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Treatment of Wastewater Contaminated with Cu(II) by Adsorption onto Acacia Activated Carbon

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معالجة المياه العادمة الملوثة بالنحاس الثنائي بالامتزاز على كربون الاكاسيا المنشط

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Abstract

In this study, the adsorption of Cu(II) ions from aqueous solutions onto Activated Carbon prepared from Acacia leaves. (AAC) was investigated. The experiments were performed in a batch system at different parameters (contact time, adsorbent dosage, initial concentration of adsorbate, agitation rate, temperature, particle diameter, and solution pH) were varied in order to establish the optimum conditions for copper removal using AAC, and the copper ions adsorption capacity was evaluated after equilibrium was attained. The results indicate that the removal was effective at low Cu(II) concentrations and a natural pH value, and the optimum conditions for Cu(II) removal operation from the synthetic solution investigated were 120 *minutes*, 300 *rpm*, and 0.375 *mm* as a contact time, agitation rate, and particle diameter respectively, and pH value equals to 6 at the temperature 30 1 ^{o}C. Also, the adsorbent dose of 0.5 *g*/100 *ml* was sufficient for the high removal of Cu(II) from the solution for studied batches which reaches up to 95.3, 77.42, 53.4, 37.6, 26.5, 18.4, 15.4, and 12.15% respectively for studied batches 100, 200, 300, 400, 500, 600, 800, and 1000 *ppm* respectively. The results obtained from this study show that the AAC can be used as a low-cost adsorbent for the complete removal of Cu(II) from an aqueous solution especially at low concentrations.

Keywords: *Copper; Acacia leaves; Adsorption; Spectrophotometer*.

الملخص

تم التحقق من عملية ازالة أيونات النحاس الثنائية من المحاليل المائية باستخدام تقنية الامتزاز على الكربون المنشط المحضر من أوراق الأكاسيا (AAC). تم إجراء التجارب بنظام الدُفعات بمعلمات مختلفة (وقت التماس، الجرعة المازة، التركيز الأولي للمادة الممتزة، معدل الخلط، درجة الحرارة، قطر المادة المازة، ودرجة حموضة المحلول) تم تنويعها من أجل تحديد الظروف المثلى لإزالة النحاس باستخدام AAC، وتم تقييم قدرة الامتزاز لأيونات النحاس بعد الوصول لمرحلة الاتزان. تشير النتائج إلى أن الإزالة كانت فعالة في تركيزات أيونات النحاس المنخفضة وقيمة pH معتدلة، وكانت الظروف المثلى لعملية إزالة ايونات النحاس من المحاليل الاصطناعية هي زمن تلامس 120 دقيقة، ومعدل خلط 300 دورة في الدقيقة، ومتوسط قطر المادة المازة 0.375 مم على التوالي، وقيمة الرقم الهيدروجيني تساوي 6 عند في درجة حرارة 30 درجة مئوية. كما كانت الجرعة المازة 0.5 جم/100 مليلتر كافية لعملية إزالة عالية من المحلول للدُفعات المدروسة التي حيث وصلت نسبة الإزالة إلى 95.3، 77.42، 53.4، 37.6، 26.5، 18.4، 15.4،

و12.15٪ على التوالي ذات التراكيز الابتدائية 100، 200، 300، 400، 500، 600، 800 و1000 مجم/لتر على التوالي. وتظهر النتائج التي تم الحصول عليها من هذه الدراسة أنه يمكن استخدام AAC كمادة امتزاز منخفضة التكلفة لإزالة أيونات النحاس من المحاليل المائية بشكل كامل عند التراكيز المنخفضة.

الكلمات الدالة: النحاس، أوراق الأكاسيا، الامتزاز، المطياف الضوئي.

1. Introduction

Wastewaters from metal industries such as metal finishing and galvanized pipe manufacturing contain toxic substances, heavy metals, acids, alkalis, and other substances. High concentrations of metals in the effluents can ultimately reach the food chain and thus become a risk factor for human health (Lai *et al.*, 1994; and Aslam *et al.*, 2004).

The removal of copper ions Cu(II) is gaining wide interest from both environmental and economic viewpoints due to its serious hazardous impacts on humans, animals, and plants. Generally, heavy metal contamination (such as Cu(II)) in the environment poses serious health problems due to their accumulation in living tissues throughout the food chain as non-biodegradable pollutants (Ho, 2003; and Gaikwad, 2011). The major sources of copper ions are products of industries such as metallurgy, wood preservation, plating, electronics plating, tanning, corrosion inhibition, wire drawing and printing operation (Gaikwad, 2011; and Ibrahim *et al.*, 2009). Typical concentrations vary from several thousand *mg/l* from plating bath waste to less than 1 *ppm* from copper cleaning operations. Copper is a heavy metal that is naturally observed in the environment and in fragmented water resources. The discharge of wastewater including heavy metals increases the environmental pollution and toxic nature of Cu(II) ions affects water resources (Ho, 2003).

Generally, conventional methods for heavy metal removal from wastewater include; reduction, precipitation, filtration, membrane technology, ion exchange, evaporation, and electrochemical treatment, all of which may be ineffective or extremely expensive when metals are dissolved in large volumes of solution at relatively low concentrations (Ossman and Mansour, 2013). Adsorption process is the most frequently applied method in industries for heavy metal removal (Ibrahim and Abushina, 2008). Though activated carbon is an ideal adsorbent, due to its organophilic character, its high costs prohibit its use in wastewater treatment. The high cost of active carbon has prompted a search for cheaper substituents (Gaikwad, 2011; and Ibrahim *et al.*, 2009, 2016]. A lot of studies on this process have been carried out (Regaraj *et al.*, 2002). Many studies have recently devoted the usage of different adsorbent materials in processes involving the removal of Cu(II) ions from aqueous effluents with the aim of finding cheaper replacements for conventional adsorbent material situations (Tamaki and Ali, 2003) such as activated carbon which is expensive for developing countries (Seco *et al.*, 1997, 1999; Rao *et al.*, 2011; and Gaikwad, 2011). Therefore, many investigators have used inexpensive adsorbent materials, such as tree fern (Ho, 2003), anaerobic sludge (Ulmanu *et al.*, 2003), waste tea (Alhluwalia and Goyl, 2005), fly ash (Al-Qodah, 2006), newspaper pulp (Chakravarty *et al.*, 2008), soil (Okasha and Ibrahim, 2008), date stones (Bouhamed *et al.*, 2012), and green waste tea (Maraie and Ibrahim, 2015). But till now, the activated carbons have a long history of use in adsorption technology which made from a wide range of natural and synthetic precursors. The use of these inert materials as adsorbents utilizes their large surface area and pore volume size for superior adsorption and avoids complications associated with leachate of plasticizers and other toxins from polymer based systems (Bhatanagar and Minocha, 2006; and Girgis *et al.*, 2007).

In this research, the feasibility of using Acacia Activated Carbon (AAC) for the removal of Cu(II) from wastewater will be investigated. The adsorption characteristics will be investigated under operating variables, as contact time, adsorbent dosage, initial concentration of adsorbate, agitation rate, temperature, particle diameter, and solution pH

2. Materials and Methods

2.1. Chemicals

The solutions of Cu^{2+} were prepared by dissolving accurately weighed amounts of copper (II) nitrate ($Cu(NO_3)_2.3H_2O$ that supplied from Across Organics, UK) in distilled water. All used chemicals were of analytical grades include Hydrochloric acid (HCl), sodium hydroxide (NaOH), ammonia solution 25%, formaldehyde, and copper (II) nitrate.

2.2. Preparation of Activated Carbon

Preparation of activated carbon done as mentioned by (Kumar *et al.*, 2008) as follows;

The acacia leaves were collected from a local farm in Zliten city, northwestern of Libya. They were washed with water to remove dust and other impurities. They were dried in the sun and then burnt in the thermal furnace at 400°*C* for 30 *min*. The acacia leaves were ground to obtain small pieces. They were then washed with the 1% formaldehyde solution to remove the color and then dried in oven maintained at temperature range of 120-140°*C* for a period of 12 *hrs*. The dried material was ground and sieved through standard sieve (AS 200) to obtain particle of sizes up to 0.375 and 1.0 *mm*.

2.3. Adsorption Experiments (Batch system)

A stock solution of Cu(II) (1000 *mg/l*) was prepared by dissolving 3.785 *g* of ($Cu(NO_3)_2.3H_2O$) in deionized water. Experimental solutions of copper which have known initial concentrations were prepared by diluting the stock solution in stoppered conical flasks (100 *ml*). The pH of the experimental solution was adjusted by using 1 *N* of HCl and NaOH solutions and measured by digital pH meter (HI 8417, HANNA Instrument, accuracy ±0.01).

Sorption experiments were carried out by adding AAC to a conical flask in various amounts containing known concentration of Cu(II) solutions. The temperature of the experiments was maintained at $30^{o}C\pm1$. The solutions were shaken in a mechanical stir at 300 *rpm*. The effects of adsorption pH solution, adsorbent dosage, initial concentration and contact time were studied. These solutions are filtered by using (FILTER-LAB) paper Cod. PN1248110 will be adding 5 *ml* of ammonia and the concentrations of residual Cu(II) were measured using spectrophotometer equipment (JENWAY 7305 Spectrophotometer) at selected wavelength λ_{max}= 615 *nm*. All experiments were carried out in duplicate and showed differences less than 1%.

The removal percentage of Cu(II) ions and capacity of AAC were computed using Eqn. (1) (Al-Meshragi *et al*., 2009);

$$Re\,\% = \left(\frac{C_o - C_e}{C_o}\right) * 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\quad (1)$$

Where C_o and C_e are the initial and equilibrium concentration of Cu(II) ions (*mg/l*) in solution. Adsorption capacity was calculated by using the mass balance equation for the adsorbent (Al-Meshragi *et al*., 2009);

$$Q = \left(\frac{C_o - C_e}{w}\right) * V \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\quad (2)$$

Where Q is the adsorption capacity (*mg/g*), C_o is the initial and equilibrium concentrations of Cu(II) in solution (*mg/l*) respectively, V is the volume of Cu(II) ions solution (*l*) and W is the weight of the adsorbent (*g*).

3. Results and Discussion

The important characteristics of AAC are presented in Table (1). Characteristic of carbon reveals that activated acacia leaves carbon (AAC) was found neutral. The characteristics of carbon reveal that the AAC possessed a good characters and agreed with the characterize estimated by Kumar *et al*. (2008).

Table 1. Characterization of AAC adsorbent

Character	***Unit***	***Value***
pH	--	7.0
Bulk density	g/cm^3	0.32
BET surface area	m^2/g	571
Pore Volume	m^3/g	4.1

The effect of different parameters carried out to identify the optimum conditions for adsorption process such as contact time, adsorbent dose, initial concentration of adsorbate, agitation rate, temperature, particle size of adsorbent, and pH.

3.1. Effect of Contact Time Variation

The removal percentage of Cu(II) from synthetic solution is investigated for 100 *ml* of solution at agitation rate 300 *rpm*, adsorbent dose 0.5 *g*, particle size (0.375<d<0.5) *mm*, pH value 6, temperature 30 ^oC, and time durations of 10, 20, 30, 50, 60, 90, 120, and 150 *min.* to evaluate the equilibrium time. Figure (1) shows the effect of contact time on Cu(II) removal from synthetic samples for eight batches. An optimum contact time of 120 *min.*, for samples corresponding to percentage removal of Cu(II) reaching 95.25, 77.04, 53.33, 36.71, 26.54, 15.22, and 12.15 % and adsorption capacity recorded at 19.06, 30.8, 32, 29.4, 26.54, 25.04, 24.46, and 24.31 $mg_{\text{Cu(II) ions}}/g_{\text{AC}}$ for initial concentrations 100, 200, 300, 400, 500, 600, 800, and 1000 *ppm* respectively.

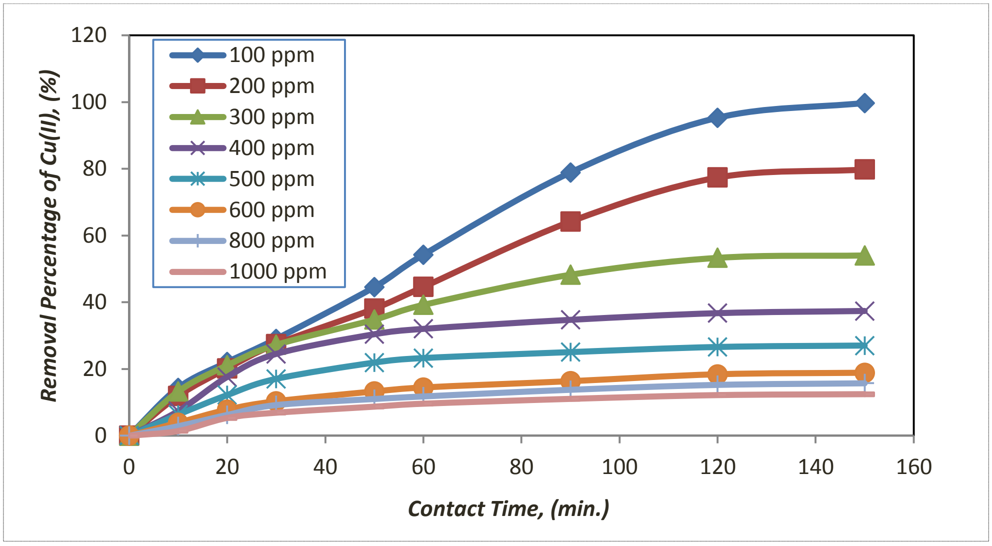

Figure 1. Effect of contact time variation on removal percentage of Cu(II).
Operating conditions: (Adsorbent dosage = 0.5 *g*/100 *ml*, 300 *rpm*, pH= 6, and Temperature 30 ^oC).

There was slow removal percentage of Cu(II) after 120 *min.* so this time period was taken as optimum time. The perusal results show higher removal rate initially and slower rate after lapse of time. Vacant adsorption sites, high solute concentration gradient, electrostatic affinity and ion-exchange may attribute to the higher removal in the initial stages (Kumar *et al.*, 2008; and Ibrahim *et al.*, 2016).

3.2. Effect of Adsorbent Dosage Variation

Cu(II) uptake by AAC at different dose of 0.25, 0.5, 1, 2, 3, and 5 *g* at 300 rpm agitation rate, particle size (0.375<d<0.5) *mm*, temperature 30 ^oC, pH value 6, and 120 *minutes'* contact time has been given in Figure (2). The results showed that increase in adsorbent dosage increased the amount of Cu(II) removal. This is due to increase the active sites of AAC and hence more active sites are available for the adsorption of more Cu(II) ions (Ibrahim *et al.*, 2016). Generally, a dose of 0.5 *g* of AAC per 100 *ml* of samples results in a relatively high values removal of 95.3, 26.5, and 15.4% respectively. For solutions that have high concentration require large amount of AAC to provide a larger surface area to allow the adsorption process to proceed. The results reveal that the optimum adsorbent dose for low initial concentrations less than 100 *ppm* was 0.5 *g* per 100 *ml* of synthetic solution corresponds to a high removal of Cu(II) ions.

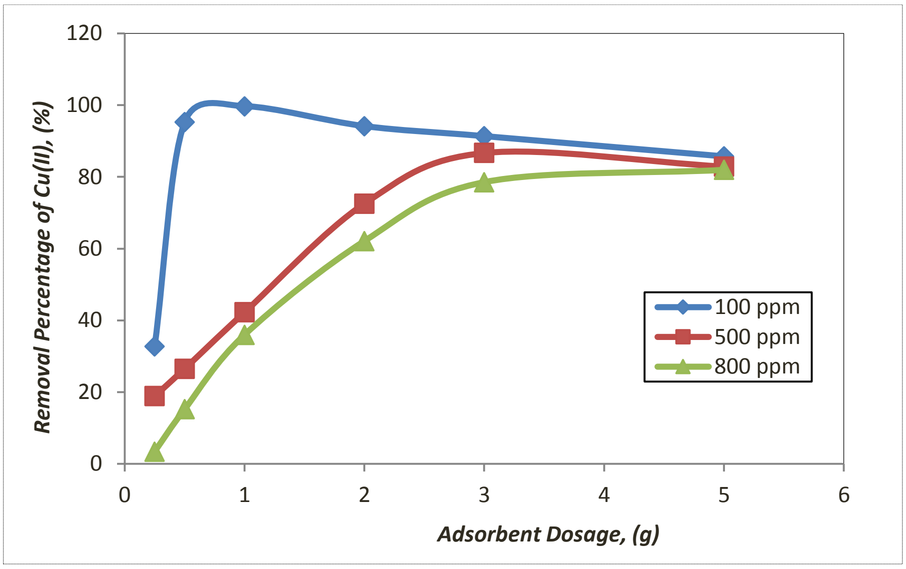

Figure 2. Variation of Cu(II) removal versus adsorbent dosage
Operating conditions: (Agitation rate=300 *rpm*, pH= 6, contact time = 120 *min.*, particle size= (0.375<d<0.5) *mm*, and temperature 30^{o}C).

3.3. Effect of Initial Concentration Variation

The effect of initial Cu(II) ions concentrations variation on the adsorption efficiency of AAC is shown in Figure (3). Adsorption experiments were carried out at different initial Cu(II) concentrations 100, 500 and 800 *mg/l* respectively for 120 *min.* as an equilibrium contact time with 0.5 *g*/100 *ml* of synthetic solution were used. The data shows that the Cu(II) uptake increases and the percentage removal of Cu(II) decreases from 95.3, 26.5, and 15.4% with increase in initial concentration of Cu(II) ions at 100, 500, and 800 *ppm*. At lower initial Cu(II) concentrations, almost all Cu(II) ions present in solution could interact with the active sites and thus the percentage removal was higher than those at higher initial Cu(II) ionic concentrations. The results behavior may be explained on the basis that the increase in the number of ions competing for the available active sites in the adsorbent, and also because of the lack of active sites on the sorbent at higher concentrations (Ibrahim *et al.*, 2016).

3.4. Effect of Agitation Rate Variation

The effect of agitation rate variation on Cu(II) removal from 100 *ml* of tanning solutions is based on agitation rates of 100, 200, 300, 400 and 500 *rpm* using 0.5 *g* of AAC of particle size (0.375<d<0.5) *mm* at temperature 30 ^{o}C, pH of 6, and 120 *minutes'* contact time.

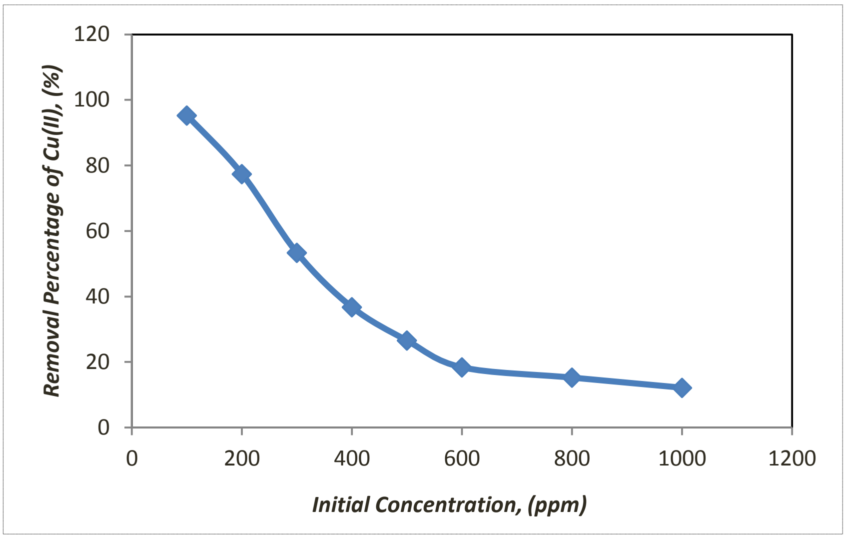

Figure 3. Effect of Initial concentration variation on removal percentage of Cu(II) Operating conditions: (Adsorbent dosage = 0.5 *g*/100 *ml*, agitation rate=300 *rpm*, pH =6, contact time = 120 *min*., particle size (0.375<d<0.5) *mm*, and Temperature 30^{o}C).

Results in Figure (4) show that, the removal percentage of Cu(II) from synthetic samples for first batch of an initial concentration 100 ppm increases from 17.57 to 99.13% as the agitation rate increases from 100 to 500 *rpm*.

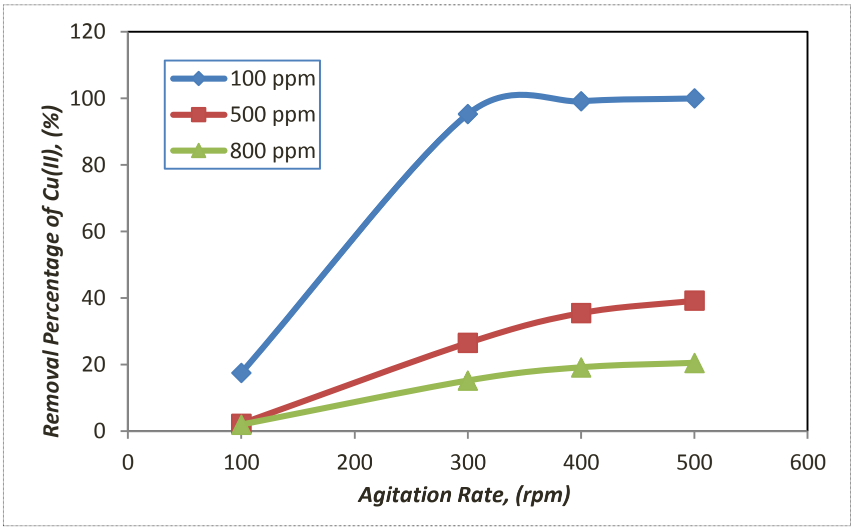

Figure 4. Effect of agitation rate variation on removal percentage of Cu(II) Operating conditions: (Adsorbent dosage = 0.5 *g*/100 *ml*, pH =6, contact time = 120 *min*., particle size (0.375<d<0.5) *mm*, and Temperature 30^{o}C).

A similar trend for the second batch with initial concentration 500 *ppm*, removal percentage increase from 1.98 to 39.23% as the agitation rate increases from 100 to 500 *rpm* and the third batch of with initial concentration 800 *ppm*, the removal percentage increase from 1.98 to 20.54% as the agitation rate increases from 100 to 500 *rpm*. These results indicate that, Cu(II) removal is controlled by the degree of agitation. Increasing of agitation rate decreases the boundary layer resistance to mass transfer surrounding AAC particles (Ibrahim *et al.*, 2016). So, the results reveal that the optimum agitation rate for batches is 300 *rpm*, corresponding to removal efficiencies 95.3, 26.5, and 15.4 % for batches respectively.

3.5. Effect of Temperature Variation

Temperature variation effect on the adsorption of Cu(II) from 100 *ml* of synthetic solutions are investigated using 300 *rpm* agitation rate, 0.5 *g* of AAC of (0.375<d<0.5) *mm* particle size, pH equal to 6, and 120 *minutes'* contact time for 25, 30, 40, and 60 *°C*.

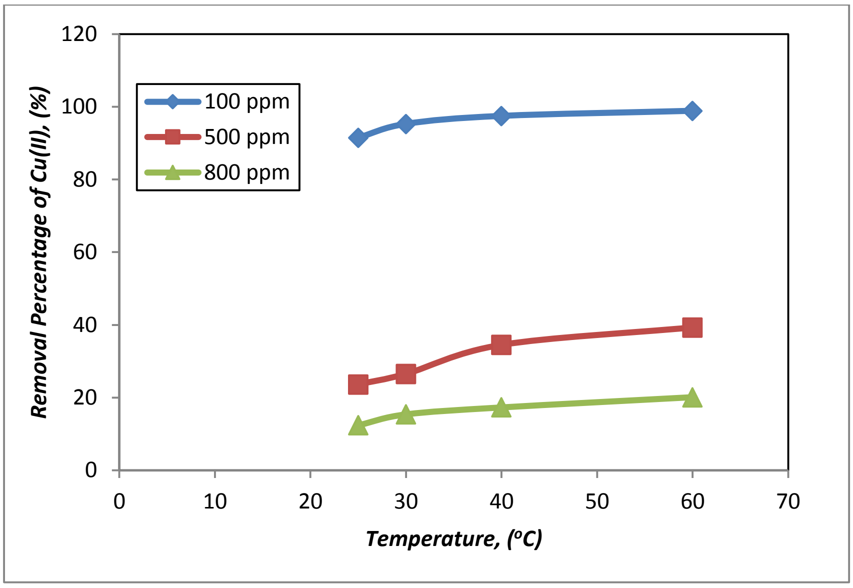

Figure 5. Effect of temperature variation on removal percentage of Cu(II)
Operating conditions: (Adsorbent dosage = 0.5 *g*/100 *ml*, pH =6, contact time = 120 *min.*, particle size (0.375<d<0.5) *mm*, and agitation rate 300 *rpm*).

The results shown in Figure (5) represent that the removal percentage increases as temperature increases as an indication that the process in endothermic in nature. An increase in the temperature of the solution causes the kinetic energy of the adsorbate particles to increase so the velocity of the adsorbate molecules also increases that leads to reduce tie needed by these particles to reach the adsorbent surface so the rate of adsorption removal will increase.

As shown in Figure (5) adsorption removal percentage increasing gradually with increase temperatures. Therefore, removal percentage at temperatures above ambient is rather cost ineffective; especially the removal percentage was completely at 30 *°C* after 120 *minutes* for initial concentrations less than 100 *ppm*.

3.6. Effect of Particle Diameter Variation

The effect of AAC particle size variation is investigated by using 0.5 *g* doses of particle sizes (0.375<d<0.5) and (0.5<d<1) *mm* and experiments are conducted at 30^oC at agitation rate 300 *rpm*, and pH 6 for 120 *minutes'* contact time.

The results in Figure (6) show that, the removal percentage increases as the particle sizes of AAC decrease. This trend can be attributed to the increase in the available surface area of contact of AAC. Higher Cu(II) adsorption by smaller particles is attributed to a greater accessibility to pores and greater surface area for bulk adsorption per unit weight of adsorbent (Manahan, 1984).

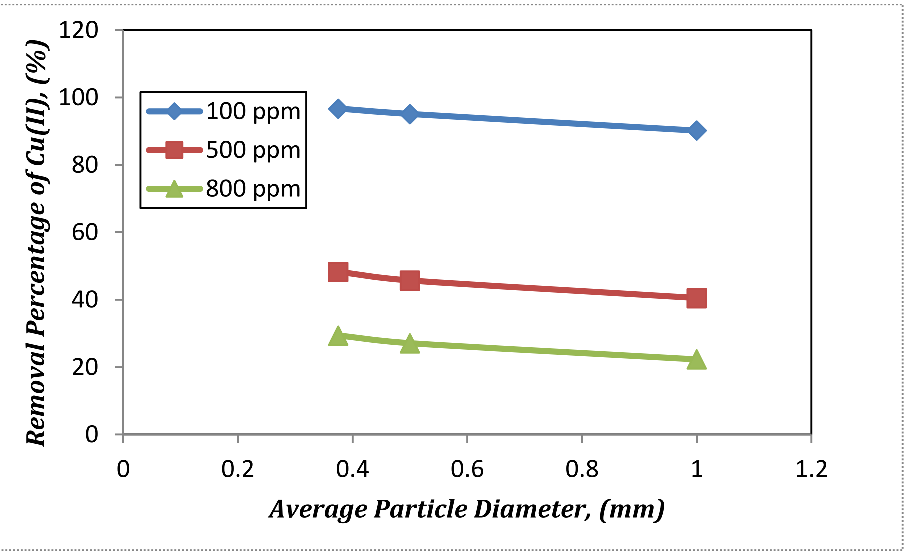

Figure 6. Effect of particle diameter variation on removal percentage of Cu(II)
Operating conditions: (Adsorbent dosage = 0.5 *g*/100 *ml*, pH =6, contact time = 120 *min*., agitation rate 300 *rpm*, and temperature 30 ^oC).

3.7. Effect of pH Variation

Batch adsorption performed to study the influence of pH on adsorption of Cu(II) ions onto AAC from aqueous solutions. The copper adsorption was conducted using an initial concentration 100, 500, and 800 *mg/l* over a pH range of 2-7 at 30 ^oC, agitation rate 300 *rpm*, adsorbent dose 0.5 *g*/100 *ml*, and 120 *min.* as a contact time. Figure (7) shows that the increase of pH leading to increase the amount of copper adsorbed upto pH 6 whereas the maximum removal of copper is 95.3, 26.5, and 15.4% for the studied batches 100, 500, and 800 *ppm* respectively. In the case of AAC a pH range of 4-6 is more suited for the quantitative removal of copper from aqueous solution. The variation in the amount of adsorbent clearly indicated the influence of pH on adsorption process. At lower values, the metal ions uptake was limited in this acidic medium, and this can be attributed to the presence of H^+ ions which compete with the Cu(II) ions for the adsorption sites. Contrarily, the metal ion was prone to

$Cu(OH)_2$ deposition through hydrolysis at higher values of pH, (pH>7) as mentioned by literatures (Gode and Pehlivan, 2003; Kumar *et al.*, 2008; and Ibrahim *et al.*, 2009). Therefore, pH 6 was selected as optimum value for conducting further adsorption experiments.

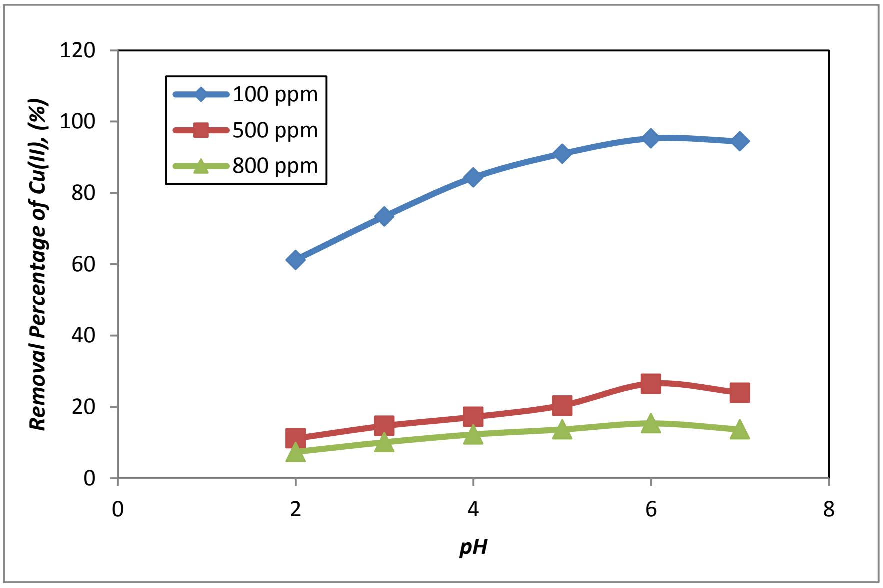

Figure 7. Effect of pH variation on removal percentage of Cu(II)
Operating Conditions: (Adsorbent dosage = 0.5 *g*/100 *ml*, pH =6, contact time = 120 *min.*, agitation rate 300 *rpm*, and temperature 30^oC).

4. Conclusion

This study aims to establish the optimum conditions for the removal of copper (II) ions on Activated Carbon prepared from Acacia (AAC). The removal of Cu(II) on AAC increases with the increase of initial solution pH, indicating that Cu(II) ions are retained mainly through the ion-exchange mechanism. The maximum retention (reaches 95.3% of Cu(II) from the initial quantity) appears at relatively low AAC dosage (0.5 *g*/100 *ml*), the optimum initial concentration of copper (II) was established to be 100 *ppm* which adsorption capacity recorded at 19.06 $mg_{Cu(II)}/g_{AC}$. The adsorption process attains the equilibrium in 120 *minutes*. The present study indicates to the amount of Cu(II) ions adsorbed onto the Acacia AC increased with an increase in pH. The optimum pH was found as pH 6 for the removal of Cu(II) ions by AAC at 30^oC±1. On decreasing the adsorbent particle diameter, the adsorption percentage also increases. So, the present study shows the feasibility of the practical use of AAC as a low cost, and natural material adsorbent for the effectively removal of Cu(II) ions from aqueous solutions.

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