



Treated Plant Waste Used as Recyclable Bio-Adsorbents for Removal of Hg (II) from Aqueous System

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ABSTRACT:

We have removed mercury from waste water by using waste fruit material as a bioadsorbent. Additionally, we have created reusable bioadsorbent. It was recycled five times. Additionally, we tested the chemically treated bioadsorbent's capacity to remove mercury using a variety of factors, such as pH optimization, solution temperature, adsorbent dosage, contact time, and solid-liquid ratio optimization.

1. Introduction:

Mercury is widely recognized for its exceptionally high toxicity, ranging from far regions of the globe to industrial areas [1]. As per USEPA guidelines, the maximum amount of mercury allowed to be released in waste water is 10.0 µg/L [3], whereas the maximum amount allowed to be in drinking water is 2.0 µg/L [2]. The WHO and China standards [4,5] state that drinking water should have an inorganic mercury concentration of 1.0 µg/L. Mercury is extremely neurotoxic, even at low doses, as compared to other heavy metal ions [6]. Moreover, it has been linked to liver, kidney, and gastrointestinal system problems [7], which can impair speech and hearing and reduce one's range of vision. A neurological illness initially identified in 1956 in Minamata, Japan, Minamata disease is caused by high concentrations of mercury in water. In severe situations, it can cause a fetus to be affected in the womb, even die, and cause insanity, paralysis, and coma [8–10]. Gaseous emissions from fossil fuels, chloro-alkali production facilities, paint, pulp and paper, pharmaceutical, and cosmetic preparations, among other industries, are the main causes of mercury contamination [11,12]. Even with the installation of costly cleaners, there is still a chance that mercury emissions will end up in the neighboring ecosystems [13]. Over the last thirty years, emerging countries have increased their mercury emissions, countering

decreases from wealthier countries [14]. Therefore, it is crucial to bring the residual mercury concentration from industrial wastewater—especially from drinking water—below the allowable level.

Numerous techniques, including precipitation reduction, solvent extraction, and membrane procedures, have been reported for the removal of heavy metal ions (15). These techniques do, however, have a number of drawbacks, including the creation of hazardous sludge and insufficient metal removal. A notable advancement has been made with the new technique of eliminating heavy metals using bio-adsorbents (16–17). Bioadsorption is the ability of biological materials to extract heavy metals from wastewater by means of metabolically or physico-chemically mediated absorption processes. This phenomenon, called bioadsorption, seems to be a good replacement for the existing methods for treating huge amounts of wastewaters with low pollutant concentrations because it doesn't produce chemical sludge and can be highly selective, efficient, affordable, and easy to operate (18–19). Fruit peels are more beneficial as adsorbents from an ecological and economic perspective since they are less expensive, minimize the quantity of agricultural waste that builds up, provide the possibility of adsorbent renewal, and make it possible to recover metals from adsorbents. Due of their widespread availability worldwide, citrus



fruit peels have lately been studied for their potential to cleanse wastewaters contaminated with heavy metals and colors (20–23). Citrus peels are high in lignin, cellulose, and pectin, which are functional groups that bind divalent cations. These groups include hydroxyl and carboxylic groups.

2. Materials and methods

Preparation of Kinnow peel adsorbent: After removing any impurities and dust particles with two or three rounds of distilled water washing, the kinnow peel (KP) was harvested from the local market. It was then chopped into small pieces and allowed to naturally dry in the open air under the sun. To reduce humidity and facilitate crushing, the peels were roasted to 100°C in an oven. Subsequently, a single sieve and crushing were performed to remove any particles larger than 0.155 mm in diameter. After that, the solid mass was stored in a desiccator so it could be used later.

Modification of bio-adsorbent with different chemicals: In order to activate the bioadsorbent (also known as AKP), the solid support is combined with 0.1 M nitric acid solution. The mixture is then subjected to a 24-hour thermochemical treatment at 120 °C. Subsequently, the mixture underwent a distilled water wash to eliminate any surplus acid, and it was then allowed to sit overnight in a 1% NaHCO₃ solution to further remove any remaining acid waste. Ultimately, the strong support was baked to dryness at 105 °C. For the activation (abbreviated as BKP), 100 g of KP is combined with one litre of 0.1M KOH solution. It is then left for 24 hours before being washed with distilled water to a neutral pH.

Preparation of Mercury solution:

A 250 mL standard flask was used to dissolve the HgCl₂ in one liter of water to create a solution containing 100 mg/L of Hg(II) ion. The solution was then made to mark. The stock solution was used to create various concentrations of mercury ion (25–250 mg/L) in 250 mL standard flasks, which were then marked.

Experimental set-up for Hg removal and analysis:

Using the batch process technique, the adsorption of mercury ion from aqueous solutions was tested at room temperature. First concentrations of mercury (II) were

created at 25, 50, 100, 150, 200, and 250 mg/L. A 100 ml flask containing the necessary quantities of Hg(II) aqueous solution was introduced for each adsorption experiment. With the use of 0.1 M HNO₃ and 0.1 M NaOH, the pH of modified kinnow peel was corrected. For three hours, these 100 ml flasks were shaken at 200 rpm in a shaker. The batch experiments was done varying in the pH, the dosage and size of the biosorbent, the initial Hg(II) concentration, the contact time, the agitation speed, the temperature, and the peel pretreatment. We looked into the impact of the adsorbent mass by adjusting the KP weight between 0.1 and 1 g. Additionally, KP's mercury adsorption capacity was investigated at various contact times (10 min, 20 min, 30 min, 45 min, 1 hr, and 2 hrs) with mercury ion solutions. The starting metal ion solution concentration (25 mg/L), pH (pH - 6), and temperature (40 °C) were maintained at the same levels in both cases.

Determination of Metals Uptake Capacity and % Removal

The Hg ion absorption was calculated using the concentration difference method. The quantity of metal ions (mg) adsorbed per gram of fruit peel is known as the "q." The initial concentration of metal ions is given by C_i (mg/L), C_e indicates the equilibrium concentration of metal ions in solution; $V(L)$ indicates the volume of the metal ions solution that is used; and $W(g)$ indicates the weight of the adsorbent. The following formulas were used to calculate the adsorbent capacity and the percentage of metal absorbed by the sorbent.

$$\%Adsorption = \frac{(C_i - C_e)100}{C_i}$$

$$q_e = \frac{(C_i - C_e)V}{1000} W$$

3. Results and discussion:

Effect of Biosorbent Particle Size: The effect of changing the sorbent particle size on the sorption capacity, q , revealed that smaller particles were able to remove more Hg(II). The sieve analyzer produced various sizes of bio-adsorbent. With smaller bio-adsorbent particles, equilibrium was attained more quickly than with bigger ones. This was most likely



caused by the increase in total surface area, which gave the metal ions additional sorption sites.

| Sieve size | % Remove |
|------------|----------|
| 0.158 | 68 |
| 0.258 | 51 |
| 0.49 | 49 |
| 0.7 | 48 |
| 0.79 | 49 |
| 2 | 49 |

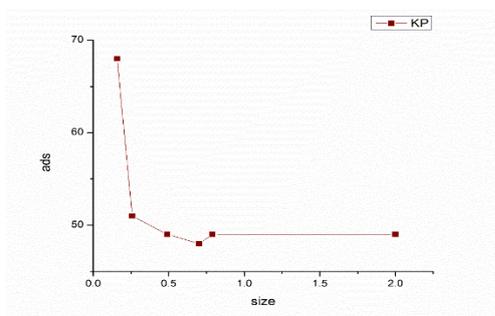


Figure 1: Impact of adsorbent size on Hg(II) ion removal from aqueous solution

The effects of primary modifications:

0.3 g/L of pretreated bio-adsorbent with a size of 0.157 mm for Hg(II) was shaken with 26 mg/L of Hg(II) for two hours at 200 rpm in order to assess the impact of pretreatment on fruit peel waste biomass. Figure 2 displays the q values of fruit peel waste biomass that has been left untreated, physically altered, and chemically altered for Hg(II) sorption. The sorption capacity of the biomass has risen during the boiling process due to the removal of mineral materials and the development of new sorption sites on the surface. Because heat treatment impeded intracellular absorption, it reduced the uptake of metals in biomass. Two parameters determine a biomass's sorption capability following an acidic pre-treatment: Acids have the ability to raise the initial sample's porosity and surface area at a given concentration, which increases biomass's potential for absorption. Furthermore, above a specific alkali concentration, the proportion of protein amino groups that could participate in metallic ion binding significantly decreased.

| Salts | % ADS |
|----------------|-------|
| Native | 55 |
| HCl | 72 |
| Nitric Acid | 95 |
| Sulphuric acid | 80 |
| NaOH | 78 |
| Ethanol | 65 |
| Methanol | 55 |

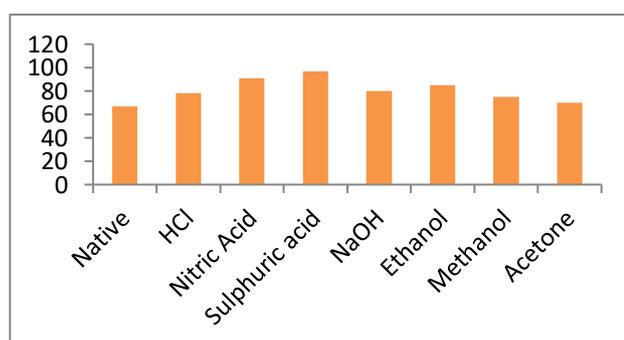


Figure 2: Effect of bio-adsorbent pre-treatment on Hg ion adsorption

The impact of pH:

Using the dried kinnow peel, the effects of pH on Mercury adsorption were examined. To do this, mix 100 ml of a 25 mg/L Hg ion solution with 0.1 g of chemically modified kinnow peel powder (particle size: 0.155 mm) and 0.1 g of dried kinnow peel. To adjust the pH between 4 and 8, samples were shaken for six hours at room temperature and 150 revolutions per minute with either 0.1 M HNO₃ or 0.1 M NaOH. The pH of the solution affects the adsorption of metal ions on adsorbents. It affects the adsorbents' surface charge and dissociation of their functional groups as



well. The adsorption capacity of *Citrus reticulata* waste biomass increased as the pH of the solution rose. Extremely little mercury was absorbed because the adsorbent's surface active sites were protonated, which made Hg ion and H⁺ compete for the same surface

active sites. When the pH rose from 4 - 8 at a fixed biomass level of 0.05 gm/L, the absorption of mercury ions increased (Fig. 3). It is evident that the efficacy of the Hg ion's adsorption increases to 78% at pH 6.

| pH | KP | BKP | AKP | MKP |
|----|----|-----|-----|-----|
| 4 | 45 | 55 | 58 | 60 |
| 5 | 51 | 60 | 62 | 63 |
| 6 | 55 | 72 | 78 | 72 |
| 7 | 58 | 68 | 75 | 68 |
| 8 | 55 | 63 | 68 | 65 |

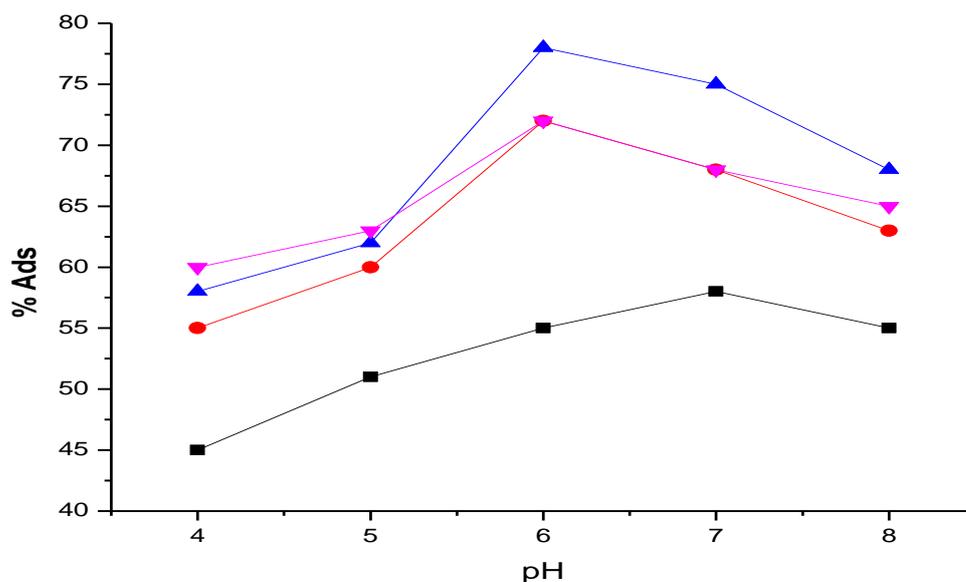


Figure 3: Adsorption of the Hg ion by modified and unmodified bioadsorbent: pH effect

Adsorbent dosage effect:

The mass of modified and unmodified KP had a different effects on the removal of Hg ions from aqueous solution, as shown in Figure 4. For 100 mL of Hg ion solution, the adsorbent dosages ranged from 0.01 to 0.1 g. Other factors, such as pH (6), contact duration (2 hours), and temperature of °C, were held constant. The findings demonstrate that when adsorbent mass grows, the removal percentage of mercury ions correspondingly rises, although

adsorption capacity falls (Fig. 5). This is because additional active sites become available for interaction with metal ions as the dose of both modified and unmodified KP is increased, as a result, a rise in the percentage of metal ions extracted from the watery solution. However, larger concentrations of the adsorbent may cause the modified and unmodified KP to aggregate and unsaturate the active sites, reducing the adsorption capacity. Aggregation results in a decrease in the adsorbent's overall surface area.



| Dose | KP | BKP | AKP | MKP |
|------|----|-----|-----|-----|
| 0.1 | 59 | 71 | 75 | 66 |
| 0.25 | 66 | 73 | 83 | 68 |
| 0.5 | 73 | 83 | 90 | 75 |
| 0.75 | 78 | 85 | 95 | 81 |
| 1 | 80 | 90 | 94 | 82 |

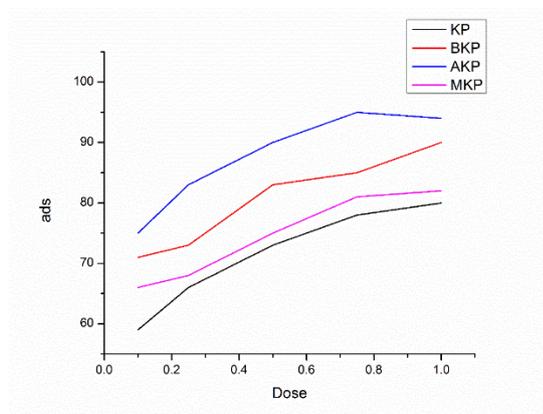


Figure 4: Effect of adsorbent dose on the amount of mercury ions removed by adsorption.

Impact of contact duration:

Figure 5 illustrates the impact of contact duration on orange peels' ability to eliminate mercury. The curve is shaped like a traditional saturation curve. The Hg ion was adsorbed very quickly for the three support ports that were activated by nitric acid and caustic soda (NaOH), reaching saturation in around the first five minutes. For the natural support, the adsorption is much slower, and saturation takes around ten minutes to reach. This is explained by the initial emptiness of the adsorption sites, which makes it simple for metallic ions to rapidly occupy them and offer a high adsorption rate. After this initial delay, the dissolved molecules may diffuse through the adsorbent's pores more slowly, which could account for the delayed adsorption.

| Time | KP | BKP | AKP | MKP |
|------|------|-----|------|------|
| 10 | 70 | 76 | 82 | 84 |
| 20 | 71 | 75 | 82.5 | 85 |
| 30 | 71.5 | 76 | 83 | 87 |
| 60 | 74 | 77 | 84 | 88 |
| 120 | 76 | 79 | 85 | 89 |
| 240 | 77 | 80 | 86 | 90 |
| 360 | 76 | 81 | 86.5 | 90 |
| 720 | 79 | 83 | 86.9 | 92 |
| 1440 | 79 | 85 | 87 | 91.4 |

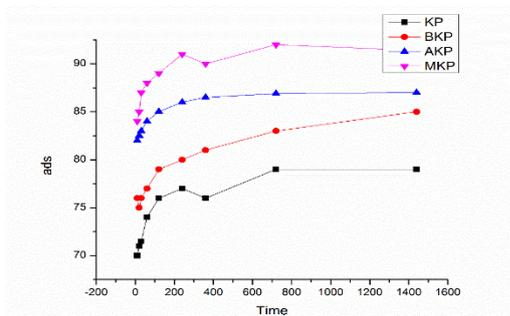


Figure 5: Effect of contact duration on the modified and unmodified bio-ability adsorbent's to adsorb Hg ions.

Effect of temperature on adsorption:

Figure 4 depicts how temperature affects kinnow peel-based Hg(II) adsorption. The highest Hg(II) adsorption was attained at 60 °C. The fact that Hg adsorption capacity grew as the temperature of the solution did indicates that the process was endothermic. Temperature rise reduced the thickness of the kinnow peel's top layer and sped up the rate at which Hg(II) ions were transferred from the solution to the peel's open spaces.

| Temp | KP | BKP | AKP | MKP |
|------|----|------|------|------|
| 20 | 69 | 81 | 76 | 86 |
| 30 | 71 | 82 | 76.7 | 86.5 |
| 40 | 72 | 83 | 76 | 87 |
| 50 | 76 | 83.5 | 77 | 88 |
| 60 | 78 | 84 | 79 | 90 |

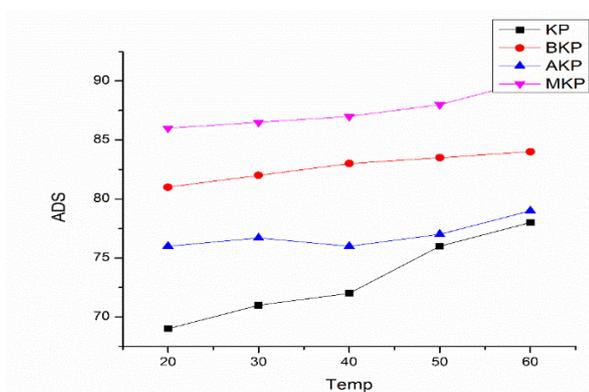


Figure 6: Effect of temperature on adsorption

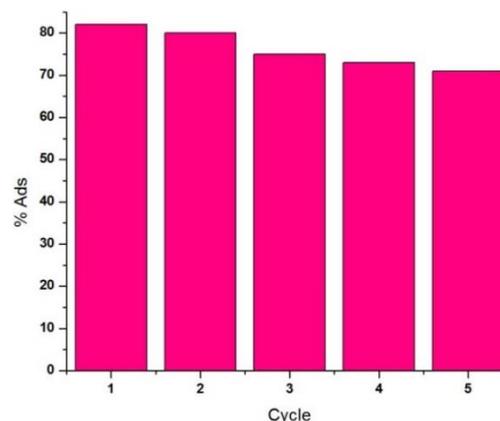


Figure 7: Recycling of AKP for removal of Hg (II) ion
Conclusion:

Recycling of Bio-Adsorbent: As shown in Fig. 7, a recycling research was carried out after the utilized AKP reacted for two hours with a saturated NaCl solution. It was found that the AKP's adsorption capability reduces with an increase in cycles. Even while the studied adsorbent's capacity to adsorb mercury diminishes with each succeeding adsorption operation, this decline was negligible, indicating that KP may be reused for multiple cycles. From 82 to 72%, the adsorption capacity dropped.

For the purpose of removing mercury ions from aqueous solutions, we have created a bio-adsorbent based on recyclable kinnow peel waste. We have a wide range of reaction parameters, such as adjusting the solution temperature, adsorbent dose, pH, contact time, and solid-liquid ratio. It is discovered that kinnow



peel is a high-capacity, commercially feasible, and inexpensive adsorbent for mercury removal.

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