efficiency of such metals by PAC was 83%, 91% showing preference over GAC which had a removal efficiency of 76%, 82% respectively.

Index Terms—Activated carbon, date stones, heavy metals, batch mode technique, adsorption.

I. INTRODUCTION

Global developments directed towards making human life increasing comfortable have greatly increased industrialization and urbanization. However, this trend has damaged the environment alarmingly, mainly due to the generation of a large amount of hazardous waste and the pollution of both usable surface water and soil. The high levels of potentially toxic trace elements in water is a very serious problem in many places around the world, sometimes in relation to natural sources and in other cases in relation to anthropogenic ones [1].

Lead and Copper ions were therefore selected in this study as modeled pollutants and the affect of some physical parameters such as pH, initial concentration and contact time, and the adsorbent dosage were investigated to examine the efficiency of date stones activated carbon (DSAC) as adsorbent materials in removing of these HMs from their aqueous solutions.

In order to avoid contaminations with hazardous metals, and keep their levels within permissible values in drinking water, great efforts in researches and developments directed towards making human life easy and comfortable were carried out. Among these efforts is the implementation of very effective treatment processes.

In this regard, some literatures research reports pointed out to the earlier techniques of heavy metals removal by the use of chemical reagents for the precipitations of these metals from its solutions [2]. Many others reported methods included coagulation-flocculation, electrocoagulation, cementation, membrane separation, solvent extraction, ion exchange adsorptions applied in fields of water treatments [3]. However, each of these methods formally mentioned has its merits and limitations in applications. Some require high capital investments, involve various and large volume of chemicals, consumes time, and/or are tedious. Besides, it was revealed that these processes when applied, some of them are usually incapable to meet the discharged standards limits laying between 0.1 – 3 mg/l for heavy metal concentrations [4].

Activated carbon (AC) materials are very popular as adsorptive media in wastewater treatments for removal of many types of heavy metals [5], [6], and gas treatments for removal of CO₂ [7]. These materials are black and solid carbonaceous substances, and have porosity, internal surface area of more than 400 m²/g and relatively high mechanical strength [8]. Most of the activated carbon product especially developed from agricultural by-products such as fruit stones [9], coconut shell [10], olive stones and walnut shells [11] and tea wastes [12] are inexpensive adsorbents and easily available.

GAC and PAC are two well-known forms of which AC are generally found. The size of a GAC particle is usually greater than 0.1 mm, about the size of coarse sand [13]. However, the particle size of a PAC, of course, is less than that. GAC is usually have larger internal surface area and smaller internal pores of those in PAC. However, the last is characterized with a faster adsorption rate [8].

Dates stones (DS) are usually disposed to landfill, environmentally causing problems. However, the stones in some very few Arabic countries are utilized as fuels, animal feeds, extraction of oil, and production of some pharmaceuticals [14].

In this present study, a batch mode technique was carried out to evaluate the efficiency of such AC in Pb (II) and Cu (II) removal from their aqueous solution.

II. EXPERIMENTAL PROCEDURES

A. Materials and Methods

The experimental part consists of two major sections, namely, preparation of AC, and adsorption efficiency measurements.

B. Preparation Method of Activated Carbon

The date stones (DS) were collected from few local manufactories of date pastes and juices in Tripoli city at the coastal region of Libya. The stones were repeatedly washed with distilled water and dried in an oven at 105°C for 24 hours. The dried stones were impregnated with phosphoric acid (85% by weight) at the weight ratio of 1:1 (stones: acid). The impregnated stones of 250 g were packed in a 15 × 15 cm² aluminum foil which was then placed inside a furnace and heated to a temperature 550 °C for 60 min for carbonization. After cooling the sample was washed thoroughly using hot distilled water until pH reached to 6.5. And finally, the carbonized stones were grinded, and sieved. Fractions of average size of 0.8 mm and 2.0 mm were used and stored in closed containers.

C. Preparation of Metal Solutions

All chemicals, supplied by Merk Company, were of high analytical grade and solutions of Pb (II) and Cu (II) were prepared by a deionized bi-distilled water with salts of Pb(CH₃COOH)₂ and Cu(NO₃)₂, respectively. They were all prepared with no further purifications.

D. Instrumentations

For the first part concerning AC final product, it was characterized for its functional groups using 1760X, Perkin Elmer, USA Fourier Transform Infrared Spectroscopy (FT-IR) at the range of 450-4000 cm⁻¹.

The pH of the solutions was measured with a 740 Inolab WTW model pH meter using a SenTix 20 pH model double electrode calibrated with standard buffer solutions. Batch mode adsorption experiments was performed using a GFL 3005 model, Germany made, thermal shaker at controlled room temperature and 100–300 rpm. Finally, determination of Pb(II) and Cu(II) concentrations were carried out by the use of Varian Liberty Series (II), Australian inductively coupled plasma atomic Absorption spectrometry (ICP-AA) with computerized programs. All tools and instruments involved in this study was supplied by Tajoura Nuclear Research Center in Tripoli-Libya.

III. EXPERIMENTAL STUDIES

Batch mode sorption experiments were conducted by mixing different quantities (10 mg, 50 mg, 100 mg and 200 mg) of activated carbon with 100 ml of synthetic solutions containing also different initial concentration of heavy metal ions (10, 25, 50, 200 mg/l). The experiments were performed in a thermal shaker at 25 °C and a constant agitation rate of 250 rpm for different periods of contact time (5–60 min) and pH range of 1.5–9.5 using 250 ml Erlenmeyer flasks.

After termination of the adsorption experiments, the remaining concentrations of the Pb(II) and Cu(II) concentrations in each sample was determined by (ICP-AA) after filtering the adsorbent with Whatman filter paper to make it carbon free. The percentage adsorption (%) was calculated using the following equation (1):

$$\% \text{ Adsorption} = (C_i - C_f) \times 100 / C_i \quad (1)$$

where, C_i and C_f are the concentrations of the metal ions in

the initial and final solutions respectively. The amount of metal adsorbed by weight of DSAC was calculated using the following equation (2):

$$Q_e \text{ (mg/g)} = \{(C_i - C_f) \times V\} / m \quad (2)$$

where, q_e is the equilibrium adsorption capacity (mg/g), C_i and C_f are the concentrations (mg/l) of the metal ions in the initial and final solutions respectively, V is the volume of the aqueous solution (ml) and m is the dry weight of the adsorbent (g/l)

IV. RESULTS AND DISCUSSION

A. Characteristics of the Activated Carbon

Fourier transform infrared (FTIR) spectroscopy was used to measure the carbons of the adsorbent within the range of 400–4000 cm⁻¹ wave number. Fig. 1 shows the spectra of the studied ACDS with a weak but sharp band at 3687 cm⁻¹ may be ascribed to isolated –OH groups. Another weak semi broad band in the 3400–3500 cm⁻¹ region assigning the O–H stretching mode from hydroxyl groups, involved in hydrogen bonding may be due to adsorbed water from the surroundings and a double peak at 2850–2950 cm⁻¹ may due to the C–H stretching vibrations. Finally, the absorbance peak of ACDS at 1597 cm⁻¹ and 1377 cm⁻¹ are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups and carboxylic moieties [15].

Fig. 1. FTIR analysis of activated carbon of dates stones.

B. Effect of pH

The pH value of the aqueous solution is an important controlling parameter in the adsorption process. These pH values affect the adsorbent surface charge, the degree of ionization and speciation of adsorbate during adsorption. Therefore, affects the adsorption efficiency of the metal pollutants from their solution media [16]. The adsorption experiments of Pb(II) and Cu(II) as a function of pH were studied between pH 1.5 and 9.5 for both GAC and PAC solution systems at room temperature of 25°C, constant HM concentrations of 25 mg/l, DSAC dose of 0.5 g/100ml and agitation rate of 250 rpm. In general, the adsorption of most metals on AC adsorbents increased with the increase of pH [17], [18]. This was attributed to the fact that, at low pH (< 4), the protonation of the active sites at carbon surface was enhanced and this refused the formation of links between cationic metals and protonated active sites.

The release of protons from the active site as the pH

increased up to 6.5, allowed more Pb(II), and Cu(II) ions to be adsorbed to the active sites on both GAC & PAC. Some authors reported that at higher pH, metal complex forms and results in precipitation and therefore the separation may not be due to adsorption [19], [20].

As shown in Fig. 2, it was apparent that the metal adsorption capacity, q , of the Cu (II) and Pb (II) was very low at strong acidic medium and the adsorption capacity increases with increasing pH value and reached its maximum at pH 6.5. It was confirmed by some authors that most Pb (II) species exist as Pb^{2+} ions, and only a small portion of $Pb(OH)^+$ are also present in case of pH approaching 6.5 [21, 22]. Similarly, It was also confirmed that the dominant Cu (II) species exist below such pH is Cu^{2+} and mainly involved in adsorption process [21].

Fig. 2. Adsorption of Pb(II) & Cu(II) using PAC and GAC as a function of pH.

It was also observed that the PAC was better than GAC in terms of the metal adsorption capacity, q , due to its larger pores and faster adsorption rate [8]. The larger pores of PAC allow by entrance additional removal of these metals from their aqueous phase to take place. Nadeem et al. [23] have reported that by applying three adsorbent particle sizes (0.25, 0.149 and 0.074 mm), the adsorbent with highest surface area i.e. 0.074 has proved maximum metal uptake capacity. The final pH values measured were always less than the initial pH, indicating that H^+ ions were released into the solution from the surface of adsorbents as Pb(II) and Cu(II) ions were adsorbed. This indicated that the type of adsorption of HMs involved in was an ion-exchange mechanism [24].

C. Effect of Contact Time and Initial HM Conc

The metal uptake by the adsorbent is particularly dependent on the HM ions concentrations. At low value concentration of HM ions, these HMs are adsorbed by specific sites on the adsorbents, while with increasing HMs concentrations the specific sites are saturated and the exchange sites become filled [25]. (Fig. 3. A, B, C & D) show the effect of contact time on the adsorbed amount of both Pb (II) & Cu (II) by DSAC from solution with different initial concentrations of Pb(II) and Cu(II) ion solutions of 10, 25, 50, 200 mg/l; once by a PAC and another time by GAC at pH of 6.5, room temperature of 25°C, DSAC dose of 0.5 g/100 ml and agitation rate of 250 rpm.

By DSAC from solution with different initial concentrations of Pb(II) and Cu(II).

From (Fig. 3. A, B, C & D), it can be obviously observed that the adsorption of both HMs was faster in adsorption and

higher in efficiency by PAC. This is in agreement with the reported fact; the smaller the particle size the higher the surface area per unit weight of the adsorbent and hence higher percentage adsorptions of HMs is expected [12]. Some other authors attributed to result to PAC larger pores permitting HMs to be faster adsorbed inside internal sites and thus fully occupying these active sites [23]. The results in (Fig. 3. A, B, C & D) indicated that the adsorption increased very fast and almost linearly by PAC with the increase of the contact time almost in the first 10 min and 20 min in respect to Cu(II) and Pb(II) ions. The majority of metal ion reached adsorption equilibrium in between 5 and 8 min for Cu^{2+} ion of the 25 mg/l and 50 mg/l samples and the sorption tends toward saturation of 73% & 80% removal at 10 min by PAC, while sorption tends toward saturation of 60% & 68% removal at 20 min by GAC for Cu^{2+} ion of the 25 mg/l and 50 mg/l samples. In contrast, the majority of metal ion reached adsorption equilibrium in between 5 and 15 min for Pb^{2+} ion of the 25 mg/l and 50 mg/l samples and the sorption tends toward saturation of 69% & 77% removal at 20 min by PAC, while sorption tends toward saturation of 61% & 65% removal at 30 min by GAC. By both types of ACs, the initial faster rate of metal adsorption may be explained as due to the availability of the large number of active sites for the ion exchange. For the bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium. Similar experimental results has been mentioned in literatures dealing with HMs adsorptions confirming that the Cu(II) percentage uptake by an AC was relatively higher than Pb(II) [26, 27]. Nevertheless, some other experimental results might have found that Pb(II) with higher affinity for some surfaces than Cu(II) [27]. The difference in selectivity between this present study and previous researches is probably a function of the different surfaces applied. It can be clearly observed that on changing the initial concentration of Cu (II) & Pb (II) solutions from 25 mg/l to 50 mg/l, the adsorption percentage increased as mentioned previously (Fig. 3. A, B, C & D). This may be attributed to fact that for higher initial concentration, more efficient utilization of sorption sites is expected due to the great driving force of the concentration gradient in order to overcome all mass transfer resistance of HM ions between the aqueous and solid phases [21]. M. Zabihi *et al.* reported that the increase in the HMs uptake capacity of AC (Derived from Wanut sell) with increasing initial ion concentration may be due to the higher collision probability between HMs ions and AC particles [28]. For the samples with higher initial concentration of 200 mg/l, the removal percentage was high for both Cu(II) and Pb(II). However, the time to reach equilibrium adsorption was quite longer and might be more than the 40 min used at the experiment. The rapid adsorption and removal of HMs by Adsorbents is one of the important factors very well considered when seeking economical wastewater treatment plants [28].

D. Effect of Adsorbent Dosage

Fig. 4 showed the effect of adsorbent doses of two types of AC (PAC and GAC) on the adsorption percentage of Pb(II)

and Cu (II) ions. The study was carried out to optimize the required amount for maximum uptake efficiency of the adsorbent at optimum pH of 6.5, initial concentrations of 50 mg/l for both HMs, contact time of 45 min (greatest uptake efficiency achieved in preceding part), room temperature of 25°C, and agitation speed of 250 rpm. Percentage of Cu (II) ions uptake by PAC increased with higher percentage from 45 to 86% and by GAC from 37 to 81% when the adsorbents doses per 100 ml of solution was increased from 0.1 to 1.0 g. A similar trend was shown by Pb (II) ions adsorptions. In general, the number of adsorption sites or surfaces area increases with the increase of the adsorbent weight and hence resulting in a higher percent of metal removal at a high dose [1], [21].

Fig. 3. A, B, C, D): The effect of contact time on the adsorbed amount of both Pb (II) & Cu

Fig. 4. Effect of adsorbent dosage on the adsorption of Cu(II) & Pb(II) by PAC & GAC

After certain adsorbent dosage of both types of AC the uptake efficiency is not increased so significantly. Efficiency (%) decrease in removal of HMs with the increase in the adsorbent dosage of AC may be as a result of clusters formations of carbon particles causing decrease of the overall surface area, as explained by other researchers [23].

V. CONCLUSION

Date stones are good materials for preparing AC as adsorbent for removal of Cu and Pb from their solutions. Powder activated carbon showed higher adsorption capacity and rate compared to granular activated carbon. The adsorption of copper and lead on the activated carbon prepared from date stones found to be activated carbon form (Powder or Granular AC), solution pH, initial HM ion concentration and contact time, activated carbon dose dependent. Adsorption process data revealed that the initial uptake of both HMs was efficient at pH 6.5, rapid and equilibrium was achieved within 30 min time for both types of activated carbons. The optimum parameters for this study were pH 6.5, 50 mg/100ml of Cu (II) & Pb(II) concentrations and around 1.0 g/100ml of adsorbent dose.

Date stones used in this work showed a good material for adsorption of toxic heavy metals. Therefore, date stones obtained from Local Libyan manufacturing date pastes and juices wastes can be used as a low cost adsorbent for removal of toxic heavy metals discharged to the environment. Date stones are available in factories dealing with manufacturing date pastes and juices and it is possible to be beneficial in stead of facing problems as when usually disposed to landfills ruining the environment.

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