# Preparation and Properties of the Chitosan/PVA Blend for Heavy Metals Chelation

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## Abstract:

Current research based on the use of extracted chitosan mixed with Polyvinyl alcohol to manufacture blend that can been used in water purification from heavy metals such as copper, this due to chitosan properties and its ability to chelation these metals because of the presence of the functional groups in their structure. The blend has been treated with borax to increase the viscosity, and then high density polyethylene granulated coated with polymer solution to increase the surface area for chelation. The ultraviolet test showed the efficiency of blend to chelation of copper ions through lower the copper ions absorbance peak after each stage where the solution of copper ions pass on the polymer blend containing chitosan.

**Keywords:** Biopolymers, Chitosan, Heavy metals, High density polyethylene, Polyvinyl alcohol, Viscosity, Ultraviolet.

## الخلاصة:

يستند البحث الحالي على مزج مستخلص الجتوسان مع البولي فينيل الكحول لتصنيع مزيج بوليمري يمكن استخدامه في عمليات تنقية المياه من المعادن الثقيلة مثل النحاس، وذلك لخواص الجتوسان وقابليته على اقتناص هذه المعادن بسبب وجود مجاميع فاعلة في تركيبه. المزيج البوليمري عولج بواسطة البوراكس لزيادة لزوجته، ولزيادة مساحة الاقتناص السطحية تم طلاء حبيبات من البولي اثلين العالي الكثافة بمحلول المزيج البوليمري. اختبار الاشعة الفوق البنفسجية اثبت كفاءة الجتوسان على اقتناص ايونات النحاس من خلال انخفاض بيك الامتصاصية لايونات النحاس بعد كل مرحلة يمرر فيها محلول ايونات النحاس على المزيج البوليمري المحتوي على الجتوسان.

**الكلمات المفتاحية:** بوليمرات حياتية، جتوسان، معادن ثقيلة، بولي اثلين عالي الكثافة، بولي فينيل الكحول، اللزوجة، الاشعة فوق البنفسجية.

## Introduction:

Pollutants like water, air and soil through their adverse effects on the environment caused by waste materials. It severity depends on several factors, such as chemical composition, concentration and its resistance to decomposition. Pollution can take the forms of air, light, littering, noise, soil contamination, radioactive contamination, thermal, visual and water pollution, and it may cause long- or short-term damage (Merriam, 2010).

There are several reasons of water pollution such as discharge of wastewater from commercial and industrial waste into surface waters, including agricultural runoff, which may contain chemical fertilizers and pesticides (West,2006). The water pollution is one of the serious problems to solved, and that caused many deaths, especially of children. The estimated number of deaths is more than 14,000 people daily (Kumar, 2013 ; Landis,2000). The wastewaters often contain amounts of toxic and polluting heavy metals such as Hg, Pb, Cr, Ni, Cu, Cd and Zn, which caused many problems when adsorbed by living organisms (Njoroge, 2000).

Heavy metals are metals that have bad effects on the environment and in general, that are greater density than iron, and include all the metals that have a toxic effect, such as lead, cadmium, antimony, mercury, cobalt, nickel, copper, zinc, arsenic, selenium, chromium, silver and thallium. The question that can be asked, what is the standard which it identifies heavy metal? Several criteria are used for this purpose, such as, density, atomic weight, atomic number, or periodic table position. Density (3.5 - 7 g/cm$^3$), atomic weight (22.98 – 40), atomic numbers (20 – 92) (Duffus, 2002; Sengupta, 2002).Heavy metals can cause large effects of on living organisms because

of the penetrated to various body tissues, which can cause cancer and inhibit the operation of the nervous or blood circulation (Pezzarossa, 2011).

Trace quantities of toxic metals ions in polluted water are difficult to be removed. Chitosan is one of these materials of biological origin that have the ability to absorb heavy metals due to the presence of has both hydroxyl and amine groups that can work as chelating sites, chitosan has been high efficiency of adsorption humic acid, proteins, dyes, metal ions and noble ions (Alan ,2006; Manfred, 2000).

Chitin $(C_8H_{13}O_5N)_n$ is a long-chain polymer a derivative of glucose, and is found in many organisms such as, fungi, crustaceans ( crabs, lobsters and shrimps), insects and squid. The structure of chitin is comparable to the polysaccharide cellulose, forming crystalline nanofibrils or whiskers. Chitin is useful for several medical and industrial application. Chitin can used in many processes such as in food processing include the formation edible films and as an additive to thicken and stabilize foods and pharmaceuticals, also used as a binder in dyes, fabrics, and adhesives, industrial separation membranes and ion-exchange media (Shahidi, 1999; Gaellstedt, 2005), its structure is shown in figure (1) (Jolanta ,2010).

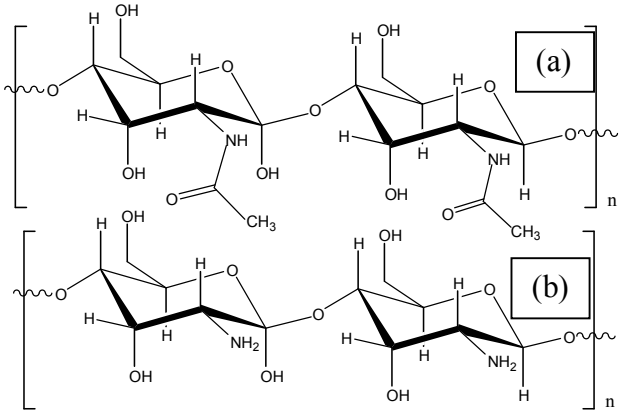


Figure (1) Structure of the (a) chitin (b) chitosan (Jolanta, 2010).

Chitosan is a linear polysaccharide . It was made by treating chitin with the alkali sodium hydroxide to remove acetyl groups of chitin by process called deacetylation, to obtain a soluble product, chitosan structure shown in figure (1).

Chitosan has a number of commercial and biomedical uses. It can been used in agriculture, winemaking, self-healing polyurethane paint coating, bandages to reduce bleeding and as an antibacterial agent, drugs deliver through the skin and use in limiting fat absorption, which would make it useful for dieting.

Chitosan can also been used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to binding together and is subsequently removing with the sediment during sand filtration. It also removes phosphorus, heavy minerals, and oils from the water. Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone, while the chitosan with sand filtration removes up to 99% turbidity (Wan Ngah, 2008).

The polyvinyl alcohol is a nontoxic water-soluble synthetic polymer, white (colourless) and odorless. Polyvinyl alcohol used in textiles, papermaking and coatings (Gert, 1996). Polyvinyl alcohol has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvents. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties.

The current research a simple contribution in this field, using a natural material was extracted from husks of fish, which considered an available and cheap biomaterial. PVA has been chosen as a medium to carry the chitosan to improve heavy metal chelation efficiency. Borax added to PVA as cross-linking agent to reduce polymer solubility in water and chitosan disparcity.

## 2. Material and methods:

2.1. Materials:

Chitin a laboratory extraction according to the method described in source (Sura, 2014), as it was been extracted from the fish scales and after the extraction process, convert the chitin to chitosan by using sodium hydroxide with a heat. PVA obtained from company. Borax obtained from BDH chemicals lit. Poole England and High density polyethylene was obtained from Sabic Company, Saudi Arabia.

2.2. Preparation of chitosan / PVA solution:

Chitosan solution was prepared by dissolving 8g of chitosan into 100 ml of 5% (v/v) acetic acid solution at 70 $^{o}$C by using magnetic stirrer, the chitosan solution was left 24 hrs at room temperature. Preparing 6% solution of polyvinyl alcohol in distilled water and agitated on a magnetic stirrer at about 500 rpm at 70 ◦C for 5 hrs. The two prepared solutions mixed by using magnetic stirrer at about 500 rpm at 70 ◦C for 2 hrs and then lift 48 hrs under room temperature for homogeneity (Wan, 2004). Borax solution (4% in distilled water) was used as a thicker materials to convert chitosan / PVA solution to gel blend, dropping 5ml of borax solution to chitosan / PVA solution, stirring until most of it is dissolved and obtained homogenies solution.

2.3. HDPE beds Coating:

To increasing absorption area the HDPE beds coated by the blend solution, HDPE beds immersed in ethanol to remove any impurities and fats then washed carefully by distilled water and dried at room temperature. The beds immersed in blend solution for 30 min at room temperature, removed the reminding blend solution and drying the coated beds.

2.4. Preparation of Cu (II) ions solutions:

The stock solution of 1,000 mg/L Cu(II) was prepared by dissolving 1 g of copper metal supplied by BDH Chemicals lit. Poole England in 10 ml of concentrated nitric acid. After the copper metal dissolved, the solution powered on 1 L distilled water (Fan Zhao, 2007).

## 3. Results & Discussion:

In this paragraph has been discussing the proposed structures resulting from the chitosan/ PVA mixing process and cross-linking structure by adding borax to the above blend. They also discussed the results of some tests that determine the efficiency of the blend in the chelation of the metal ions from aqueous solutions such as UV, FTIR and viscosity test.

3.1 Chitosan/ PVA Blend:

The presence of OH groups in both polymers leads to hydrogen bond formation, which caused chemical interactions between them. These proposal interactions, which convert the polymers solutions to gel like, as shown in, figure (2).

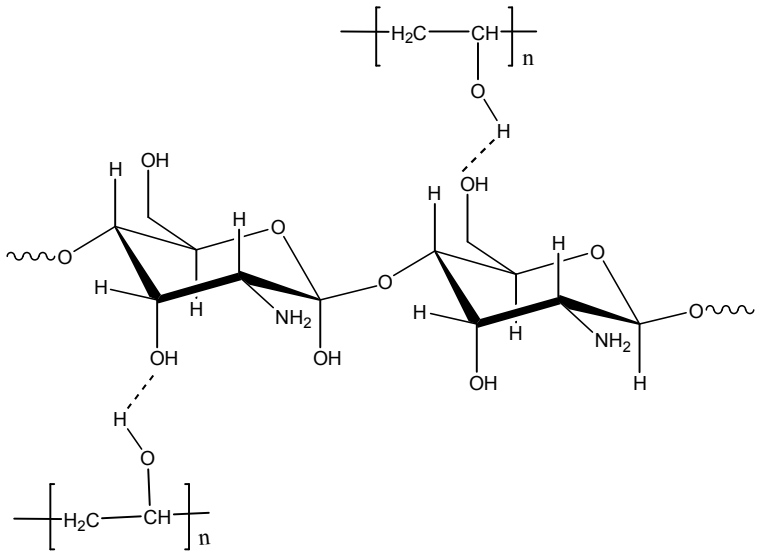

Figure (2) Proposed Structure of Chitosan/ PVA blend.

The polymer solution treated with borax to make more viscous solution, so that it can be used as a surface coating for polyethylene granules, in water borax dissolves to form the borate anion, a boron atom surrounded by OH (hydroxyl) groups , it leads to be cross-linking by hydrogen bonds formation, which increases the polymer solution viscosity, as shown in figure (3).

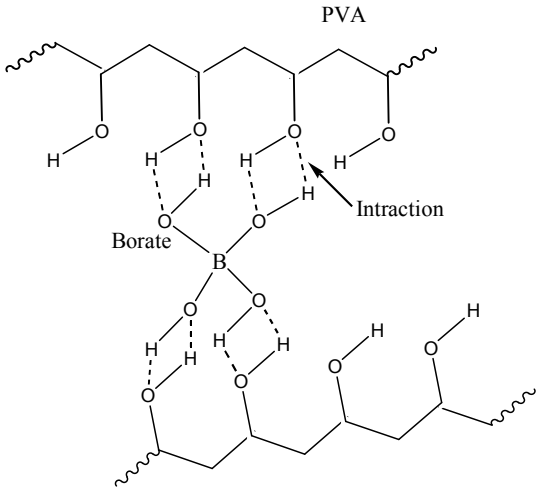


Figure (3) Borate cross-linked polyvinyl alcohol polymer (Fan Zhao, 2007).

3.2 $Cu^{++}$ Chelation:

The mechanism of copper ions chelation can thought that, shared four groups of amino or hydroxyl in chitosan to chelation copper ions from aqueous solution as shown in proposal figure (4).

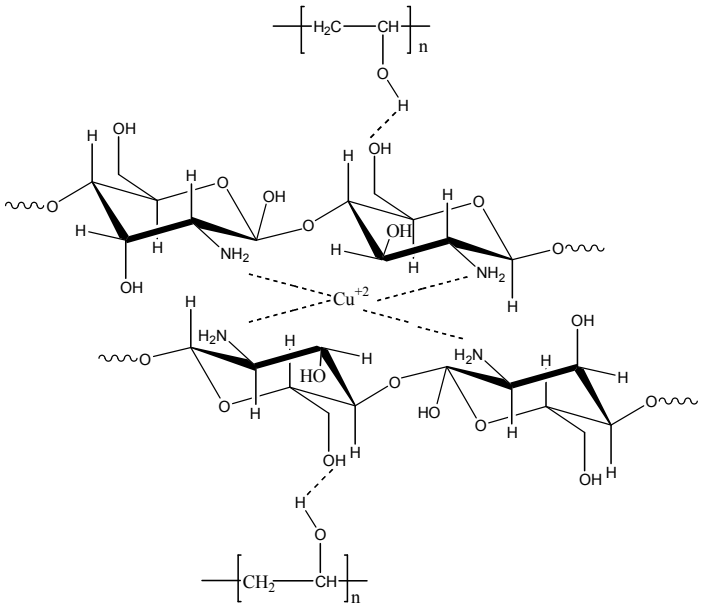


Figure (4) Proposed Structure of Chelation of Chitosan with Copper Ion.

3.3 Viscosity Test:

The viscosity device type brookfield viscometer (model, DV-III ULTRA PROGRAMBAL RHOMETER) achieved this test. Results showed that, a viscosity of polymer solutions increase with addition of PVA, and a larger increase after the addition of borax, this due to cross-linking as explained above, and as shown in Figure (5).

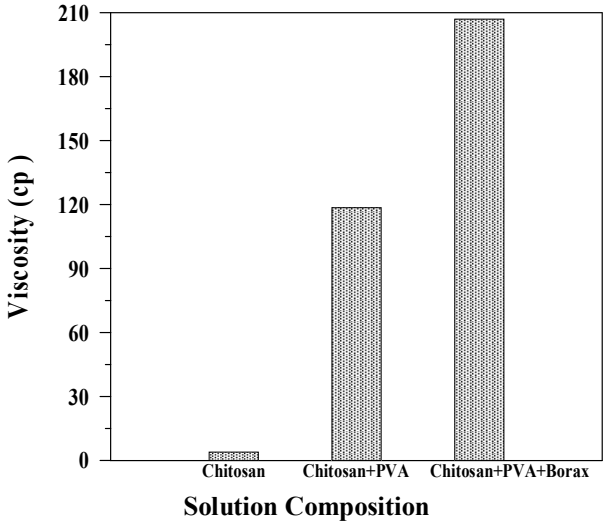


Figure (5) Viscosity of polymers solutions.

3.4 Tensile Test:

The samples test according to ASTM D638-IV and the universal testing machine (model WDW 5 E) was used for testing with test rate 0.5 mm/min. The mechanical properties of the PVA/Chitosan blend are significantly increased compared to those of the pure PVA, the chitosan enhanced the tensile strength of the PVA this due to strong hydrogen bonding between them. The elongation at break is decreased by the same reason that caused restricted and hardly sliding polymer chins, as shown in figure (6).

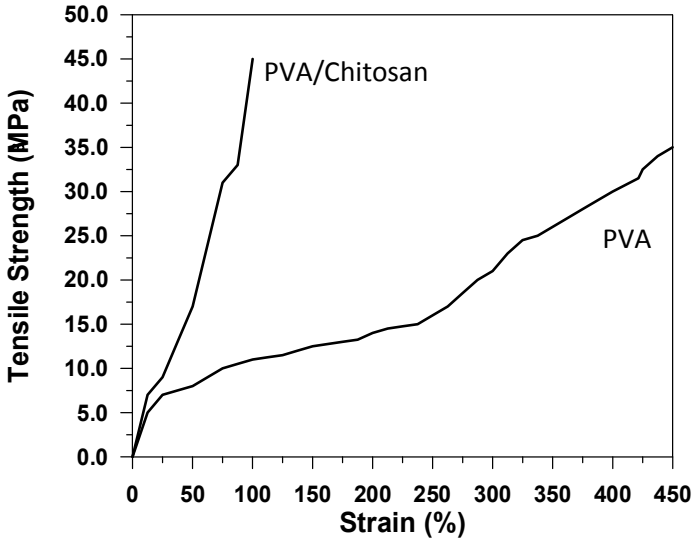


Figure (6) Stress- Strain Curve of PVA and PVA/Chitosan blend.

3.5 UV Test:

Shimadzu UV Prob 2.34 was use in this test. The maximum absorption for the copper solutions is at range 600-950 nm. The test solution absorbs strongly in the red regions of the visible spectrum, which confirms the blue-color that we see as it transmits light of only that color or absorbs light of a complementary color (John, 2008).

Figure (7) shows the results of an ultraviolet radiation test. The results show absorption beaks at wavelength 804 nm this beak due to the presence of copper ions dissolved in water and the absorption value was 1.052 for the solution of copper before passed it on the blend beds. This absorption value decreases after passing ions copper solution on the polymer beads and disappear completely after 5 cycles (each cycle requires one minute for the passage of the solution through the beads). This a clear evidence of the disappearance of these ions due to catching by chitosan molecules.

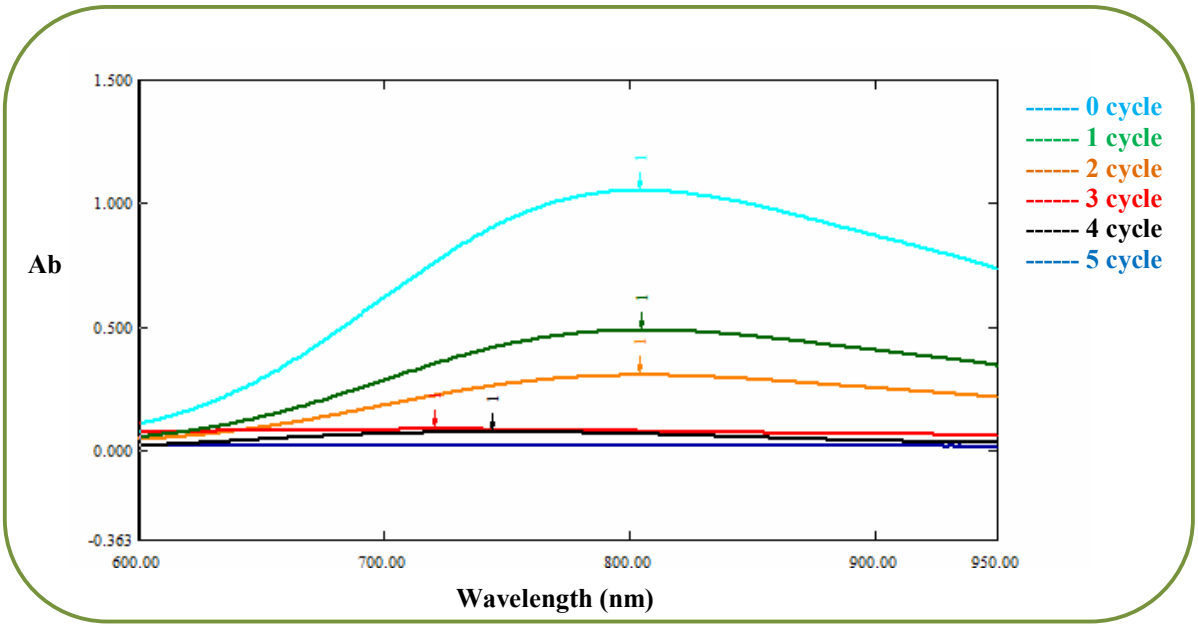


Figure (7) UV Test of polymers solutions.

3.5 Atomic Absorption Test:

Atomic absorption Spectrophotometer is a spectroanalytical procedure for the quantitative determination of chemical elements. Atomic Absorption Spectrophotometer type (AA320N, Hanker, Hongkong) was used. Standard solution was prepared by using high-purity of ($CuSO_4$) which dissolved in deionized water. Four blanks prepared for calibration with concentration (2, 4, 4, 8) ppm.

The copper concentration decrease with increased number of cycles (The number of times the contaminated water passes through the chitosan granules), this due to chelation of copper ions. Figure (8) shows the initial copper concentration is 110.25 ppm while became 96.55 ppm after treated with chitosan. This is evidence of the efficiency of chitosan to chelation this ions from contaminated water and purifying it from heavy metals.

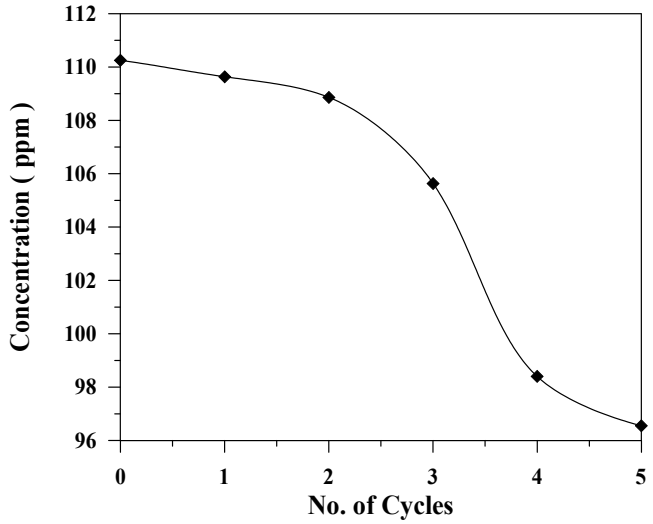


Figure (8) Atomic Absorption Test of Polymers Solutions.

Conclusion:

The current research demonstrates the preparation of polymeric blend from chitosan (prepared from a natural source) and polyvinyl alcohol to be used in the purification of polluted water with heavy metals, so by taking advantage of adsorption property of chitosan. Results proved good scalability of the blend on the adsorption of copper ions, proved this by the UV test, lowering the copper ions absorption beck with each stage where the water passes on the blend, evidence of the efficiency of the chitosan on the adsorption of heavy metals. This result is confirmed by atomic absorption test, which showed similar results.

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