# A Study on Sustainable Adsorbents for Heavy Metals Removal

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**Abstract.** Adsorption techniques are widely used in the treatment of wastewater for the removal of heavy metals. These days the extensively used adsorbent is activated carbon, which can be extracted from various agricultural by-products such as walnut shells, groundnut shells, coconut shells, which gives best results in treating heavy metals. But the process of obtaining activated carbon into its finite form and regeneration requires high cost. In the era of advanced development, the world at present faces the scarcity of freshwater resources; it is essential to examine other possibilities that decrease the burden on existing resources. Furthermore, because heavy metals are hazardous even at trace levels, an environmentally safe removal technique required the use of inexpensive adsorbents. Adsorption has acquired popularity as a low-cost waste disposal method. The adsorption process and the many adsorbent kinds that are now on the market are the main topics of this chapter. It also includes low-cost adsorbents that explain the adsorption reaction situation, such as industrial and agricultural waste. When choosing adsorbents, the following factors are important: cost-effectiveness, technological application, and ease of access to raw materials with minimal adverse effects on the system. The chapter is interested in that it discusses a variety of adsorbents and how well they remove heavy metals from wastewater.

## 1. INTRODUCTION

Toxic elements such as Zn, Fe, Cu, Cr, Hg, Pb, Ni, Co, and others with specific gravities greater than 5g/cm3 are known as heavy metals. Soil erosion, rock weathering, and volcanic processes are the primary natural sources of heavy metals. Contrarily, industrial processes such as mining, metal processing, chemical fertilizers, dye manufacture, and fuel burning are examples of anthropogenic sources. Because heavy metals are resistant, non-biodegradable, and highly mobile in aqueous conditions, they tend to accumulate in soils and living things, which can have an adverse effect on the environment. Plants absorb heavy metals, which bio magnify through animal and human food chains and have major detrimental health effects since they are carcinogenic.
The USEPA's maximum contamination level (MCL) in drinking water is listed in Table 1, along with the detrimental consequences of each contaminant.

**Table 1. Harmful Effects of Heavy Metal**

| S. No. | Heavy Metal | MCL (mg/L) | Harmful effects |
|---|---|---|---|
| **1** | Zn | 0.80 | Skin irritation, nausea, depression, anemia, neurological symptoms |
| **2** | Hg | $3.0 \times 10^{-5}$ | Neurotoxin, Kidney dysfunction, Circulatory & Neurological Disorder |

| | | | |
|---|---|---|---|
| **3** | Pb | 6.0 X $10^{-3}$ | Central Nervous System Damage, Cerebral Disorders, Kidney, Liver Reproductive System Dysfunction |
| **4** | Ni | 0.20 | Carcinogen, Dermatitis, Gastrointestinal Disorder, Lung, Kidney Damage |
| **5** | Cu | 0.25 | Liver Damage, Convulsions, Insomnia |
| **6** | Cr | 0.05 | Carcinogen, Nausea, Diarrhea |
| **7** | Cd | 0.01 | Carcinogen, Kidney Dysfunction |
| **8** | As | 0.05 | Skin Problems, Visceral Cancer |

**Table 1.** Harmful Effects of Heavy Metal

Heavy metals are extremely persistent in the environment due to their strong propensity to form complexes, high reactivity, and elevated metabolic activity. They can concentrate on soil and water resources and are carried by aqueous media. Because of this, they pose a serious threat to the ecosystem and all living species. Therefore, to avoid more negative effects, these hazardous metals must be eliminated from wastewater before to discharge. Heavy metals have been eliminated from wastewater using conventional techniques including membrane filtration, chemical precipitation, ion exchange, etc. However, these techniques have several drawbacks, such as low effectiveness, high energy consumption, harmful chemical precipitation, cost inefficiency, etc.
It is an economical and effective method for removing heavy metals from wastewater. Another benefit of the adsorption process is that it is frequently reversible, meaning that the adsorbent can be recycled back into use. The effectiveness of adsorbents is influenced by numerous variables, including temperature, pH, initial concentration, contact time, and rotation speed.

### 1a. Overview of adsorption process

A solution containing the adsorbate is adsorbed on the surface of an adsorbent in a process known as adsorption. There are two types of adsorption phenomena: chemisorption, which happens when the adsorbate and adsorbent undergo chemical interactions, and physiosorption, in which the adsorbate attaches to the adsorbent because of van der Waals forces. Chemisorption is irreversible, selective, and exothermic, whereas physiosorption is weak, reversible, and typically endothermic.

### 1b. Models and adsorption isotherms

The amount of solute adsorbed on the adsorbent surface per unit weight as a function of equilibrium concentration at a certain temperature is estimated via adsorption isotherms. The adsorption process is described by the most widely used Langmuir and Freundlich isotherms. Additional models like Redlich and Peterson, Radke and Prausnitz, Sips, Toth, and Koble and Corrigan are also utilized.

### 1c. Adsorbent types

Usually, adsorbents are categorized as either natural or synthetic based on where they come from. Clays, minerals, charcoal, ores, and zeolites are examples of natural adsorbents. On the other hand, waste sludge, industrial waste, and agricultural waste are used to make synthetic adsorbents.

## 2. DETECTION OF HEAVY METALS IN WASTEWATER

### LIMIT TESTS

Limit tests are quantitative or semi-quantitative procedures used to regulate trace amounts of inorganic contaminants that are anticipated to be found in pharmaceutical products. The Indian pharmacopeia's individual monograph of medicinal substances includes information on the official tests for limit testing for arsenic, heavy metals, lead, iron, sulphates, and chlorides.

In terms of parts per million (ppm ≡ 1 µg ≡ 10–6g), the impurity limit is given.

In these tests, the test opalescence, turbidity, colour, and stain obtained by reacting a specific quantity of test sample (pharmaceutical substance) with the reagent are compared to the standard opalescence, turbidity, colour, and stain obtained by reacting a known quantity of impurity with the reagent. As a result, limit tests are comparison assessments that require the simultaneous preparation of the test and the standard under identical circumstances. The reaction is slow and sensitive since the reagents are diluted solutions. Furthermore, a less specific reagent should be chosen to achieve limits of many probable contaminants.

Nessler cylinders are used for both the test and the standard in limit tests for iron, heavy metals, sulphates, and chlorides. Nessler cylinders are identical clear, colourless glass tubes with a flat, transparent base and a consistent internal diameter. They have a 50 ml nominal capacity and are made of transparent glass. About 150 mm is the total height, 110 to 124 mm is the external height to the 50 ml mark, 1.0 to 1.5 mm is the wall thickness, and 1.5 to 3.0 mm is the base thickness. The cylinders used for a test must have an exterior height variation of no more than 1mm from the 50 ml mark.

Note:

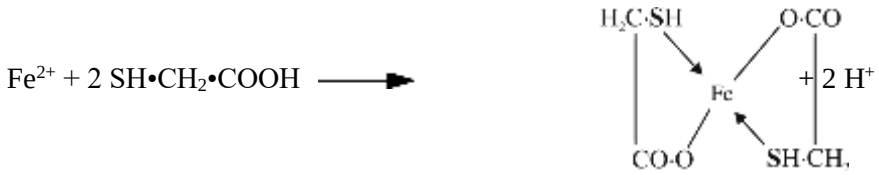
- When conducting limit tests, special adjustments should be made, particularly when dealing with medicinal compounds that are coloured and insoluble. In case of insoluble pharmaceutical ingredients (ex: activated charcoal), it is properly extracted with boiling water and afterward the water is used for performing limit tests. Coloured medicinal compounds (such potassium permanganate) undergo chemical treatment, such as ethyl alcohol, to eliminate the colour before a limit test is conducted. Additionally, keep in mind that each pharmaceutical substance has a predetermined limit of impurity, but each monograph specifies the quantity of pharmaceutical substances to be examined for the limit test.
- As instructed in monographs, use the sample straight away if it is liquid or in solution form.
- Add a small amount of a standard impurity to the test sample and run the test if a test sample needs to be produced to fail the limit test for a specific impurity.
- A non-clear solution is called a turbid solution. Opalescence is a colour shift.
- Choose identical Nessler cylinders that are similar to one another and keep them close to one another. The distance between the 50 ml marks on the two cylinders should not be greater than 1 mm.

### 2a. LIMIT TEST FOR IRON

Principle: The experiment's basic idea is to compare the standard colour, which is produced by reacting a known amount of iron with mercaptoacetic acid, with the test colour, which is purple and results from the reaction of iron impurities with thioglycolic acid.

If there are any metal cations present, they are complexed with citric acid (iron-free).

2 Fe2+ + HOOC•CH2•S•S•CH2• COOH + 2 H+ 2 Fe3+ + 2 SH•CH2•COOH




Ferrous Mercapto acetate/ Ferrous thioglycolate

Thioglycolic acid functions as a reducing agent and transforms any Fe3+ into Fe2+ in addition to establishing a compound with Fe2+. When citric acid is present, the ferrous mercapto acetate that is produced takes on a purple hue. Apart from the creation of metal complexes other than iron, citric acid also creates ammonium citrate buffer, which stabilizes the complex created when ammonia is added to make it alkaline.

**Test colour:** Transfer the provided sample to a Nessler cylinder after dissolving it in 20 millilitres of water. Add 0.1 ml of thioglycolic acid and 2 ml of a 20% w/v solution of iron-free citric acid, stir, make alkaline with iron-free ammonia solution, dilute to 50 ml with water, let stand for 5 minutes, and check the colour transversely.

**Standard colour**: Fill a Nessler cylinder with 2.0 ml of iron standard solution (20 ppm Fe). Use 20 ml of water to dilute. Make an alkaline solution using iron-free ammonia solution, add 2 ml of a 20% w/v solution of iron-free citric acid and 0.1 ml of thioglycolic acid, mix, dilute to 50 ml with water, let stand for 5 minutes, and check the colour transversely.

**Reagent Preparation**

- 0.05 M sulphuric acid: To make solutions of any molarity xM, carefully add 54 ml of sulphuric acid to an equal volume of water, then dilute with water to make 1000 ml.
- 20% w/v iron-free citric acid: In 100 millilitres of water, dissolve 20 grams of iron-free citric acid.
- Iron-free ammonia solution: This solution has around 10% w/w of iron-free NH3. Make 1000 ml by diluting 425 ml of strong ammonia solution.
- 20 ppm Fe iron standard solution: Ten litres of water should be added to one volume of a 0.1726% w/v solution of ferric ammonium sulphate in 0.05 M sulphuric acid. Includes iron in its ferric form.

**Table. 2 Iron Content Determination**

| **Test solution** | **Standard solution** |
|---|---|
| Transfer the provided sample into Nessler's cylinder after dissolving it in 20 millilitres of water. | Fill a Nessler's cylinder with 2.0 ml of iron standard solution (20 ppm Fe). |
| Include 2 millilitres of 20% w/v iron-free citric acid. | Include 2 millilitres of 20% w/v iron-free citric acid. |
| Include one millilitre of thioglycolic acid. | Include one millilitre of thioglycolic acid. |
| Next, use an iron-free ammonia solution to turn the solution alkaline. | Next, use an iron-free ammonia solution to turn the solution alkaline. |
| Watch the colour transversely after diluting to 50 ml of water and letting it stand for five minutes. | Watch the colour transversely after diluting to 50 ml of water and letting it stand for five |

| | |
|---|---|
| | minutes. |

**Observation**

Compared to the standard colour, the test colour is not more vivid.
The test colour is more intense than the standard colour.

**Result**

If compared to the standard colour, the test colour is not more vivid. Then the provided sample passes the limit test.
Else the test colour is more intense than the standard colour. The provided sample does not pass the iron limit test.

**2b. Limit Test for Lead**

Principle: It is to compare the test colour in the chloroform layer, which is produced when lead impurities react with diphenyl thiocarbazone (dithizone), with the standard colour in the chloroform layer, which is produced when a known amount of lead reacts with diphenyl thiocarbazone (dithizone). Lead is extracted from an alkaline aqueous solution as the violet-coloured lead dithizone complex by dithizone in chloroform. In this experiment, any interfering metal ions (apart from lead) are extracted and disposed of in the form of complex at the ideal pH using ammonium citrate, potassium cyanide, and hydroxyl amine hydrochloride. Lead-dithizone exhibits a violet colour in chloroform, whereas the original dithizone is green. The amount of lead in the solution determines how intense the colour is. Here, the sample is dissolved in water and the reagents are added according to the protocol so that the dithizone extract solution can be extracted. After separating the dithizone extract solution from the water layer (in chloroform), the organic layer is separated from the aqueous layer and a fresh dithizone extract solution is added to the sample solution that was previously extracted.
The first layer is joined with the organic layer, also known as the di-thizone lead complex layer. The extraction process is carried out repeatedly until the freshly drawn di-thizone extract solution does not turn violet when extracted with the sample solution, signifying that all the lead has been removed. To extract the lead from the chloroform layer into the aqueous layer by creating lead nitrate (soluble in water), all the combined chloroform layers containing the lead-thizone complex (violet) are now removed using an aqueous solution of nitric acid. Since the lead is no longer in the organic layer following nitric acid extraction, the combined di-thizone
Now, precisely 5 millilitres of dithizone standard solution are used to extract the aqueous solution, which is then separated and compared to the standard solution. It is important to remember that the amount of di-thizone extract solution used for extraction does not have to be precise; nonetheless, 5 millilitres of di-thizone standard solution must be taken to compare colours. extraction solutions can be thrown away.

**Procedure**

**Test colour**: As directed in the monograph, dissolve the provided sample in water, then transfer it to a separator. Add 2 millilitres of hydroxyl amine hydrochloride solution Sp. and 6 millilitres of ammonium citrate solution Sp. After adding two drops of phenol red solution, add strong ammonia solution to make the solution only alkaline (red). If required, chill the mixture before adding two millilitres of potassium cyanide solution Sp. Extract the solution right away using multiple amounts, each containing five millilitres of

dithizone extraction solution. Drain each extract onto a separate funnel until the solution maintains its green hue. Discard the chloroform layer after shaking the combined dithizone solutions for 30 seconds with 30 millilitres of a 1% v/v nitric acid solution. Add precisely 5 millilitres of the dithizone standard solution to the acid solution, then shake for 30 seconds. Take note of the chloroform layer's colour.

**Standard colour:** Fill a separator with a volume of lead standard solution (1 ppm Pb) equal to the quantity of lead allowed in the material under investigation. Then, add 2 ml of hydroxyl amine hydrochloride solution Sp. and 6 ml of ammonium citrate solution Sp. After adding two drops of phenol red solution, add strong ammonia solution to make the solution only alkaline (red). If required, chill the mixture before adding two millilitres of potassium cyanide solution Sp. Extract the solution right away using multiple amounts, each containing five millilitres of dithizone extraction solution. Drain each extract onto a separate funnel until the solution maintains its green hue. Discard the chloroform layer after shaking the combined dithizone solutions for 30 seconds with 30 millilitres of a 1% v/v nitric acid solution. Add precisely 5 millilitres of the dithizone standard solution to the acid solution, then shake for 30 seconds. Take note of the chloroform layer's colour.

| **Table. 3 Lead Content DeterminationTest solution** | **Standard solution** |
|---|---|
| 1. After dissolving the necessary amount of sample in water, it is moved into a separating funnel. | 1. Transfer required amount of lead standard solution<br>(1 ppm lead) equivalent to the amount of lead permitted in the substance being examined into a separating funnel |
| 2. Include 6 ml of solution of ammonium citrate (Sp). | 2. Add 6 ml of ammonium citrate solution (Sp). |
| 3. Include two drops of phenol red solution together with two millilitres of hydroxylamine hydrochloride solution (Sp). | 3. Add 2 ml of hydroxyl amine hydrochloride solution (Sp), and add two drops of phenol red solution. |
| 4. Add strong ammonia solutions to make the solution just alkaline, and if needed, chill it. | 4. Make the solution just alkaline by the addition of strong ammonia solution to cool it if necessary. |
| 5. Include 2 ml of solution of potassium cyanide (Sp). | 5. Add 2 ml of potassium cyanide solution (Sp). |
| 6. Extract right away using multiple amounts of 5 ml of dithizone extraction solution till it becomes green. | 6. Extract immediately with several quantities, each of 5 ml of dithizone extraction solution until it becomes green. |
| 7. Mix the dithizone extracts with 30 millilitres of a 1% v/v nitric acid solution, shake for 30 seconds, and then discard the chloroform layer. Lead nitrate stays in the aqueous layer, while dithizone stays in the chloroform layer. | 7. Combine the dithizone extracts and shaken for 30 seconds with 30 ml of 1 % v/v solution of nitric acid and discard the chloroform layer (dithizone remains in chloroform layer, lead nitrate in aqueous layer). |
| 8. Add 5 millilitres of standard dithizone solution to this acid solution. | 8. Add 5 millilitres of standard dithizone solution to this acid solution. |

| | |
|---|---|
| 9. After 30 minutes of vigorous shaking, check the colour of the chloroform layer. | 9. After 30 minutes of vigorous shaking, check the colour of the chloroform layer. |

**Obse**

**rvation**

The standard colour of the chloroform layer is not more vivid than the test colour.
The chloroform layer's test colour is more vivid than its typical colour.

**Result**

If the standard colour of the chloroform layer is not more vivid than the test colour. Then the provided sample passes the lead limit test.
Else the chloroform layer's test colour is more vivid than its typical colour. The provided sample does not pass the lead limit test.

**Reagent Preparation**

1. 1% v/v nitric acid: Use water to dilute one volume of nitric acid to one hundred volumes.
2. A solution of ammonium citrate Sp: In 90 millilitres of water, dissolve 40 grams of citric acid. Then, add two drops of phenol red solution. Finally, gradually add strong ammonia solution until the solution turns reddish. Remove any lead that may be present by extracting the solution using 30 ml increments of dithizone extraction solution until the orange-green colour of the dithizone solution is retained.
3. Dithizone extraction solution: Add 5 ml of 95% ethanol after dissolving 30 mg of dithizone in 1000 ml of chloroform. The solution should be kept refrigerated. Before using, shake an appropriate amount of the solution with roughly half as much nitric acid (1% v/v) solution, then throw away the acid.
4. Dithizone standard solution: Mix 1000 millilitres of chloroform with 10 milligrams of dithizone. The solution should be kept in a refrigerator in a glass-stoppered, lead-free, light-resistant bottle.
5. Solution of hydroxyl amine hydrochloride Sp: Make roughly 65 ml by dissolving 20 g of hydroxyl amine hydrochloride in enough water. To make the solution yellow, move it to a separator and add five drops of thymol blue solution and strong ammonia solution. After adding 10 millilitres of a 4% w/v sodium di-ethyl-di-thio carbonate solution, let it stand for five minutes. Add 10 millilitres of chloroform at a time until a 5-milliliter piece of the extract does not turn yellow when agitated with a diluted cupric sulphate solution. After adding diluted hydrochloric acid until the solution becomes pink, add enough water to make 100 millilitres.
6. Lead standard solution (0.1% Pb): Make 250.0 ml by dissolving 0.400 g of lead nitrate in water with 2 ml of nitric acid and adding enough water.
7. 1 ppm Pb lead standard solution: One volume of the lead standard solution (10 ppm Pb) should be diluted with ten litres of water. 8. Lead standard solution (10 parts per million Pb): Use water to dilute 1 volume of lead standard solution (100 parts per million Pb) to 10 volumes.
8. 100 ppm Pb lead standard solution: dilute 1 volume of 0.1% Pb lead standard solution with 10 litres of water. A solution of potassium cyanide. Sp: Make 100 ml by dissolving 50 g of potassium cyanide. in enough water. Using consecutive amounts of 20 millilitres of dithizone extraction solution, remove the lead from this solution until the dithizone solution maintains its orange-green hue. Shake with chloroform to remove any dithizone that is still present in the cyanide solution. This cyanide solution should be diluted with enough water to yield a solution that contains

10 g of potassium cyanide per 100 ml.

**2c. Limit Test for Arsenic**

Principle: In this experiment, a known quantity of arsenic (in the form of arsine gas) is reacted with mercuric chloride to create a standard stain, which is then compared to the test stain produced by reacting arsenic impurities in the form of arsine gas with mercuric chloride (paper).
The limit test is conducted using a specifically made device. The mercuric chloride paper also develops a yellow or brown stain due to the formation of AsH (HgBr)2, As (HgBr), and As2Hg3.

$H_3AsO_4 \longrightarrow H_3AsO_3$

Arsenic acid Arsenous acid

Here, the arsenic that is present is changed into arsenic acid. Arsenous acid is subsequently produced by reducing the arsenic acid. Arsenous acid is reduced to arsine gas by the nascent hydrogen created when zinc and hydrochloric acid combine.

$H_3AsO_3 + 3\,H_2 \longrightarrow AsH_3\uparrow + 3\,H_2O$

Traces of hydrogen sulphide, which are created when sulphide impurities are present, are eliminated from hydrogen gas and arsine using lead acetate cotton.

$Pb(CH_3COO)_2 + H_2S \longrightarrow PbS\downarrow + 2\,CH_3COOH$

The Gutzeit method (modified) is the name of the technique.
For the consistent and continuous release of hydrogen gas from zinc, stabilized hydrochloric acid is utilised. Tin creates a Sn/Zn couple and speeds up the reaction between zinc and hydrochloric acid because zinc is not particularly reactive with it.
Arsenic (As5+) is reduced to arsenous (As3+) by stannous chloride, which is found in stannated hydrochloric acid. The released hydrogen gas also serves as an arsine carrier gas.

In an arsenic apparatus, a side hole at the tube's bottom end keeps condensed liquid from being pushed up the tube by the hydrogen pressure, preventing blocking. To convert arsenic to arsenous, potassium iodide is also added.

**Description of the Apparatus**
The apparatus (shown in the figure) is made up of a glass tube that is around 20 cm by 5 mm and is sealed with a rubber or ground-glass stopper. The bottle or conical flask holds 100 ml. A lateral aperture with a diameter of 2 to 3 mm is located 15 mm from the tube's tip, while the bottom portion is pulled to an internal diameter of 1.0 mm. The lateral opening should be at least 3 mm below the stopper's bottom surface when the tube is in place.
At right angles to the tube's axis, the upper end of the tube features a flawlessly smooth surface. Two spiral springs or clips secure a second glass tube that is 30 mm long, has a comparable flat surface, and has the same internal diameter as the first. Put 50–60 mg of loosely packed lead acetate cotton or a small cotton plug and a 50–60 mg rolled piece of lead acetate paper into the lower tube. A disc or a little square of mercuric chloride paper, large enough to cover the tube's aperture (15 mm x 15 mm), should be placed between the tubes' flat surfaces.
**Procedure**

Test stain: Transfer the provided sample into the arsenic apparatus bottle after dissolving it in 50 millilitres of water and adding 10 millilitres of stannated hydrochloric acid. Add 10 g of zinc AST and 5 ml of potassium iodide (1 M). As soon as possible, put the equipment together and submerge the bottle in a water bath that is heated to a temperature that maintains a consistent gas evolution. Examine the stain that forms on the mercuric chloride paper after 40 minutes.

Standard stain: Fill an arsenic apparatus bottle with 1.0 ml of the arsenic standard solution, then dilute it with 50 ml of water. 10 ml of stannated hydrochloric acid should be added. Add 10 g of zinc AsT and 5 ml of potassium iodide (1 M). As soon as possible, put the equipment together and submerge the bottle in a water bath that is heated to a temperature that maintains a consistent gas evolution. Examine the stain that forms on the mercuric chloride paper after 40 minutes.

**Observation**

Compared to ordinary stain, the test stain is not more intense.

The intensity of the test stain is higher than that of the regular stain.

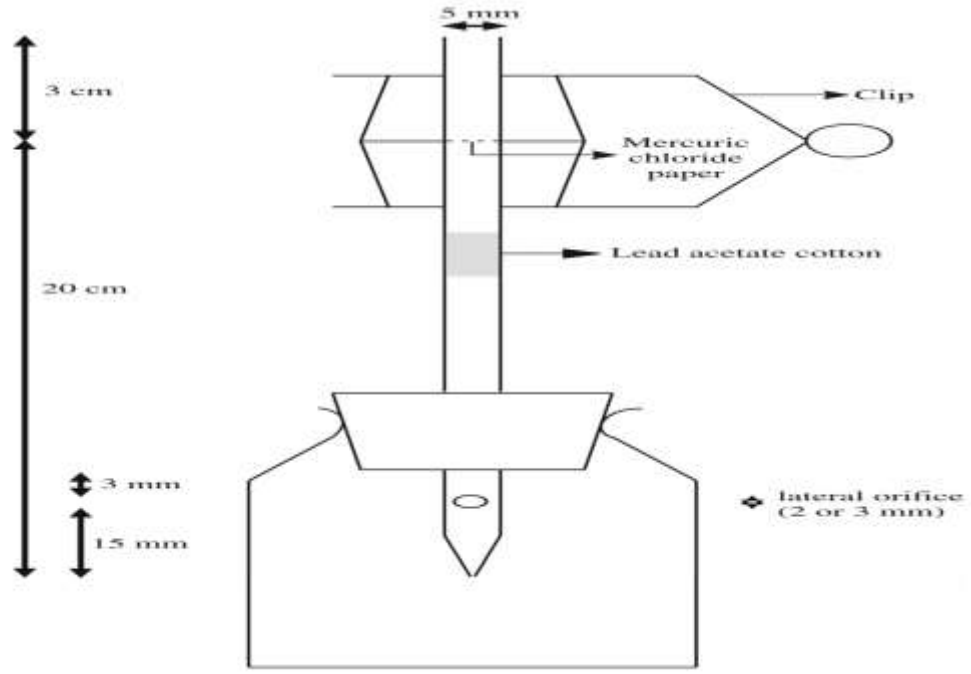



**Figure-1: Diagram of Arsenic Apparatus**

**Result**

If compared to ordinary stain, the test stain is not more intense. Then the provided sample passes the arsenic limit test. Else the intensity of the test stain is higher than that of the regular stain. The provided sample does not pass the arsenic limit test.

**Reagent preparation**

1. 1M potassium iodide: Make 1000 ml by dissolving 166.0 g of potassium iodide in enough water.
2. 2 M sodium hydroxide: 40x sodium hydroxide can be dissolved in enough water to yield 1000 ml of solution, which can have any molarity xM.

3. Standard solution of arsenic (10 ppm As): In 5 millilitres of 2 M sodium hydroxide, dissolve 0.330 grams of arsenic trioxide, then dilute with water to 250.0 millilitres. Use water to dilute one volume of this solution to one hundred volumes.
4. Lead acetate cotton: Soak absorbent cotton in a solution of led acetate (10 volumes) and 2 M acetic acid
5. (1 volume). Without pressing the cotton, spread the liquid on multiple layers of filter paper to drain off any extra. At room temperature, let it dry. Keep in containers that are well sealed.
6. Lead acetate paper: Make the impregnated paper using the lead acetate solution, and then dry it at 100 degrees without coming into contact with any metal.
7. Lead acetate solution: A 10.0% w/v lead acetate solution in water devoid of carbon dioxide.
8. Mercuric chloride paper: White filter paper that is smooth and at least 25 mm wide, soaked in a saturated solution of mercuric chloride, pressed to remove excess solution, and then placed in a dark environment to dry at around 60˚. The filter paper grade is such that its weight ranges from 65 to 120 g per square meter; the thickness of 400 sheets, measured in millimetres, is roughly equivalent to its weight in grams per square meter.
9. Stannated hydrochloric acid: This low-arsenic hydrochloric acid can be made commercially or by mixing one millilitre of stannous chloride solution AsT with one hundred millilitres of hydrochloric acid AsT.
10. Solution of sodium chloride AsT: A low-arsenic stannous chloride solution that can be purchased commercially or made by adding an equivalent volume of hydrochloric acid AsT to stannous chloride solution, boiling it to its original volume, and then filtering it through fine-grain filter paper.

Note: When dealing with liquids, use the sample directly.

**2d. Limit Test for various Heavy Metals**

Principle: To compare the colour of the test, which is produced when heavy metal impurities react with a saturated solution of hydrogen sulphide, with the colour of the standard, which is produced when a known amount of lead reacts with a saturated solution of hydrogen sulphide.

$$Pb + H_2S \longrightarrow PbS\downarrow + 2\,H^+$$

colour (brown)

Colour is produced by the heavy metal sulphide precipitate. To ensure that the precipitate is uniform and colloidal, diluted acetic acid and ammonia are added to keep the pH between 3.0 and 4.0. For the experiment, a fresh saturated solution of hydrogen sulphide must be made. Here, ferrous sulphide sticks are designed to react with equal amounts of strong hydrochloric acid and water to produce hydrogen sulphide gas using a specially designed device known as Kipp's apparatus.

The 1996 Indian Pharmacopoeia offers four different approaches based on the substance's final solution (i.e., based on solubility, colour, etc.). Hydrogen sulphide solution is used in method A, hydrogen sulphide solution is used in method B after the substance has been ignited, sodium sulphide solution is used in method C after the substance has been treated with sodium hydroxide solution, and thioacetamide solution is used in method D.

In a concise way, the methods can be categorized as follows:

Method I: It is applied to substances that, under certain circumstances, yield a clear, colourless solution.
Method II: This approach is applied to substances that do not yield a colourless, transparent solution.
Method III: This method is applied to substances that produce a colourless, transparent solution in a sodium hydroxide medium.

**Procedure**

Test colour: Transfer the provided sample into a Nessler cylinder after dissolving it in 25 millilitres of water. To get the pH between 3.0 and 4.0, adjust with diluted acetic acid or diluted ammonia solution. Then, dilute with water to about 35

ml and stir. After adding 10 millilitres of freshly made hydrogen sulphide solution, mix it with 50 millilitres of water, let it rest for five minutes, and then look down over a white surface.
Standard colour: Fill a Nessler cylinder with 1.0 ml of lead standard solution (20 ppm Pb), then dilute it with 25 ml of water. To get the pH between 3.0 and 4.0, adjust with diluted acetic acid or diluted ammonia solution. Then, dilute with water to about 35 ml and stir. After adding 10 millilitres of freshly made hydrogen sulphide solution, mix it with 50 millilitres of water, let it rest for five minutes, and then look down over a white surface.

Method I: It is applied to substances that, under certain circumstances, yield a clear, colourless solution.

**Table. 4: Lead Determination by Hydrogen Sulphide Method (Method I)**

| Test solution | Standard solution |
|---|---|
| A Nessler's cylinder is filled with 25 millilitres of the sample solution, which has been produced in accordance with the monograph. | Dilute 1.0 ml of the standard lead solution with 25 ml of water. |
| Adjust the pH between 3 and 4 by adding diluted ammonia or acetic acid solution. | Adjust the pH between 3 and 4 by adding diluted ammonia or acetic acid solution. |
| Mix thoroughly after diluting with 35 cc of distilled water. | Mix thoroughly after diluting with 35 cc of distilled water. |
| Mix in 10 ml of the recently made hydrogen sulphide solution, then dilute with 50 ml of water. | Mix in 10 ml of the recently made hydrogen sulphide solution, then dilute with 50 ml of water. |
| After five minutes of standing, look down on a white background. | After five minutes of standing, look down on a white background. |

Method II: This approach is applied to substances that do not yield a colourless, transparent solution.

**Table. 5: Test Solution and Standard Solution Preparation (Method II)**

| Test solution | Standard solution |
|---|---|
| Fill a crucible with the specified amount of sample. | Neutralize 1.0 ml of standard lead solution with diluted ammonia solution. |
| Apply sulphuric acid to the sample and light it over a low flame until it is completely charred. | Adjust pH to 3-4 and Filter. |
| After heating to 500 degrees Celsius and cooling, add two to three drops of nitric acid. After that, add 4 millilitres of diluted hydrochloric acid, digest for two minutes, and then evaporate until completely dry. After | Mix thoroughly after diluting with 35 cc of distilled water |

| | |
|---|---|
| that, digest the residue for two minutes with 10 millilitres of diluted hydrochloric acid. | |
| Just acidify with acetic acid after neutralizing with a diluted ammonia solution. | Mix in 10 ml of the recently made hydrogen sulphide solution. |
| If required, adjust the pH from 3 to 4 and filter. Use water to dilute to 35 ml. | Dilute with 50 ml of water |
| Ten millilitres of recently made hydrogen sulphide solution should be added. Use water to dilute to 50 ml. | Mix thoroughly to ensure uniform colour development. |
| After five minutes of standing, look down on a white background. | After five minutes of standing, look down on a white background |

Method III: It is applied to the material that produces a colourless, transparent solution in a sodium hydroxide media.

**Table. 6: Lead Determination in Sodium Hydroxide Media (Method III)**

| **Test solution** | **Standard solution** |
|---|---|
| After dissolving the necessary amount of sample in 20 millilitres of water, add 5 millilitres of sodium hydroxide solution, or make the sample solution according to the monograph. | Five millilitres of sodium hydroxide solution are added to one millilitres of standard lead solution to create the standard solution. |
| Add enough water to make 50 ml. | Add enough water to make 50 ml. |
| Mix thoroughly and set aside for five minutes after adding five drops of sodium sulphide solution. | Mix thoroughly and set aside for five minutes after adding five drops of sodium sulfide solution. |
| Over a white background, view downward. | Over a white background, view downward. |

**Observation**

The sample satisfies I.P. standards if the colour generated in the test solution is not more vivid than that of the standard solution, or vice versa.

**Result**

Compared to standard colour, the test colour is not more vivid. The provided sample then passes the heavy metal limit test. Standard colour is less bright than test colour. The provided sample does not pass the heavy metal limit test.

**Reagent preparation**

1. Diluted acetic acid: contains around 6% of CH3COOH by weight. Use water to dilute 57 millilitres of glacial acetic acid to 1000 millilitres.
2. Dilute ammonia solution: Has around 10% NH3 by weight. Make 1000 ml by diluting 425 ml of strong ammonia solution. Keep in a cool location in well-sealed containers.

3. Lead Standard solution (0.1% Pb): Mix 0.400 g of lead nitrate with 2 ml of nitric acid in water, then top off with enough water to make 250.0 ml.
4. 100 ppm Pb lead standard solution: dilute 1 volume of 0.1% Pb lead standard solution with 10 litres of water.
5. Lead Standard solution (20 parts per million Pb): Use water to dilute 1 volume of lead standard solution (100 parts per million Pb) to 5 volumes.

## 3. METHODOLOGY

### 3a. Nut Shells as Pollutant Adsorbents

The process of creating activated carbons from leftover biomass waste is attracting the attention of many academics. Nutshells are one kind of this biomass (Figure 1). The health advantages of nuts are becoming more and more clear. Their production has significantly increased due to their nutritional qualities, which have been supported by science. However, efforts to continuously improve people's quality of life continue to follow paths that encourage excessive packing and the usage of single-use, disposable items. This has led to significant solid waste accumulation as well as increased air and water pollution. Solid waste management involves creative solutions, some of which may be inspired by cycle economy concepts. Additionally, the scientific community is under pressure to create new techniques and tools for the decontamination and purification of waters due to the growing pollution of these bodies of water. As a result, it becomes clear that research aimed at creating reusable products using a systems approach is essential. Accordingly, the latter two issues may be resolved by using leftover nutshells for water purification and decontamination (Santzouk et al., 2019; Coelho et al., 2020; Criado and Martin, 2020; Roda-Serrat et al., 2020; Madeddu et al., 2021).

This study focuses on the possible use of castor seed hulls, pistachio, cashew, and pecan nutshells, particularly as adsorbents of contaminants in surface waters and wastewater. Once gathered, these chemicals can be employed with only a small amount of physical processing. Contrarily, they can be utilised as precursors for activated carbon, which can then be utilised for a number of purposes. The efficiency of these materials as adsorbents is reviewed in this article.

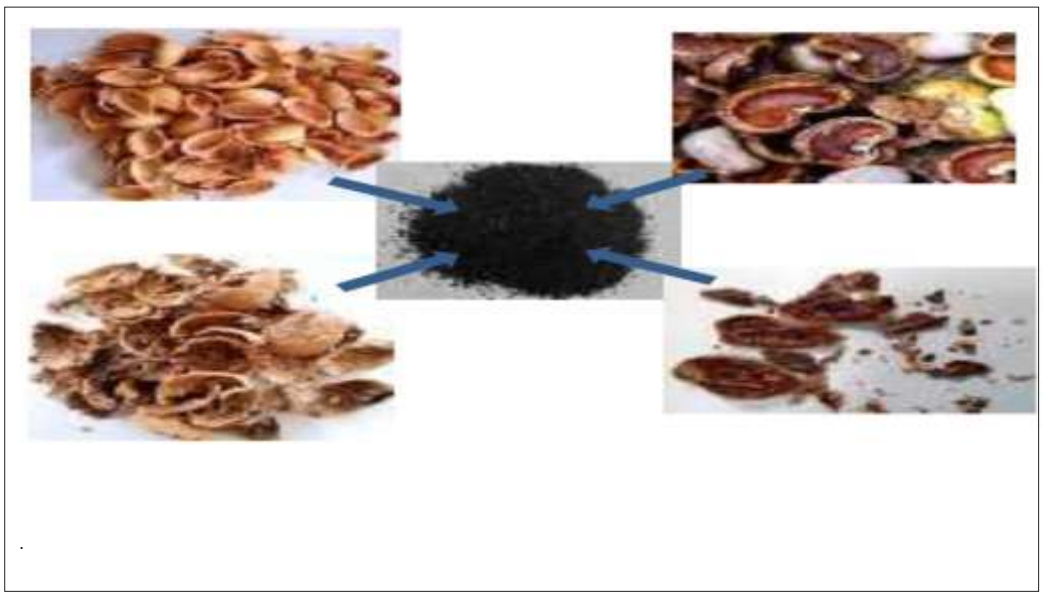
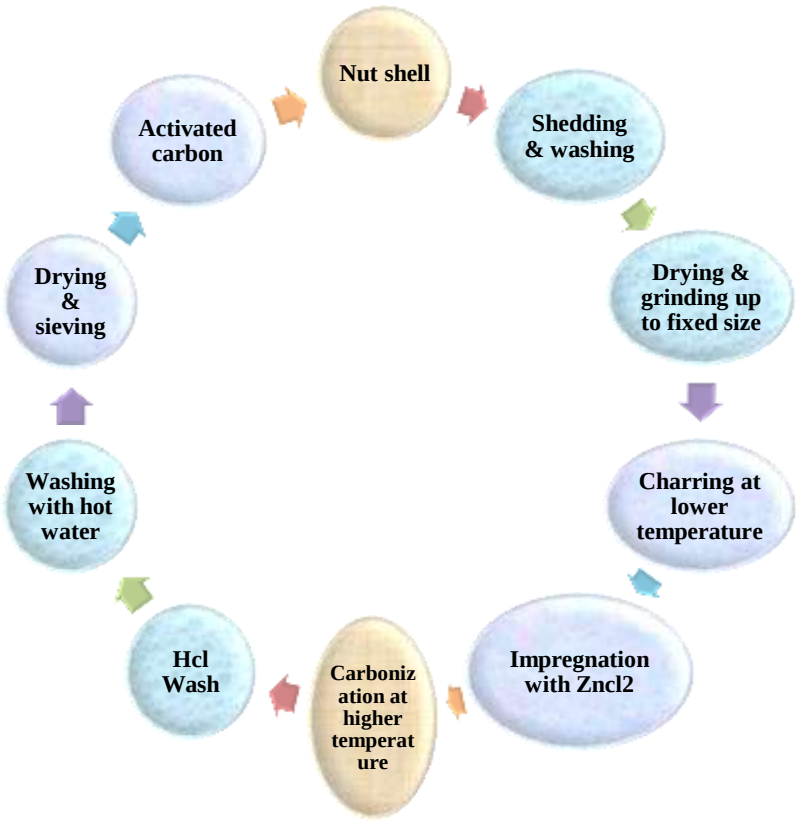


**Figure-2: Activated Carbon for various Nutshells**

**Figure-3: Activated Carbon**

### 3b. Preparation of Adsorbent



The groundnut shell is completely cleaned, dried, crushed, ground into a powder, and sieved to a size of 2 mm. For 30 minutes, heat at 400 degrees Celsius in an electrical furnace. The powder is carbonized for 15 minutes at 650°C after being impregnated with zinc chloride for 24 hours at 100±5°C. After that, HCL is applied to remove the zinc chloride. Hot distilled water is used to treat the char to eliminate acidity and chloride. Analysis is done on the characterization of adsorbent characteristics. Recently, attempts have been made to remove heavy metals from wastewater by using inexpensive and easily accessible agricultural wastes as adsorbents, such as sawdust, rice husks, orange peels, coconut shells, and peanut husks. The absorbent that we utilise is groundnut shell.

The water from the flocculation process is combined with the activated carbon that has been manufactured. The interaction between the activated carbon and the waste-treated water begins as soon as the carbon is combined with the solution. Zinc and chromium, two heavy, concentrated elements found in industrial wastewater, are absorbed by activated carbon made from groundnut shells. The activated carbon procedure only helps those who have heavy hazardous metals because it absorbs them and lowers their concentration. Consequently, the ash (activated carbon) that is added to the water causes it to become muddy and changes colour following the absorption process. After the adsorption process, we filter the water to separate the water that is free of the ash particles. As a result, water with minimal levels of toxicity is collected. Methodology for experiments:

The collected water is first tested for pH and concentration, and then sodium hydroxide is added to raise the water sample's pH range to 9 and raise its alkalinity. The flocs are then created on the water's surface, where the chemical precipitation process occurs. The metals that have a high concentration float as flocs.

After a few hours, the filters are used to remove the flocs that have formed. To remove the residual heavy concentration of metals, the produced activated carbon is then added to the water.

### 3c. Methodology for experiments

The collected water is first tested for pH and concentration, and then sodium hydroxide is added to raise the water sample's pH range to 9 and raise its alkalinity. The flocs are then created on the water's surface, where the chemical precipitation process occurs. The metals that have a high concentration float as flocs.

After a few hours, the filters are used to remove the flocs that have formed. To remove the residual heavy concentration of metals, the produced activated carbon is then added to the water.

### 3d. Results and Testing

**The concentration test and the pH test**

The pH metre can be used to determine the hydrogen power, and the Atomic Adsorption Equipment is utilised for the concentration test. The test's equipment and procedures are as follows.

a. Water samples
b. A pH metre
c. Adsorption of atoms
d. Beaker
e. Coagulants
f. Electrodes

**pH Adjustment Results**

| SAMPLE | INITIAL pH VALUE | FINAL pH Value |
|---|---|---|
| **Zinc Plated Water** | 6.63 | **12** |
| **Chrome Plated Water** | **5.82** | **9** |

**Heavy Metal Concentration Test Results**

| PARA METER mg/L | INITIAL VALUES | | FINAL VALUES | |
|---|---|---|---|---|
| **SAMPLE** | 1 | 2 | 1 | 2 |
| **Arsenic** | 0.01 | 0.01 | 0.01 | 0.01 |
| **Cadmium** | 0.017 | 0.01 | 0.08 | 0.01 |
| **Chromium** | 0.024 | 136 | 0.012 | 0.85 |
| **Lead** | 0.016 | 0.03 | 0.014 | 0.03 |
| **Zinc** | 285 | 37 | 0.75 | 1.2 |

1- Zinc plated water

2- Chromium plated water

## 4. RESULTS AND DISCUSSION

It is possible to eliminate the hazardous metals from industrial wastewater up to the pollution control board's minimum concentration level. The normal limits of CGWB have been analysed using the pH and concentration test. Here, we gathered steel effluents from the Auto Nagar, Anantapur, and electroplating industry. And a sample of agricultural water from a paddy field in Anantapur's Reddy Palli. Concentrates and chemical precipitation are efficient techniques that do not harm the environment. At last, the groundnut shell ash has fully absorbed the harmful metals. The pH and concentration of the water vary from normal. According to the pollution control board, the number of harmful metals in the treated water should not be higher than that. It has no effect on the environmental system and should not have any negative effects on living things. The pH and concentration of the treatment should be balanced. After the treatment process, the pH range of zinc-plated water is 6.8, compared to its initial range of 6.63. The initial pH range of chrome-plated water is 5.82, and the final pH range is 6.1. After the treatment process, the concentration range of zinc-plated water is 0.75, compared to the starting concentration range of 285 (zinc). The starting concentration of chromium in chrome-plated water is 136, and the end concentration range is 0.85.

## 5. CONCLUSIONS

To use nutshells as adsorbents for various pollutants, primarily heavy metals and dyes, researchers have looked into using them as raw materials or as precursors for the production of activated bio-carbons and biochar. They seem to be a promising alternative to conventionally activated carbons in terms of efficiency. The majority of the studies reported in this article used nutshells to form activated carbons after various types of treatment; some used the natural shells in a powder form, others activated varieties of them, and other works involved modifying the adsorbent.

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