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Orange Peels as Biosorbent for Heavy Metals and Its Application in Water Pollution Remediation Studies

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Abstract

Ecosystems and public health are seriously threatened by heavy metal poisoning of water sources, which is growing. Heavy metal removal from wastewater using conventional technologies is either costly, ineffective, or results in secondary pollutants. In this regard, biosorption has become an affordable and environmentally beneficial substitute. The mitigation study of heavy metals from wastewater is crucial for the protection of the environment and human health. Efforts have been made to use the effectiveness of orange peels for the removal of Cu^{2+} ions from synthetic wastewater. By emphasizing the advantages of using agricultural waste and providing low-cost, sustainable solutions to water contamination, this research opens the door for future advancements in environmental bioremediation methods. The residual metallic ions concentration was determined using UV spectrophotometer. Different reaction parameters were examined such as metal ions concentration in solution, pH, contact time and effect of pretreatment. Pretreatment of orange peels was done with 0.1 N HCl and same mentioned parameters were studied. Maximum percent uptake is 29.60% and adsorption capacity (0.00074 mg/g) after 24 h at pH 5.5 for 0.01 M concentration of Cu^{2+} ions by pretreated orange peels as biosorbent. Physical characterization of orange peels and HCl-treated orange peels was done by using Fourier transform infrared spectroscopy.

Keywords: Water pollution, heavy metals, pretreatment, adsorption, orange peels

INTRODUCTION

Water contamination is one of the most serious problems faced by society today. Among the various contaminants, heavy metals have received special attention, since some of them are extremely toxic for a large variety of organisms, even at very low concentrations. Metals once released into the environment pose many problems as they can accumulate and circulate in the food chain. So, elimination of heavy metals from industrial wastewater is important for the safety of the environment and human health [1–3].

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Heavy metals are used as raw materials in a variety of industries and the main reason of industrial pollution is the effluents emerging out of these industries, such as fertilizers, stabilizers, mining, textile dyeing and processing, paints, pigment, etc. [4–6]. These heavy metals released from industrial wastewater contaminated various water bodies and therefore toxic to many life forms. As most heavy metals are non-degradable into non-toxic end products so before discharging them into the environment their concentrations must be reduced to acceptable levels. According to World Health Organization (WHO) the metals Cd^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Hg^{2+}, and Pb^{2+}[(6)]. Pb^{2+}, Cd^{2+}, Zn^{2+}, and

Cu^{2+} are the most immediate concern amongst various toxic metals because of different health disorders connected with them [7].

Heavy metals cannot be metabolized, and they bio-accumulate in organism bodies. These toxic metals can move up the biological chain, thereby reaching human beings where they produce chronic and acute ailments. Heavy metal toxicity can give rise to damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, liver, kidneys, and other vital organs [8]. Copper participates in the physiological processes such as formation of blood and utilization of iron in hemoglobin synthesis, etc. The higher concentrations of copper have been linked with different disorders, for example, nephritic syndrome, copper intoxication, and burn injuries.

Orange Peels as a Biosorbent

Orange peels may be used as a natural source and low-cost substitute to more costly materials for the mitigation studies of dyes and other unsafe or undesirable species present in the waste effluents [9].

Composition of Orange Peels

Orange peels mainly consist of cellulose, proteins, essential oils, simple carbohydrates, hemi-cellulose, pectin, chlorophyll pigments and other low molecular weight compounds like limonene. In cellulose the active binding sites for metals are supposed to hydroxyl and carboxyl functional groups and chemical modification has exposed great results in improving the cation exchange capacity of these functional groups.

Structure and Composition of Pectin

Pectin is a key ingredient of fruit preserves, jellies, and jams. Pectin is a polysaccharide and present in the cell walls of all plant tissues as a cementing material. Approximately 30% pectin is there in the white portion of the peel of lemons and oranges. Pectin is the methylated ester of polygalacturonic acid and consists of chains of 300 to 1000 galacturonic acid units joined with $\alpha 1 \rightarrow 4$ linkages. Gelling properties of pectin are controlled by degree of esterification. Pectin is also composed of other neutral sugars xylose, galactose and arabinose present in the most common side chains. The side chains occurred in groups so pectin molecule as having hairy and smooth regions.

In the structure of pectin (Figure 1) presented here has three methyl ester groups ($-COOCH_3$) for every two carboxyl groups ($-COOH$), so it has a 60% degree of esterification (DE) and is usually called a DE-60 pectin.

REVIEW OF LITERATURE

Marshall and Champagne [10] focused their studies for metal ion adsorbent in aqueous solutions on the byproduct of soyabean and cottonseed hulls, rice straw and sugarcane bagasse. They found that the adsorption capacities for Zn^{2+} was higher (0.52–0.06 meq/g.) than the rice straw and sugarcane bagasse (0.12 meq/g). At sub saturating concentration of metal ion (100 mg/L), soyabean and cotton seed hulls absorbed high levels (95.6%–99.7%) of Cr^{3+}, Cu^{2+}, Co^{3+}, Ni^{2+}, Zn^{2+}. The percentage of metal ion adsorbed in a particular test was depending on the wastewater and metal ion. Orhan and Büyükgüngör [11] were removed heavy metals from wastewater by using waste tea, Turkish coffee, exhausted coffee, nut and walnut shells as adsorbent. Batch studies were performed by shaking adsorbent (0.3 g) in synthetic wastewater (100 mL) containing Cr^{6+}, Cd^{2+}, and Al^{3+} metal ions at room temperature. The residual concentration of heavy metals after adsorption ratio of Al^{3+} are in the order nut (99.5%) > Turkish coffee (98%), waste tea (96%) = exhausted coffee (96%) = walnut shells (96%).

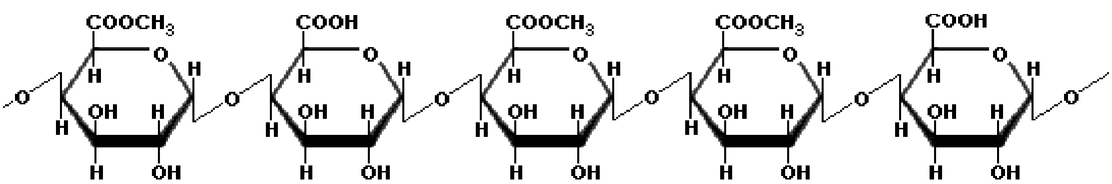

Figure 1. Structure of pectin.

Kratochvil and Volesky [12] prepared biosorbent from sargassum algal biomass for the elimination of Cr^{3+}, Cd^{2+} and Fe^{2+} by ion exchange method and investigated that the binding capacity of metals is in the order $Cr^{3+} > Cd^{2+} > Fe^{2+}$ towards the biosorbent. Selective biosorption of chromium, lead, and copper ions by microorganism from industrial wastewater had been investigated by Ilhan et al. [13]. They used *Staphylococcus sarprophyticus* for their study and observed maximum adsorption for Cr^{6+}, Pb^{2+} and Cu^{2+} as 50%, 90% and 50%, respectively [13].

Tsekova and Petrov [14] removed heavy metals (Cu^{2+}, Co^{2+}, and Fe^{2+}) using *Rhizopus delemar* mycelia in free and polyurethane-bound form from aqueous solution in their studies. Heavy metal uptake experiments were performed in the immobilized column, and they observed that more than 92% of heavy metal removal occurred during the five cycles.

Qaiser et al. [15] used *Ficus religiosa* leaves powder as adsorbent for Cr^{6+} and Pb^{2+}. It has good sorption capacity for both metals. The sorption capacity for Cr^{6+} was 5.66 ± 0.43 mg g^{-1} and for Pb^{2+} was 16.95 ± 0.75 mg g^{-1}. Optimum pH for Pb^{2+} and Cr^{6+} was 4 and 1, respectively. The optimum temperature was 40ºC for Cr^{6+} and 25ºC for Pb^{2+}. An ion exchange mechanism was found between protons and metal cations in case of Pb^{2+} and in case of Cr^{6+} between metal anions and hydroxyl ions. This result is also reflected by the change of pH at the end of biosorption process [15].

Sour sop seeds were used as biosorbent by Oboh and Aluyor for the removal of heavy metal ions from aqueous solutions. They investigated that sour sop seeds absorbed Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} ions with 77.6%, 68.5%, 56.4%, and 40.6% removal, respectively, in 120 minutes contact time. The residual metallic ion concentrations were carried out using an atomic absorption spectrophotometer [16]. Kyncl et al. had used typically cheap substances such as synthetic zeolite, bentonite, or slovakite for the removal of Cu^{2+}, Zn^{2+} and Pb^{2+} from wastewater. The best sorbent for elimination of Cu^{2+}, Zn^{2+} and Pb^{2+} ions from waste waters is slovakite. Its efficiency exceeded 91% for all those three heavy metals (98.6% for Cu^{2+}, 91.5% for Zn^{2+}, and 99.48% for Pb^{2+}) [17]. Activated carbon prepared from raw pomegranate peel and chemically treated pomegranate peel was used for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solutions by Ashtoukhy et al. Batch adsorption experiments were carried out by variation of pH, contact time, solute concentration and adsorbent dose. Maximum adsorption was observed at the optimum pH 5.6 and 5.8 for Pb^{2+} and Cu^{2+}, respectively [18].

The removal of Cu^{2+} ions from aqueous solution was studied by Islam et al. [19] by using adsorbents such as orange peel, sawdust, and bagasse. They found optimum conditions for the removal of Cu^{2+} by varying contact time, pH, concentration, dose, and ionic strength. These adsorbents showed excellent adsorption capacity with small variations due to the presence of different percent of the constituents in them which are bind with the Cu^{2+} ions [19]. The usefulness and shortcomings of conventional and non-conventional methods for heavy metal removal are significantly discussed by Banerjee et al. [20]. Pathy et al [21]. determined promising results by adsorption of heavy metals on biochar's surface in the remediation of contaminated soil and water.

This work was carried out with the objective to use the usefulness of orange peels for the removal of Cu^{2+} ions from synthetic wastewater. Various reaction parameters for obtaining maximum percent uptake such as concentration of metal ions in solution, pH, and contact time were considered. Orange peels were pretreated with 0.1 N HCl and same mentioned reaction parameters were studied. Physical characterization of orange peels and HCl-treated orange peels was done by using Fourier transform infrared (FTIR) spectroscopy.

EXPERIMENTAL PROCEDURE

Materials

Orange peels were collected from local market nearby Mohali, Punjab. Orange peels were dried in sun light for 2 to 4 days and dried peels were crushed in pestle mortar. These crushed orange peels were used as sorbent in two forms, that is, directly and pretreated (with HCl). Copper sulfate pentahydrated (Qualigens Fine Chemicals, Mumbai), sodium hydroxide (Qualigens Fine Chemicals, Mumbai), sodium acetate (Qualigens Fine Chemicals, Mumbai), glacial acetic acid (Qualigens Fine Chemicals, Mumbai), and ammonia solution (Qualigens Fine Chemicals, Mumbai) were used as received for experiments. A Shimadzu balance was used for all the weights having minimum readability of 0.01 mg.

Determination of Cu^{2+} ions

The metal ions uptake studies with orange peels (0.200 g) were studied at different concentrations (0.01 M, 0.05 M and 0.1 M) using 50 mL of $CuSO_4.5H_2O$ solution in a 100 mL beaker. Solution was prepared in acetate buffer. A standard curve of the 0.01 M aqueous solution of $CuSO_4.5H_2O$ solution in acetate buffer (pH 3.6 and 5.5) were obtained by measuring the optical density (OD) of the solution at λ_{max} (625 nm) by using UV spectrophotometer (Elico, Dolphin PG College of Life Sciences, Chunni Kalan, Punjab). OD is measured after specified time intervals 1 h, 2 h, 4 h, 6 h, and 24 h by taking 1.0 mL from above solution, 4.0 mL of sodium acetate buffer solution, and 5.0 mL of ammonia solution. Blank measurement was taken by using equal amount of buffer and ammonia solution at λ_{max} 625 nm. The same procedure was repeated for $CuSO_4.5H_2O$ solution at different concentration (0.05 M and 0.1 M).

Relationships Used to Express the Adsorption Results

The OD of the left-out solution, that is, residual solution relates to the loss in concentration of the metal solution from which metal ions uptake was calculated by using the following equation:

$$\text{Percentage Uptake (Pu)} = \frac{\text{Amount of metal ions sorbed}}{\text{Total ions in the feed solution}} \times 100$$

$$\text{Adsorption capacity (Q) (mg/g)} = \frac{(C_0 - C_t)\,V}{m} \times 100$$

where,

Q = Amount of Cu^{2+} ions adsorbed on to unit dry mass of the hydrogels (mg/g).
C_o = Concentration of the ion in the feed solution (initial concentration)
C_t = Concentration of the ion in the aqueous phase.
V = Volume of the aqueous phase
m = Weight of the dry polymer

Pretreatment of Orange Peels with HCl

The crushed orange peels were treated with 0.1 N HCl (50 mL) for 30 minutes to study the effect of pretreatment. The bloated orange peels were dried in an oven (35ºC).

Characterization of Modified Orange Peels

Orange peel and pretreated orange peel samples were characterized by FTIR spectroscopy (Perkin Elmer, Panjab University, Chandigarh).

RESULTS AND DISCUSSION

Effect of Contact Time

Contact time plays a significant role in adsorption studies so it is important to study its variation on the percent uptake of Cu^{2+} ions by orange peels. The effect of time was studied by keeping the amount of adsorbent constant at (0.200 g), pH (3.6), and concentration (0.01 M) of Cu^{2+} ions. The results (Table 1) show that the percent uptake increases with increase in time but to a certain limit, that is, 6 h after that saturation is reached. This is due to deposition of Cu^{2+} ions on the available adsorption sites on adsorbent material. The maximum percent uptake (29.0%) and adsorption capacity (0.00072 mg/g) of Cu^{2+} ions are observed in 6 h.

Effect of pH

The pH of the aqueous solution was considered as controlling parameter in the adsorption experiments and hence the effect of different pH, that is, at pH 3.6 and 5.5 has been studied at 0.01 M concentration (Tables 1 and 2). The results showed that the percent uptake of Cu^{2+} by the non-treated orange peels increases as the pH of solution increases. The maximum percent uptake (36.2%) and adsorption capacity (0.00089 mg/g) (Tables 1 and 2) were obtained at pH 5.5. It may be due to the ion exchange interaction and hydrogen bonding mechanism of these species Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$ with surface active functional groups present on the non-treated orange peels.

Ion Exchange

$$(-RO^+H_2) + Cu^{2+} \rightarrow (RO)_2Cu + 2H^+$$

$$-RO^+H_2 + Cu(OH)^+ \rightarrow (RO)Cu(OH) + 2H^+$$

Hydrogen Bonding

$$2(-ROH) + Cu\ (OH)_2 \rightarrow (ROH)_2\text{---}Cu(OH)_2$$

where -R represents the matrix of absorbent.

Also, the presence of carboxylic groups in the pectin causes electrostatic interaction with the Cu^{2+} ions.

Effect of Concentration

The effect of Cu^{2+} ions concentration (0.01 M, 0.05 M, and 0.1M) on the percent uptake at pH 5.5 is presented in Table 2. The effect of concentration showed that high percent uptake (36.2%) and adsorption capacity (0.00089 mg/g) was observed for lower concentration (0.01 M) of Cu^{2+} ions in the solution.

Effect of Pretreatment on Adsorbent

Metal affinity to the orange peels was checked by pretreating the orange peels with HCl which causes increase in the percent uptake of Cu^{2+} ions at concentration of 0.01 M. Maximum percent uptake is 29.60% and adsorption capacity (0.00074 mg/g) after 24 h at pH 5.5 are presented in Table 3.

Fourier Transform Infrared Analysis

Evidence of pretreatment of orange peels is given by FTIR analysis and spectrum of orange peels and HCl-treated orange peels. On comparison of spectra, it is observed that there is shifting of IR peaks on HCl pretreatment. The peaks of orange peels at 3406.4 cm^{-1} (-OH stretching), 1442.9 cm^{-1} ($-CH_2$ bending) and 1376.3 cm^{-1} ($-CH_3$ bending) shift towards lower wavenumbers 3368.0 cm^{-1}, 1425.3 cm^{-1} and 1372.9 cm^{-1} in HCl pretreated sample.

Percentage uptake and adsorption capacity of $CuSO_4.5H_2O$ at pH 5.5 at λ_{max} 625 nm by taking orange peels as biosorbent at different concentrations are shown in Tables 2 to 4.

Table 1. Percentage uptake and adsorption capacity of $CuSO_4.5H_2O$ at pH 3.6 at λ_{max} 625 nm by taking orange peels as biosorbent.

S.N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.094	5.4	0.00013
2	1 h	0.091	10.1	0.00025
3	2 h	0.089	13.9	0.00034
4	4 h	0.080	26.4	0.00066
5	6 h	0.078	29.0	0.00072
6	24 h	0.079	27.7	0.00069
Concentration of $CuSO_4.5H_2O$ solution = 0.01 M				

Table 2. $CuSO_4 \cdot 5H_2O$ solution at a concentration of 0.1 M.

S.N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.582	10.7	0.0026
2	1 h	0.556	15.6	0.0037
3	2 h	0.540	17.8	0.0044
4	4 h	0.532	19.0	0.0047
5	6 h	0.528	19.6	0.0049
6	24 h	0.526	19.7	0.0049
Concentration of $CuSO_4.5H_2O$ solution = 0.1 M				

Table 3. $CuSO_4 \cdot 5H_2O$ solution at a concentration of 0.05 M.

S.N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.316	10.2	0.0012
2	1 h	0.311	12.4	0.0015
3	2 h	0.300	15.6	0.0019
4	4 h	0.290	19.3	0.0023
5	6 h	0.258	20.6	0.0025
6	24 h	0.286	20.3	0.0024
Concentration of $CuSO_4.5H_2O$ solution = 0.05 M				

Table 4. $CuSO_4 \cdot 5H_2O$ solution at a concentration of 0.01 M.

S.N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.102	10.2	0.00025
2	1 hr	0.098	15.7	0.00039
3	2 hrs	0.096	18.6	0.00046
4	4 hrs	0.087	34.0	0.00084
5	6 hrs	0.085	36.2	0.00089
6	24 hrs	0.087	34.0	0.00089
Concentration of $CuSO_4.5H_2O$ solution = 0.01 M				

Table 5. $CuSO_4 \cdot 5H_2O$ solution at a concentration of 0.1 M.

S.N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.604	13.1	0.0032
2	1 h	0.590	15.4	0.0038
3	2 h	0.572	17.9	0.0044
4	4 h	0.566	18.9	0.0047
5	24 h	0.560	19.8	0.0049
Concentration of $CuSO_4.5H_2O$ solution = 0.1 M				

Table 6. $CuSO_4 \cdot 5H_2O$ Solution at a Concentration of 0.05 M.

S.N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.347	5.9	0.00073
2	1 h	0.339	8.6	0.0010
3	2 h	0.332	11.5	0.0014
4	4 h	0.304	19.6	0.0024
5	24 h	0.303	19.5	0.0024
Concentration of $CuSO_4.5H_2O$ solution = 0.05 M				

Percentage uptake and adsorption capacity of $CuSO_4.5H_2O$ at pH 5.5 at λ_{max} 625 nm by taking pre-treated orange peels as biosorbent at different concentrations is shown in Tables 5 to 7.

Table 7. $CuSO_4 \cdot 5H_2O$ solution at a concentration of 0.01 M.

S. N.	Time (t)	Optical Density (nm)	Percentage Uptake (P_u) (%)	Adsorption Capacity (Q) (mg/g)
1	30 min	0.106	6.1	0.00015
2	1 h	0.098	17.9	0.00044
3	2 h	0.096	23.1	0.00057
4	4 h	0.092	27.7	0.00069
5	24 h	0.091	29.6	0.00074
Concentration of $CuSO_4.5H_2O$ solution = 0.01 M				

CONCLUSION

The research demonstrates that orange peels, particularly when pretreated with HCl, are an effective and low-cost biosorbent for the removal of copper (Cu^{2+}) ions from synthetic wastewater. The study evaluated the performance of orange peels under various conditions, including different pH levels, contact times, and metal ion concentrations. It was found that the maximum adsorption capacity occurred at pH 5.5, with a peak copper ion uptake of 36.2% for non-treated peels and 29.6% for HCl-treated peels after 24 hours. The findings highlight that agricultural waste like orange peels can offer a sustainable, environmentally friendly solution for water purification, particularly for heavy metal mitigation. These results pave the way for further exploration of orange peels in environmental bioremediation strategies, providing an affordable alternative to conventional methods of wastewater treatment.

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