

Preparation of nano-activated carbon from carbon based material for copper decontamination from wastewater

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Abstract: This investigation deals with preparation of an activated carbon in nano-scale from natural waste bio-materials of water hyacinth segments through chemical modification of water hyacinth followed by chemical and thermal activation of the material. The different parameters affecting in the chemical and thermal activation processes such as chemical types used for activation process, activation time and temperature and carbonization time and temperature for the thermal activation process were optimized to produce nano-size activated carbon. All prepared materials were evaluated as adsorbent materials for copper decontamination from industrial wastewater. The produced nano-activated carbon was characterized using X-ray diffraction (XRD), Morphological characterization (SEM), Thermal Analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The performance of the prepared nano-activated carbon was evaluated for copper ion sorption from aqueous solution using batch technique. The influence of the different parameters affecting the copper sorption process was examined. The results indicated that the prepared nano-activated carbon recorded high copper removal of 86.12% within 4hours.

Keywords: Nano-Activated Carbon, Water Hyacinth, Chemical and Thermal Activation Processes Copper Removal

1. Introduction

The occurrence of heavy metal ions such as copper, iron, nickel, lead, etc in the environment are of major concern due to their toxicity to many life forms. Unlike organic pollutants, which are susceptible to biological degradation, metal ions do not degrade into any harmless end products [1] and tend to accumulate in living organisms, causing various diseases and disorders [2]. The rapid pace of industrialization and urbanization activities has become a major environmental concern due to dispersal of wastes generated on the ecosystem. Heavy metals are one of the most hazardous contaminants that may be present in the aquatic ecosystem. Heavy metals are elements having an atomic weight between 63.54 and 200.59 and a specific gravity greater than 4 [3]. These heavy metals are highly toxic to the aquatic biodiversity, and drinking contaminated water containing heavy metal poses severe health hazards in humans. According to the World Health Organization (WHO), the

most immediate concern and abundant metals are cadmium, chromium, copper, lead, nickel, and zinc. Copper is an essential micronutrient to the plants but at higher concentrations they may become toxic. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operation and tanneries. Therefore, elimination of heavy metals from water and wastewater is important [4]. The most widely used methods for removing heavy metals from wastewater include ion exchange, chemical precipitation, reverse osmosis, evaporation, and membrane filtration and adsorption [5]. Most of these methods suffer from some drawbacks such as high capital, operation cost and the disposal of the residual metal sludge which are not suitable for small-scale industries. Moreover, sometimes the above-mentioned methods fail to meet the Environmental Protection Agency requirements [6]. Considering limitations of conventional methods for metal removal, the most promising alternative appears to be the adsorption process. The adsorption process used exclusively

in water treatment and many studies investigated that this process is mainly chemico-physically feasible process [4–5]. This method is a cost-effective and user friendly technique for the removal of metallic micro pollutants from water. Additionally, adsorption has been found to be superior to other techniques for water re-use in terms of the initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [7]. Activated carbon (AC) is the most commonly used and most effective adsorbent [10, 12, 13]. The nature of activated carbon surfaces especially the nano-size activated carbon materials have made them potential adsorbents for the removal of heavy metals from industrial wastewater. Nevertheless, its application fields are restricted due to its high cost. Many reports have appeared on the development of low cost activated carbon from cheaper and readily available materials [8]. The use of low-cost wastes and agriculture by-products to produce activated carbon has been shown to provide economical solution to this problem [14, 15]. The adsorption of organic micro pollutants by activated carbon is being widely used in water and wastewater treatments and the advantages of this adsorbent have been well documented [16]. In other respect, there is evidence in the literature that activated carbon can remove metal ions, especially Cu^{2+} , from aqueous solution [12, 16]. However, sorption capacity of untreated activated carbons towards heavy metals is rather low [16].

Several researchers have reported metal ion adsorptive properties of water hyacinth waste material. Accordingly, this waste material will be tested for copper removal from polluted industrial wastewater through this investigation. Also, the sorption properties of the water hyacinth will be improved through its chemical modification. Moreover, thermal treatment for these waste materials will be takes place through the carbonization process, in order to attain activated carbon with nano-size structure and has high copper adsorption properties. The copper sorption affinity of all prepared materials driven from water hyacinth will be tested to determine the most efficient one. The processing parameters affect in the sorption process using the prepared most efficient sorbent material will be optimized and modeled.

2. Experimental

2.1. Water Hyacinth Plant

The raw water hyacinth was collected from Alexandria Canal. The collected water hyacinth was thoroughly washed with water to remove dust, fungus, and other foreign materials, and then it was dried in electrical oven at 40°C for several days to insure complete removal of surface water.

2.2. Chemicals and Reagents

The chemicals used are copper chloride ($\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$), hydrochloric acid (HCl, El Nasr Pharmaceutical Company), sodium hydroxide (NaOH, Chemajet Chemical Company), phosphoric acid (H_3PO_4 ,

Lab Chemical Trading Company, 85%), and zinc chloride (ZnCl_2 , Riedel-De HAEN AG, SEELZE, HANOVER, Germany). Distilled water was used to prepare the solutions and to wash the glassware in all experimental runs.

2.3. Preparation of Adsorbent Materials

Firstly, collected water hyacinth from Alexandria canal was washed to avoid any surface contamination. Then it was dried for 72 hours at 60°C. The water hyacinth roots and shoots were separated and crushed into fine powder to obtain two different adsorption segments. Then studying the affinity of the separated two water hyacinth segments both (roots and shoots) toward different heavy metal such as Copper $\text{Cu}(\text{II})$ and Cobalt $\text{Co}(\text{II})$ to determine the most selective heavy metal to be adsorbed onto the water hyacinth.

2.3.1. Raw Water Hyacinth as an Adsorbent Material

Both raw water hyacinth shoots and roots powdered materials which have average particle size of 1mm were used as a natural sorbent material for heavy metals (copper, cobalt) removal. The sorption capacity of the two different water hyacinth segments toward the most selective heavy metal will be determined using batch techniques.

2.3.2. Preparation of Nano-Activated Carbon from Water Hyacinth

Firstly, the two different segments of water hyacinth were chemically modified using either alkaline treatment with 1M NaOH or using acidic treatment with 1M. The alkaline or acidic activation processes were carried out under heating at 60°C for one hour or without heating for 4hours. The yielded chemically modified material was further chemically activated using either phosphoric acid (H_3PO_4) or zinc chloride (ZnCl_2) for (6-8) hours to treat the parent adsorbent materials prior to the carbonization process. The produced powder materials after chemical activation were filtered, washed and then dried at 100°C for 24 hours. The dried materials were burned for carbonization at different temperatures (350-400°C) for 2hours.

2.4. Characterization of Adsorbent Material

The physical and chemical properties of both two different raw segments of water hyacinth (shoots and roots) and the prepared nano-activated carbon were compared using different characterization techniques namely X-ray diffraction, scanning electron microscope, thermal gravimetric analysis, and infrared spectroscopy. This comparison between the properties of water hyacinth in its original raw form and that of the most efficient prepared nano-activated carbon was investigated to display the effect of the carbonization process on the morphology, surface and inner structure and thermal stability on the water hyacinth.

2.5. Evaluation the Prepared Materials as Adsorbent Materials

In order to screen all the produced materials to determine their efficiencies as adsorbent materials, all materials were

tested for copper adsorbent from aqueous solutions. 0.25 gm of adsorbed material was agitated at 200rpm with 25ml Cu(II) solution of 100ppm for 4hours. The solid adsorbent material was separated using centrifugation force then the remaining copper concentration at the solution was determined using the atomic adsorption and the copper lamp (Shimadzu model (AA-6650)). The percentage removal of Cu^{++} onto the different prepared materials was calculated using the following relationship:

$$\text{Percentage removal \%} = \left[\frac{C_i - C_f}{C_i} \right] * 100 \quad (1)$$

Where C_i : the initial concentration of copper, C_f the final concentration of copper.

The different factors affecting at the batch process for copper removal using the most efficient prepared material of nano-activated carbon will be tested such as effect of contact time, temperature, initial copper concentration, weight of sorbent material.

3. Results and Discussion

3.1. Water Hyacinth as Adsorbent Material

The affinity of the separated two raw water hyacinth segments (roots and shoots) for copper and cobalt sorption was tested to determine the most selective heavy metal to be adsorbed by the water hyacinth. Table (1) showed that the water hyacinth segments attain high copper sorption capacity compared with cobalt ions. This result indicated that copper ion is more selective than cobalt ion to be adsorbed onto the water hyacinth segments.

Table (1). sorption of Cu(II) and Co(II) by water hyacinth segments.

Element	Water hyacinth	% metal removal
Copper	Roots	74.08%
	Shoots	55.56%
Cobalt	Roots	28.13%
	Shoots	26.54%

3.2. Preparation of Nano-Activated Carbon from Water Hyacinth

Firstly, the two water hyacinth segments were chemically activated using either alkaline or acidic treatment to induce new exchangeable (H^+) and (OH^-) ions into the sorbent material that improve its active surface area. This active surface of the modified water hyacinth increases its copper sorption capacity. Figure (1) represents the sorption capacity of the chemically modified water hyacinth segments with and without heating. It was indicated that the acidic chemical treatment of drying roots with heating at 60°C recorded the highest copper removal compared with its shoot segment. From the previous result, it can predict that the water hyacinths root segments is more efficient than its shoot segments for heavy metal adsorption.

As an attempt to improve the oleophilic behavior of water hyacinth sorbent material, nano-activated carbon will be

prepared from water hyacinth plant and evaluated as sorbent material for copper decontamination. The activated carbon was prepared from both two different acidified treated water hyacinth segments that followed with chemical activation using either Phosphoric acid or zinc chloride prior to carbonization process. Figure (2) illustrates the effect chemical activation process prior to the carbonization process on the copper adsorption process. It is observed that the activated carbon produced after zinc chloride activation of acidified water hyacinth roots recorded the highest copper removal of 93.62%. This is may be due to the chemical activation with zinc salt may increase the micro pores and macro pores of the produced activated carbon. Moreover, the chemical activation with phosphoric acid may increase the ash content of the resulting activated carbon consequently the carbon content decreased that decline its sorption capacity for copper sorption [16]. Accordingly, the most proper activated carbon sample that produced after chemical acidification of root segments followed by zinc salt activation prior to the carbonization process.

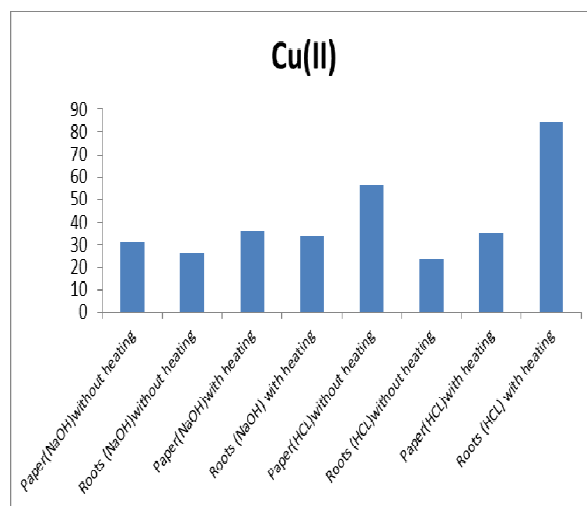


Figure (1). sorption of copper ions onto chemically modified water hyacinth segments

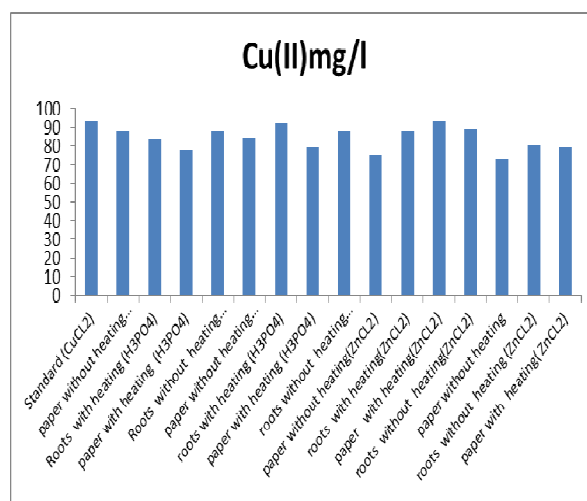


Figure (2). copper sorption onto the different prepared activated carbon from water hyacinth segments.

3.3. Characterization of Prepared Nano-Activated Carbon

3.3.1. XRD Analysis

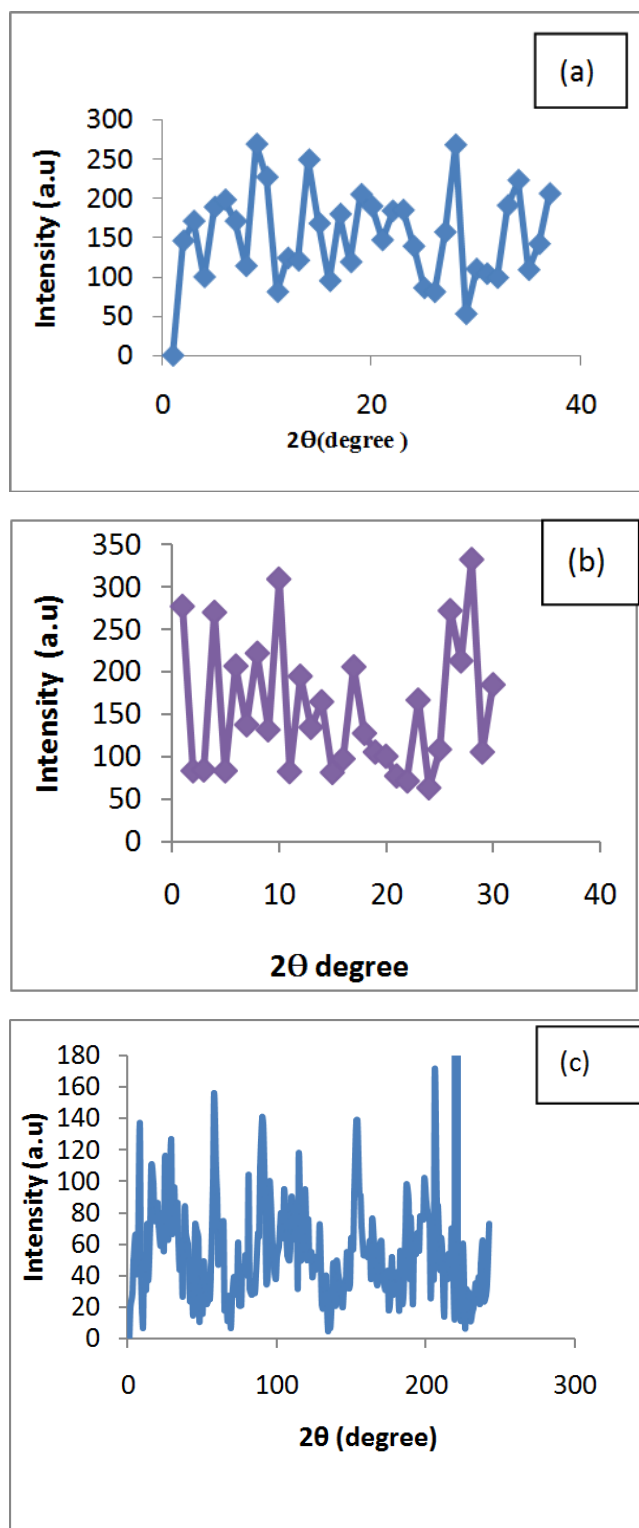


Figure (3). X-ray diffraction patterns of (a) Shoots segments, (b) roots segments, (c) activated carbon product

Figure (3) indicates the XRD patterns of the two raw segments and the activated carbon product. The XRD of water hyacinth roots and shoots showed typical spectrum of

cellulosic material having the main characteristics peaks at $2\theta = 79.93^\circ$ and 21.9552° the secondary peaks at $2\theta = 24.6874^\circ$ respectively. The main peak is taken as indicative of the presence of highly organized crystalline cellulose, while the secondary (un sharp) weak peak is a measure of a organized polysaccharide structure and assigned to broad peak with low angle. This refers to that particles are ordered in the preferred orientation to give very thin peaks besides each other because of instrumental resolution the peak as seemed with this shape. On the other hand the produced activated carbon seems to have very sharp peaks which indicate the improvement at the crystalline structure of prepared activated carbon sample after the carbonization process. This crystalline structure of activated carbon may be due to the breaks down of more amorphous cellulose under the chemical activation conditions using zinc chloride prior to carbonization process and the thermal effect of the carbonization process.

3.3.2. Fourier Transform Spectrometer (FT-IR)

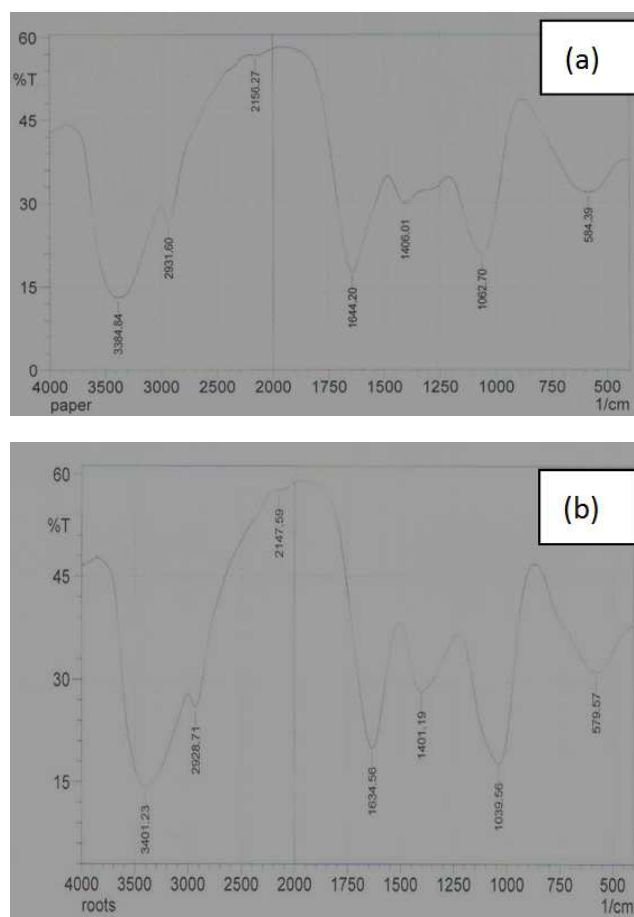


Figure (4). Infrared Spectroscopy (IR) of two raw water hyacinth segments (a) shoots and (b) roots

Fourier transform infrared (FT-IR) spectrum of water hyacinth is recorded over wavelength range of $4000\text{--}500\text{ cm}^{-1}$. This spectrum serves as a direct means for the identification of the organic function groups on the material surface. The chemical structure of the adsorbent material is of vital importance in standing the mechanism of the

adsorption process. It can be indicated from Figure (4) that there is great similarity between the FT-IR for the two water hyacinth segments. This figure displays a number of adsorption peaks indicating the complex nature of the examined biomass as; the peaks appear at 3384.84cm^{-1} (shoots) and 33401.2cm^{-1} (roots) represent the existence of free OH and NH bonded. In the water hyacinth, for the two segments, the CH_3 stretching vibration around 2931.6cm^{-1} indicates the presence of alkenes functional group. The adsorption peak appear around 1406.01cm^{-1} indicates the bonds of $\text{P}=\text{O}$ phosphonate or phospho amide. The C-O of aliphatic alcohol is represented by 1062.70cm^{-1} adsorption peak. The strong asymmetric stretching of R-COO^- , aromatic $\text{C}=\text{C}$, $\text{C}=\text{O}$ in $\text{R}=\text{O}$, of aqinones or in conjugation with alkenes represented by adsorption peak appear at 1644.2cm^{-1} [17]. On the other site, figure (5) illustrated the FT-IR spectrum of the prepared activated carbon. A weak but sharp adsorption bands at 3415.7cm^{-1} which appeared in the spectrum of the activated carbon may be ascribed to isolated OH groups [17,18]. The FITR spectrum contains absorbance peak at 1607.56cm^{-1} which is characteristics of C-O in union structure. The band at 1413.72cm^{-1} shows an aromatic ring of activated carbon. The broad band at 1157cm^{-1} has been assigned to C-O starching vibrations confirming the OH group in the activated carbon.

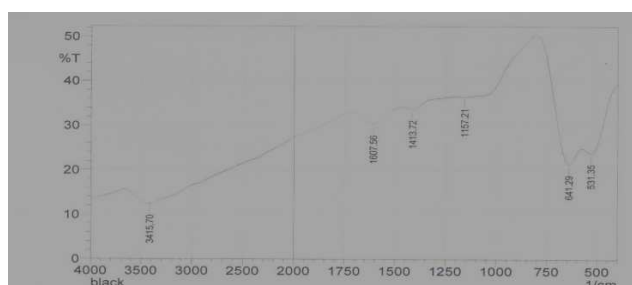
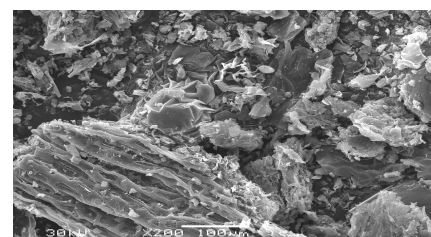


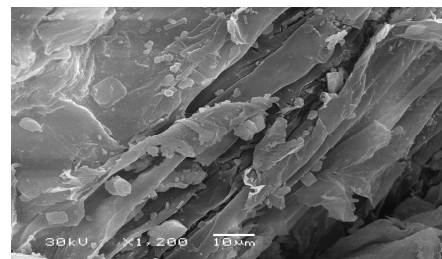
Figure (5). Infrared Spectroscopy (IR) of the most efficient prepared activated carbon

3.3.3. SEM Imaging

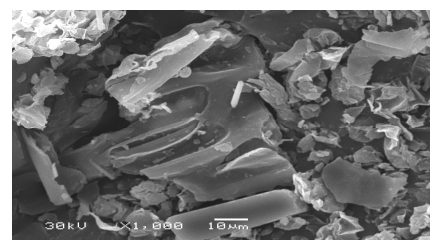
SEM is widely used to study the morphological feature and surface characteristics of the adsorbent material. In this study the surface structure of water hyacinth roots was analyzed by scanning electronic microscopy. The structure examination of water hyacinth can be observed from the SEM photographs (figure 6a-d). These figures reveal that the water hyacinth segments were irregular in shape and seem to have some degree of porosity. Figure (7) shows the surface texture of the most efficient prepared activated carbon product. The carbon particles are an assemblage of fine particles, which have regular spherical shape with average diameter of 50nm. It can be seen from the micrographs that the external surface of the chemically activated carbon is full of cavities. According to this micrograph, it seems that the cavities resulted from the evaporation of ZnCl_2 during the carbonization process.



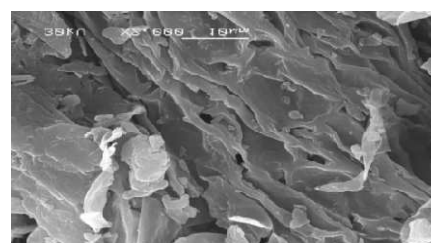
(a)



(b)



(c)



(d)

Figure (6). scanning electron microscope photographs of raw water hyacinth segment with different magnification factors .(a) 200X ,(b) 1200X,(c) 1000X,(d) 5000X.

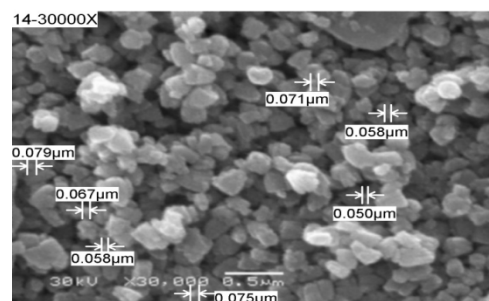


Figure (7). scanning electron microscope photographs of prepared activated carbon.

3.4. Copper Sorption Process onto Nano-Activated Carbon

The different processing parameters affecting on the

copper sorption process as function of contact time using the batch technique were optimized.

3.4.1. Effect of Initial Copper Concentration

Figure (8) showed the effect of variation the initial copper concentration on the %removal as function of contact time onto prepared nano-activated carbon. The data showed that the contact time necessary for the % removal to reach maximum value within 240minutes (4hours). Figure (8) showed the effect of initial copper concentration as function of time. It was evident that the increment at the initial copper concentration declines the percentage copper removal at the fixed contact time. The maximum copper removal was recorded for 100ppm copper concentration of 86.12% within 240minutes. So, the equilibrium time for copper sorption onto activated carbon is 4hours for the different studied copper concentration.

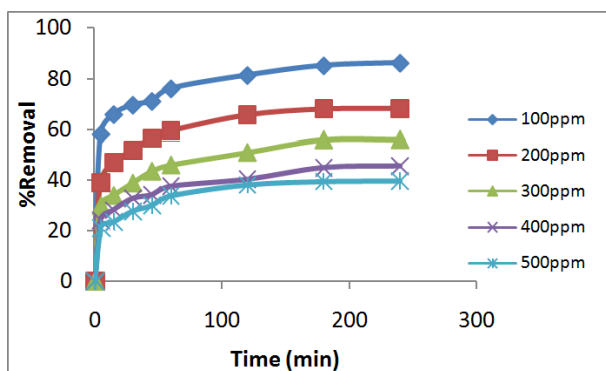


Figure (8). Effect of initial Cu(II) concentration as function of time onto the prepared nano-activated carbon

3.4.2. Effect of Dosage of Nano-Activated Carbon

The adsorbent material dosage has great influence on the percentage pollutant removal. Figure (9) indicated that the improvement of the nano-activated carbon dosage enhance the percentage copper removal for the same contact time. This is due to the availability of more active sites for copper adsorption.

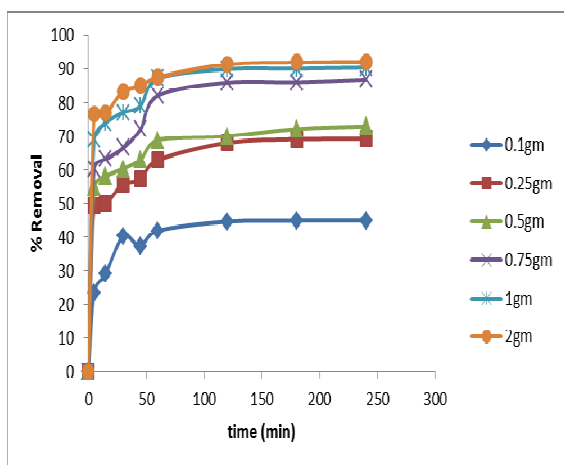


Figure (9). Effect of nano-activated carbon dosage on the percentage copper removal as function of time.

3.4.2. Effect of Solution Temperature

Figure (10) represents the effect of solution temperature variation on the copper sorption process onto the prepared nano-activated. It was indicated that as the solution temperature increased the residual concentration in solution decreased, which means that the copper adsorption process favored the increase in temperature. This behavior may be regarded to the improvement at the kinetics energy of the adsorbate particles of copper ions that increase the velocity of the copper molecules to the nano-activated carbon surfaces and lead to decrease the time need by this particles to reach the adsorbent surface. Accordingly, the rate of copper sorption increased with the increase at solution temperature especially for the low values of contact time. The enhancement at the copper adsorption process with temperature gives prediction that the copper sorption process onto the prepared activated carbon is an endothermic process [20].

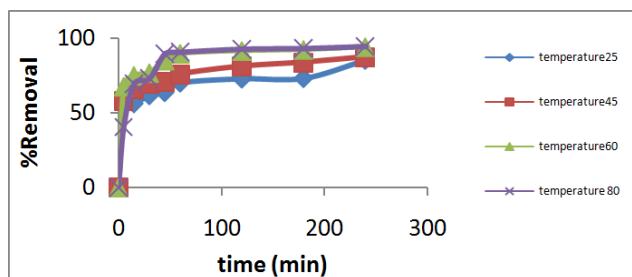


Figure (10). Effect of solution temperatures on the percentage copper removal as function of time.

5. Conclusion

Nano-activated carbon was successfully prepared from water hyacinth collected from Alexandria canal using chemical and thermal modification process. It was evident from scanning electron microscopic analysis that the external surface of prepared material has large cavities and high porosity. Both XRD and FITR confirm the chemical and crystalline structures of the prepared nano - activated carbon .The different parameters affecting the copper removal onto the prepared nano-activated carbon using the batch technique was optimized. The equilibrium copper sorption was recorded at 240min .The improvement at both the material dosage and solution temperature enhances the copper sorption process onto the prepared activated carbon.

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