ХИМИЧЕСКИЕ НАУКИ

DENDRITIC POROUS SILICON AS A HEAVY METAL REMOVAL (COPPER ELEMENT)

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ANNOTATION.

Using prepared dendritic porous silicon powder as a promise adsorbed material for heavy elements (i.e. Cu) from wastewater. The maximum removal percent of Cu (II) reached 1383.9 mg/g and 92.5%, respectively, at an initial Cu (II) concentration of 200 mg/L, adsorption time of 10 min.

АННОТАЦИЯ.

Использование приготовленного дендритного пористого порошка кремния в качестве перспективного адсорбированного материала для тяжелых элементов (т.е. Cu) из сточных вод. Максимальный процент удаления Cu (II) достиг 1383,9 мг / г и 92,5% соответственно при начальной концентрации Cu (II) 200 мг / л, время адсорбции 10 мин.

ABSTRACT.

New and inexpensive dendritic Porous Silicon powder (dendritic PS) powder is prepared by alkali chemical etching using ball milling technique and is subsequently investigated as an adsorbent in batch systems for the adsorption Cu (II) ions in an aqueous solution. The optimum conditions for the Cu (II) ion adsorption capacity of the dendritic PS powder are studied in detail by varying parameters such as the initial Cu (II) concentration, the solution pH value, the adsorption temperature and contact time. The results indicated that the maximum adsorption capacity and the maximum removal percent of Cu (II) reached 1383.9 mg/g and 92.5%, respectively, at an initial Cu (II) concentration of 200 mg/L, adsorption time of 10 min and no effect of the solution pH and adsorption temperature.

Keywords: dendritic morphology, porous silicon, heavy metals, copper element, water treatment.

Ключевые слова: морфология дендритов, пористый кремний, тяжелые металлы, медный элемент, водоподготовка.

Introduction

Porous silicon (PS) presents an artificially structured material formed by alkali stain etching of commercial polycrystalline silicon powder. The variety of the preparation conditions provides the growth of PS layers characterized by a wide range of pore sizes and structural types [6, p. 10]. The dendritic shape of PS is highly branched constructed with a well-defined symmetrical structure consisting of a central core, repeating units, and terminal functional groups while hyper-branched materials share analogous structural features but are non-symmetric. [1, p. 10]

The physicochemical properties of PS could be quite dissimilar to those of bulk silicon and are strongly affected by the type of surface orientation of the initial silicon powder. PS has exceptional properties such as the extremely high effective surface area, large adsorption capacity and unique optical properties, especially the dendritic shape of PS. [4, p. 10]

Nowadays, fast urbanization, industrialization, and unplanned activities of human beings have increased the environmental pollution especially air and water. These are generally caused by effluents from various industries and a major part is constituted by the dye industries. [10, p. 10]

The presence of heavy metals in wastewater, resulting from mining operations, various manufacturing industries, leather tanning, paper production, fertilizers, photographic materials, explosives, is a major environmental concern. The admissible levels of heavy metals are regulated in most countries, during the wastewater treatment. With water playing a crucial role in a sustainable development, the removal of heavy metals from contaminated waters has been the subject of many studies [2, p. 10]. The development of novel Sorbents, able to remove organic or heavy metal pollutants from wastewaters, represents an intensive and popular research field during the last years. [3, p. 10]

Adsorption, on the other hand, has emerged as a potential alternative to conventional physicochemical technologies in waste-treatment facilities. Adsorption is an effective separation process that has advantages in terms of cost, flexibility and simplicity of design, and ease of operation compared to other techniques. Adsorption also does not result in the formation of harmful substances. [7, p. 10]

The presence of the copper element (as a heavy metal) at a higher rate than allowed globally leads to change in the nasal mucous membranes, brain damage, demyelization, renal disease, and copper deposition in the cornea. It had to strive to remove it from the water, as shown in this study. The present study includes the adsorption studies on Cu using dendritic PS powder. The efficiency of this adsorbent is studied and maximum adsorption and lowest equilibrium time for this adsorbent is recorded.

Materials & Methods:

- *The dendritic PS Powder Preparation as an Adsorbent Material*

The ball mill technique is used in this work, because of its simplicity. To prepare (dendritic PS) powder, we used a commercially available Si-powder [Silicium, Pulver – 99%]. It is prepared via wet alkali chemical etching. Briefly, appropriate amount of Si powder is dispersed in a solution of KOH, n-propanol and distl. H_2O. The resulting powders are filtrated and washed, and then dried overnight at 40°C to obtain PS powder. The structure of producing powder is characterized by XRD (X-ray 7000 Schimadzu diffractometer). XRD equipped with a Cu anode operated at 40 kV and 30 mA; the samples were scanned at a rate of 4 °/min. The PS-powder morphology is investigated using SEM (Scanning electron microscopy, JEOL (JSM 5300).

Preparation of Metal Ion Solutions

The Cu is synthesized using standard methods. The double distilled water was used for all the analyses. The concentrations of the metal ions are estimated using UV-Visible Spectrophotometer Double Auto cell (Labomend. INC, USA). Standard Copper Solution: Cu solution is prepared by using Copper sulfate; 0.15 g of Copper sulfate is taken into a 1000 ml volumetric flask.

- ### *Batch Procedure for Cu Element Removal*

Batch Equilibrium Method: All experiments are carried out at room temperature (27 °C) in batch mode. Batch mode is selected because of its simplicity and reliability. The experiments are carried out by taking 40 ml metal ion sample in a 100 ml Erlenmeyer flask and after pH adjustments; a known quantity of solution dried adsorbent (PS) is added. The flasks are agitated at 200 RPM for predetermined time intervals using a mechanical shaker until equilibrium conditions are reached. After shaking, the suspension is allowed to settle. The residual biomass adsorbed with metal ions, the filtrate is collected and subjected for metal ion estimation using UV- Visible Spectrophotometer Double Auto cell (Labomend. INC, USA). The values of percent metal uptake by the sorbent (Sorption efficiency) and the amount of metal ion adsorbed has been calculated using the following relationships: [8, p. 10]

$$Sorption\ efficiency = \frac{c_i - c_f}{c_i} \times 100 \quad Eq.1$$

$$Amount\ Adsorbed\ (Q_e) = \frac{c_i - c_f}{w} \times V \quad Eq.2$$

Where, C_i= Initial concentration of metal ion in the solution (mg/L), C_f = Final concentration of metal ion in the solution (mg/L), W = Weight of adsorbent (g), V = Volume of solution (L) and Q_e =Amount of metal ion adsorbed per gram of adsorbent.

Results & Discussion:

- ### *Adsorbent Powder Study*

The XRD pattern of fabricated PS powder, before using it as an adsorbent, is shown in FIGURE 1. All the diffraction peaks can be well indexed to the cubic phase PS reported in (JCPDS Card No. 01-079-0613 and 00-027- 1402). Before removal process, the strongest peak is appeared at 2θ = 28.22° correspond to (111), and other peaks are appearing at 2θ = 47.173°, 56.02° and 69.12°, which correspond to (220), (211) and (400), respectively. No diffraction peaks arising from any impurity can be detected in the pattern confirming that high purity PS powdered material has been obtained. Either after the Cu-removing process using PS powder, noticeable, the appearance of the diffraction peaks at 2θ = 30.48°, 31.6° and 38.16° arising from the Cu (110), (111) and Cu (200) planes (JCPDS Card No. 00-001-1241and 00-001-1142), respectively.
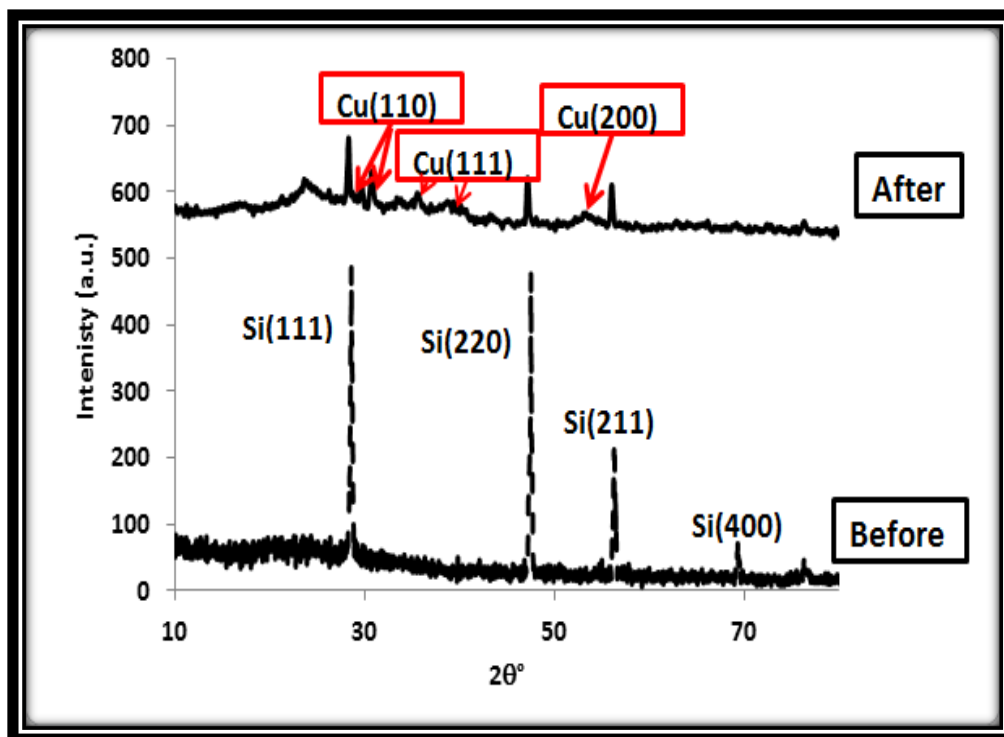

Figure 1. X-ray diffraction patterns of (a) PS powder; (b) adsorbed Cu on the PS powder.

Figure 2 shows the surface morphology of PS powder. The dendritic shape of PS surface is recorded in figure 2.a, that has many active sites of adsorption process as a result of high surface area. The Cu particles

appear on the dendritic PS surface, as shown in figure 2.b, the Cu particle size on the dendritic PS surface is in the range 0.1-0.23 μm.
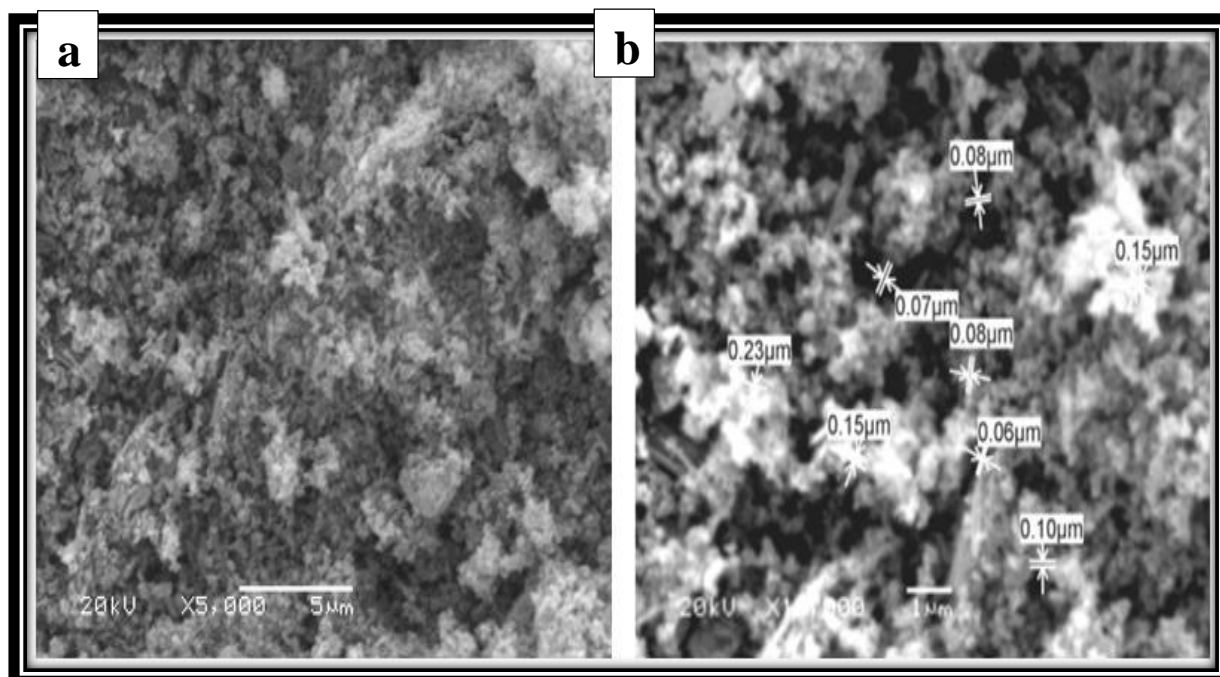

Figure 2. SEM micrographs of (a) dendritic PS powder before adsorption;
(b) adsorbed Cu on the dendritic PS powder.

- ***Adsorption Study***

Uptake of the Cu (II) by PS as a function of contact time in different Cu concentrations; as it can be seen, in all of the Cu concentrations (30, 50, 100, 200 ppm), removal process took place. Cu (II) is removed faster; it exhibited a subsequent removal until equilibrium is reached. The main reason for the appearance of rapid process, the plenty active sites on the dendritic PS powder and gradual occupancy of these sites causes of emerging [9, p. 10]. In fact Cu ions, form a molecule (actually ion) layer on the adsorbent surface. After that, the uptake rate is controlled by the rate at which the Cu (II) ions are transported from the exterior to the interior sites of the dendritic PS powder particles.

- ***Effect of initial Cu (II) concentration on adsorption:***

The initial Cu (II) concentration serves as an important driving force for overcoming mass transfer resistance of Cu (II) between the aqueous and solid phases. The effects of different initial Cu (II) concentrations on the dendritic PS adsorption capacity are shown in FIGURE 3. The adsorption capacity of the dendritic PS powder toward Cu (II) is directly proportional to the initial Cu (II) concentrations at a constant value of dendritic PS dose. As shown in figure 3.b, the adsorption capacity value at dendritic PS dose = 0.07 gm/l is the best one (1383 mgm/gm) at 10 min.

Noticeable, the removing percent of Cu (II) at several concentrations is nearly similar values at a time (10 min). Studies are carried out to obtain optimum conditions for the adsorption of Cu (II) using 0.09 g of adsorbent (dendritic PS) in a 1L solution of 50 ppm of Cu (II) concentration adjusted to different contact time values from 2 to 10 min, which produce Cu removal percent is 92.5% and the value of the adsorption capacity of PS is 513.9 mg/g. This result is observed because higher Cu (II) concentrations result in an increased concentration gradient, which, leads to a higher probability of collision among Cu (II) ions and the active adsorption sites on the PS powder, thereby increasing adsorption capacity. With further increases in Cu (II) concentration than 50 ppm, the adsorption capacity remained constant because the active adsorption sites became saturated [7, p. 10], as shown in figure 4.
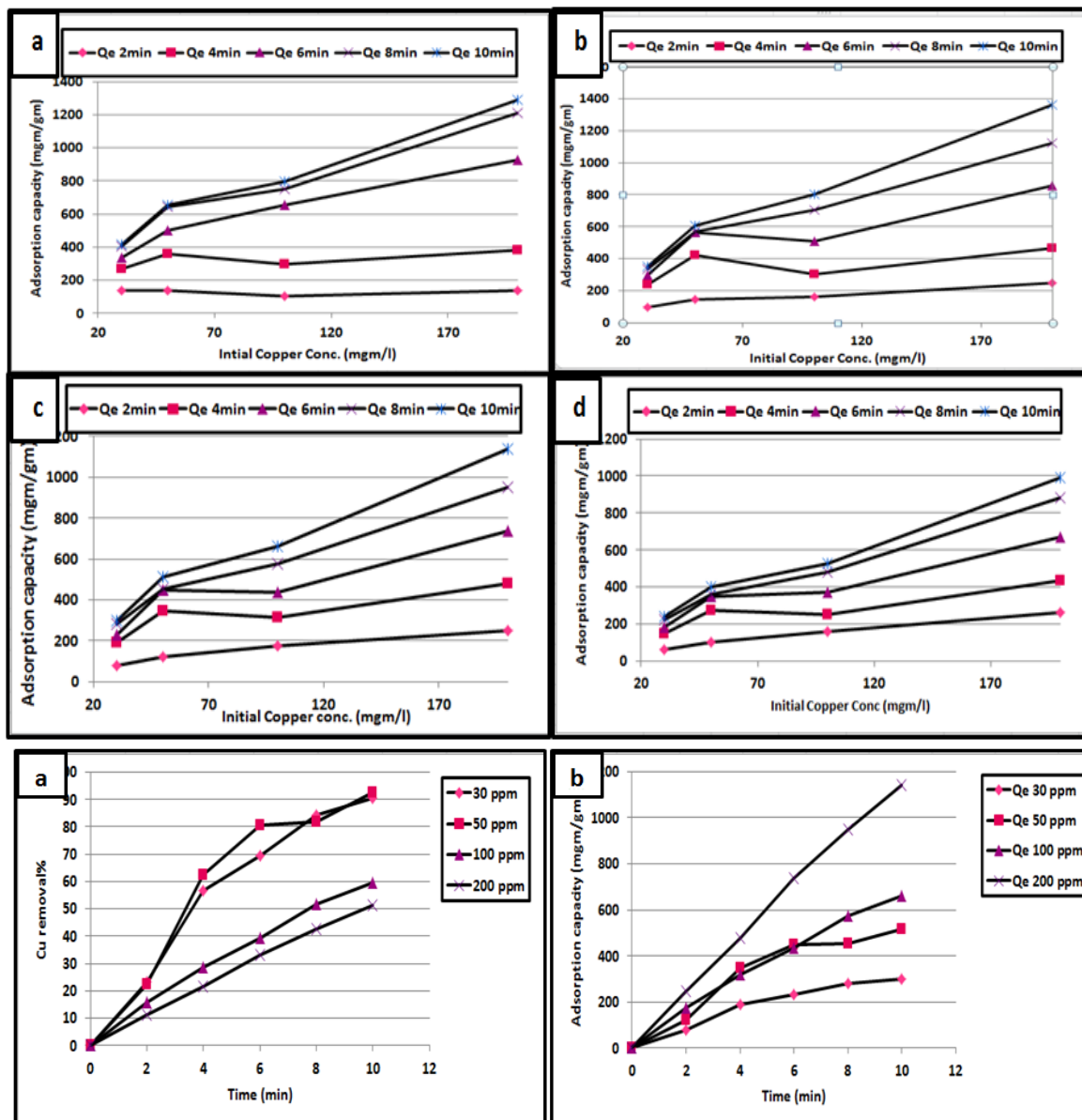
Figure 3. The effect of the initial copper concentrations on the values of the adsorption capacity value of PS each gm; initial copper concentration (Cu_conc)= (a) 0.05; (b) 0.07; (c) 0.09 and (d) 0.12 gm/l.

Figure 4. At the dendritic PS powder dose 0.09 g/L, a) Cu removal concentration percent as a function of contact time (min), b) Effect of contact time on desorption capacity of NPS.

Effect of contact time on adsorption:

The effects of different adsorption times on the dendritic PS powder adsorption capacity toward Cu (II) are shown in FIGURE 4. At prolonged adsorption times, the Cu (II) adsorption capacity of the dendritic PS powder initially increased rapidly and then decreased slowly because the surface of the dendritic PS powder is covered with a large quantity unsaturated functional groups. Cu (II) ions are adsorbed by diffusing into the microporous adsorbent (dendritic PS); thus resulting in a sharp adsorption equilibrium that decreased with the saturation of the functional groups on the dendritic PS powder surface. [5, p. 10] Therefore, the optimum contact (adsorption) time is 10 min, the studies are carried out to obtain optimum conditions for the adsorption of Cu (II) using 0.09 g of adsorbent (dendritic PS) in a 1L solution of 50 mg/L of Cu (II) concentration adjusted to different contact time values

from 2 to 10 min, which produce Cu removal percent is 92.5 % and the value of adsorption capacity of dendritic PS is 513.9 mg/g.

In addition, the effect of acidity and temperature on the adsorption value of copper is studied. It has been shown that by changing the pH value and temperature values, there is no obvious effect at the varying process of the Cu adsorption values, which are the same as in case of the room temperature and pH = 7.

Conclusion:

A new dendritic PS powder is prepared by alkali chemical etching using the ball mill technique. The results of this study show that the synthesized dendritic PS powder can be used effectively for the adsorption of Cu (II) ions from aqueous solutions. The maximum Cu (II) ion adsorption capacity for the dendritic PS powder reached to 1383 mg/g under an initial Cu (II) concen-

tration 200 mg/L and adsorption time is 10 min, in addition, no effect of pH and at adsorption temperature. Only using 0.09 g of adsorbent (dendritic PS) in a 1L solution of 50 mg/L of Cu (II) concentration at contact time 10 min, which produce Cu removal percent is 92.5 %.

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КИНЕТИКА ПРОЦЕССА АЦЕТИЛТИОМОЧЕВИННОГО ВЫЩЕЛАЧИВАНИЯ ЗОЛОТА ИЗ ХВОСТОВ ФЛОТАЦИИ НИЖНЕГО ГОРИЗОНТА ДЖИЖИКРУТСКОГО МЕТОРОЖДЕНИЯ

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АННОТАЦИЯ

В данной статье приведены полученные результаты экспериментальных и кинетических исследований по изучению общих закономерностей процесса растворения золота в кислых растворах ацетилтиомочевина с последующей разработкой технологии извлечения металлов из хвостов флотации включая кинетические закономерности протекания процесса, влияние продолжительности времени выщелачивания и влияние температуры на основе ацетил-тиомочевинного выщелачивания. На основе кинетических экспериментов и расчётов, определены порядок химической реакции, константа скорости реакции и энергия активации.

ABSTRACT

This article presents the results of experimental and kinetic studies on the general laws of the process of dissolution of gold in acid solutions of acetylthiourea, followed by the development of technology to extract metals from flotation tailings, including the kinetic laws of the process, the effect of temperature based on acetyltiourea leaching. Based on the kinetic experiments and calculations, the order of the chemical reaction, the reaction rate constant and the activation energy are determined.

Ключевые слова: ацетилтиомочевина, кинетика, температура, графический метод Вант-Гоффа, порядок химической реакции, константа скорость реакции и энергия активации.

Keywords: acetylthiourea, kinetics, temperature, graphical Vant-Hoff method, chemical reaction order, reaction rate constant and activation energy.

Ацетилтиомочевинное выщелачивание применяемое при выщелачивании хвостов флотации золото-сурьмяно-ртутных руд, является весьма сложным процессом [1, с. 7]. Проблемой данного способа является сложность подбора оптимальных

условий извлечения золота из продукта, удовлетворяющей требованием технологического процесса [2, с. 35]. Поэтому для строгой оптимизации процесса необходимы кинетические исследования.

Результаты по выщелачивание золота подробно освещены в соответствующих публикациях