The utilization of cost-effective natural sorbents for the eradication of heavy metal contaminants from the real world-based adsorbate system

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Abstract

In India, Industrial growth has resulted towards the release of numerous contaminated heavy metals into the environment. Various industries directly discharged the effluents containing harmful pollutants such as toxic heavy metals into the aqueous medium. There are numbers of treatment methods available to remove toxic elements from effluents before disposal. Several research investigations have been conducted to determine the capacity of unconventional absorbents to remove various wastewater impurities. Bio-sorption technique uses agricultural and natural left-over materials as adsorbents since they remain considerably less expensive, supportable, and available than traditional effluent treatment technologies. This study concentrates removal efficiency of orange peels (OP), rice husk (RH) and sugarcane bagasse (SCB) from the industrial effluents. Adsorption studies have been conducted for OP, RH and SCB with differing dose, pH, and contact duration, determined to be appropriate and leading to the highest levels of removal effectiveness. At 1.00 gm dosage, the maximum % removal efficiency of Cu, Cr, Ni, Cd and Zn removal for OP, RH and SCB were 84.90%, 90.45%, 86.21%, 98.00% and 74.11% respectively by using OP, RH and SCB the max. percentage removal efficiency of Cu, Cr, Ni, Cd and Zn for OP, RH were 82.81%, 76.80%, 76.16%, 78.46%, 78.59% at a pH value of 5, 6, 5, 7 and 7 respectively. The max. percentage removal efficiency of Cu, Cr, Ni, Cd and Zn using OP, RH and SCB were 93.45%, 93.05%, 77.66%, 94.62%, 85.10% at the contact time of 120, 60, 120, 60 and 80 minutes respectively.

Keywords: Industrial wastewater; Physicochemical parameters; Heavy metals; Adsorbents

1. Introduction

Over the past few decades, the escalation in global industrial operations and water consumption has resulted in the discharge of numerous harmful substances into the aquatic ecosystem. These pollutants include contaminated heavy metals, pesticides, dyes, besides various other hazardous contaminants [1]. Due to industrialization and the excessive usage of chemicals globally, heavy metals and other dangerous pollutants have been discharged into the environment. Heavy metals offer a serious problem that must to be addressed right now because of their high toxicity, lack of biodegradability and mobility in the environment. Even at small amounts, the presence of heavy metals originating from electroplating, refineries, mining, tanneries, and other industrial discharges has the potential to cause damage to the ecosystem, posing risks to the health of both humans and animals [2]. The density serves [>5 g cm$^{-3}$] as the most utilized parameter in the categorization of metals as heavy metals. Due to their harmful attributes, toxic metals, specifically cobalt (Co), cadmium (Cd), antimony (Sb), mercury (Hg), lead (Pb), copper (Cu), arsenic (As), manganese (Mn), chromium (Cr), selenium (Se), nickel (Ni), zinc (Zn), and silver (Ag) all of considered [32-35]. Escalating concentrations of heavy metal ions have adverse consequences on organisms. These metals pass in the body through physical mechanisms by means of respiration, ingestion of food, consumption of liquids, and absorption through the skin [3-11]. When present in high concentrations, most heavy metal ions have been connected to a variety of health problems, including kidney and cancer, skin lesions, liver damage, growth retardation that causes impairments, and birth
abnormalities. They alter enzyme activities, upset cellular function and can also harm cell membranes [12, 13]. WHO has set out highest permitted amounts for certain hazardous metals and the impact that exceeding those limits in water used for drinking and waste water from industries would have on human health. The toxicity threshold of alloy compositions for various organisms corresponds to their respective elemental compositions in a systematic manner Zn<Fe<Cu>Mn< Ni<Cr<Pb< Cd<Hg [14, 15]. In developed nations, there is a growing trend towards more stringent regulations concerning the permissible thresholds of toxic metals existent in effluent. If we talking about India, the prevailing maximum acceptable limit for heavy metals stands at 0.00003, 0.006, 0.05, 0.050, 0.01, 0.20, 0.25, 0.80 (ppm-mg/mL) for mercury, lead, chromium, arsenic, cadmium, nickel, copper, and zinc respectively [16]. The physiological processes of existing matter depend on the zinc metal, and it also controls several biochemical procedures. On the other hand, too much consumption of zinc can result in grave concerns for one’s health like anemia, nausea, vomiting, and an increase in stomach pains and skin rashes [17]. Copper is a key component of mammal metabolism. However, extreme copper consumption raises major toxicological issues like convulsions, cramping, nausea, or can be responsible for death [18]. Along with gastrointestinal upset, pulmonary fibrosis, and skin rashes, nickel levels that are too high might cause major lung and kidney issues [19]. Mercury, a potent neurotoxin, can inflict harm upon the central nervous system. Elevated levels of this element can lead to compromised pulmonary and kidney function, triggering symptoms such as chest discomfort and dyspnoea [20]. A noteworthy case of its harmful consequences is the infamous case of mercury poisoning in Minamata Bay. Conversely, Cd has garnered classification by the United States Environmental Protection Agency (EPA) as a potential human carcinogen, thereby posing significant health hazards to individuals. Persistent exposure to Cadmium is recognized for its propensity to induce renal dysfunction, and in severe instances, it may culminate in mortal outcomes. Lead, conversely, is known to instigate deleterious effects on the system of central nervous, impacting various human organs and systems, including the reproductive system and the liver. The harmful consequences of lead poisoning encompass a wide range of symptoms such as sleeplessness, headache, anemia, weakness in the muscles, dizziness, hallucinations, and renal impairments [21]. As per guidelines established by the WHO, sustained exposure to chromium hexavalent (Cr⁶⁺) concentrations exceeding 0.1 parts per million (ppm) may result in an array of adverse health effects, encompassing hepatic and renal impairments, alongside respiratory complications. In order to lessen the level of Cr⁶⁺ in freshwater and effluent before its following procedure, it is crucial to treat effluents [22]. In aquatic environments, chromium predominantly exists in two oxidation states, namely chromium (III) represented as Cr³⁺ and chromium (VI) represented as Cr⁶⁺. Human physiological function gets impacted by Cr⁶⁺, which also develops in the food chain and causes serious illnesses including mild skin irritation and lung cancer [23]. By adopting effective and affordable technology for the treatment of industrial effluent in an ecologically sustainable manner, a more environmentally friendly and sustainable development can be achieved [24]. Heavy metals can be eliminated from aqueous systems using several traditional physical and chemical wastewater mitigation techniques, like filtration, oxidation/reduction, precipitation, ion exchange, electrochemical treatment, coagulation, in addition reverse osmosis. These techniques, meanwhile, are only employed circumstances of wastewater treatment because they are either difficult to implement or economically undesirable [25]. The drawbacks or constraints associated with conventional practice involve chemical consumption, the emergence of highly toxic sludge, high initial operating costs, the need for adsorbent elimination, expenditures related to sludge treatment using membrane clogging, electro-coagulation, reduced productivity of concentrate elimination in membrane processes [26]. These traditional methods have limitations in terms of price, viability, dependability, effectiveness, influence on the environment, operational difficulty, handling of harmful byproducts. [27, 28]. Hazardous metals can be effectively separated from wastewater using the adsorption process. Bio-sorption technique uses agricultural and natural waste resources as absorbents since they remain considerably less expensive, readily available, and ecological than traditional effluent treatment technologies. The creation of novel materials that can eliminate dangerous heavy metals from contaminated water has recently attracted more attention [29]. Adsorption process is a very effective process to eliminate heavy metals from effluent, according to investigation on the processing of effluent containing toxic heavy metals. One or both components of a combination can be retained or condensed on a solid surface by the process of adsorption. Usage of activated carbon is popular. Given its extensive application in wastewater treatment industries, it continues to be an expensive substance. A safe and affordable alternative, such as using low-priced farming left-over products to eliminate toxic metals from contaminated streams, is required according to recent research efforts. Proteins, polysaccharides, and lignin are examples of agricultural products that have functional groups that are associated to metal ion adsorption. Due to their vast number of suitable surface groups and abundance of natural occurrences, agricultural wastes are acceptable substitutes for adsorbents.

2. Material and methods

2.1. Industrial effluent collection

Industrial effluent sample was collected from a discharge outlet of treated industrial effluents from the well-known treatment effluent facility of Unnao region, Uttar Pradesh, India (Lattitude 26.559911N, Longitude 80.513713E). The
treated wastewater directly discharged into the Ioni drain. The effluent sample was collected in accordance with normal procedures and quickly delivered to the lab under standard circumstances. Traditional procedures have been used to apply and test wastewater samples.

![Image](image.png)

**Figure 1** Sample collection point (CETP, Unnao)

### 2.2. Apparatus and Instruments used

Weighing machine (Wensar), pH indicator (Lab man, LMPH-12) to determine the solution pH, The Perkin Elmer Analyst 800 atomic absorption spectrophotometer (AAS) is employed for the quantitative determination of heavy metal concentrations, Rotary mover and shaker (SO1 Orbital) to stir the sample, Electrical mill to crush sample, To dry sample hot air oven (JSWG), Microwave oven (R-1514 JSW), Conductivity meter (Labtronics LT-5) and Whatman filter paper. The Millipore water purification system, specifically the Milli-Q system, was employed for the preparation of all samples to mitigate potential interference from extraneous ions.

### 2.3. Physicochemical parameters and heavy metal analysis

The effluent was tested in the lab for pH, the amount of total dissolved solids (TDS), total solids in suspension (TSS), oxygen that was dissolved (DO), biological demand for oxygen (BOD), overall hardness (TH), and electrical conductivity (EC) levels. By using AAS heavy metals were evaluated from the effluent. It found Cu, Cr, Ni, Cd, Zn and Pb concentrations.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Physicochemical properties of treated industrial wastewater (CETP, Unnao)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. No.</td>
<td>Parameters</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
</tr>
<tr>
<td>1</td>
<td>Colour</td>
</tr>
<tr>
<td>2</td>
<td>Odour</td>
</tr>
<tr>
<td>3</td>
<td>pH</td>
</tr>
<tr>
<td>4</td>
<td>EC (mS/m)</td>
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<tr>
<td>5</td>
<td>TDS (mg/L)</td>
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<tr>
<td>6</td>
<td>TSS (mg/L)</td>
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<tr>
<td>7</td>
<td>Total Hardness (mg/L)</td>
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<tr>
<td>8</td>
<td>DO</td>
</tr>
<tr>
<td>9</td>
<td>BOD (mg/L)</td>
</tr>
</tbody>
</table>

Table 1 displays Physicochemical properties of treated industrial wastewater (CETP, Unnao), whereas Table 2 depicts the initial presence of heavy metals amount in the sampled effluent and their maximum tolerable levels in the surface waters according to WHO and US EPA regulations (mg/L) [ministry of Jal shakti report 2019].
Table 2 Initial concentration of heavy metal ions

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Heavy metals</th>
<th>Initial concentrations (mg/L)</th>
<th>maximum permissible levels of heavy metal in surface water according to WHO and US EPA regulations (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu</td>
<td>0.667</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Cr</td>
<td>7.891</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>Ni</td>
<td>0.497</td>
<td>0.07</td>
</tr>
<tr>
<td>4</td>
<td>Cd</td>
<td>1.254</td>
<td>0.003</td>
</tr>
<tr>
<td>5</td>
<td>Zn</td>
<td>1.562</td>
<td>NGL</td>
</tr>
<tr>
<td>6</td>
<td>Pb</td>
<td>0.063</td>
<td>NGL</td>
</tr>
</tbody>
</table>

NGL: no guideline

2.4. Preparation of adsorbent

Three distinct adsorbents, specifically orange peels (OP), rice husk (RH), and sugarcane bagasse (SCB), were collected from various sources in the Lucknow region. Subsequently, each of these adsorbents underwent a meticulous purification process involving multiple rinses with water to eradicate impurities and contaminants which are soluble in water. Following this, they were roughly chopped into smaller fragments using a knife and finely ground using a blender or food processor. The resulting material was then subjected to drying in a controlled environment at 60°C for 24 hours duration, having been previously sun-exposed for a week until achieving a state of crispness. To eliminate any residual coloration and turbidity, the materials underwent pulverization and subsequent rinsing in separate batches with distilled water, a process repeated three times. To achieve uniform particle sizes, the materials were mechanically comminuted and sieved through a 75-micron screen. Finally, the produced sorbents were stored in an evaporator for subsequent testing and analysis.

2.5. Preparation of effluent

A 10 mL effluent sample, obtained from the collection process, was carefully transferred into a 50 mL beaker. Subsequently, 5 mL of concentrated nitric acid was introduced into the beaker. The resulting mixture was subjected to gentle heating on a hot plate, maintaining a temperature range of 60-70°C for a duration of 1-2 hours. After this heating step, the sample was subjected to filtration. Subsequently, a digestion mixture was prepared in a ratio of 1:3, consisting of 1 ml nitric acid (HNO₃) and 3 ml perchloric acid (HClO₄).

2.6. Adsorption studies

A 250 mL conical flask was employed as the vessel for the adsorption analysis, wherein 25 mL of wastewater sample was introduced. Subsequently, various adsorbents were introduced into the wastewater sample. To verify the achievement of a state of equilibrium, a comprehensive analysis must be conducted, the conical flask containing the adsorbent-infused wastewater was placed upon a rotator shaker and subjected to rotation at a rate of 120 revolutions per minute, maintaining the ambient room temperature for a duration of 120 minutes. Following this period, the suspension was subjected to filtration utilizing Wattman filter paper. The resultant filtered solution underwent analysis by AAS to quantitatively determine concentration of heavy metals present within the wastewater. The study also encompassed the investigation of the influence of adsorbent dosage, pH conditions, and contact time, with each aspect being assessed utilizing the identical procedural methodology. Subsequent to the completion of the adsorption procedure, a mathematical equation was employed to calculate the removal percentage (%). [32-36]

\[
\text{Removal efficiency of adsorbents} = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

Where

- \( C_i \): Concentration of heavy metal initially within the sample is expressed in mg/L.
- \( C_f \): Concentration of heavy metal finally within the sample is expressed in mg/L.
2.6.1. Variation of adsorbent dosage

The investigation of metal ion adsorption was conducted using varying dosages of 0.20, 0.40, 0.60, 0.80, and 1.0 grams. Adsorption experiments were conducted by introducing 25mL of effluent sample into the falcon tubes and different dosage vary from 0.2g to 1g of adsorbents were added in falcon tubes respectively. In the rotater shaker the mixtures were uniformly agitated for 120 min at speed of 250 rpm at a room temperate of 27 °C. The falcon tube is subsequently subjected to filtration through a designated filter paper, followed by analysis after a specified duration at pH 6. Each falcons’ tubes containing adsorbents were filtered after each adsorbent weight analysis, by means of AAS the residual metal ion concentrations were measured. The quantity of metal ions adsorbed was estimated through empirical assessment.

2.6.2. Variation of pH

This study involved the examination of metallic ions adsorption by means of various adsorbents across a range of pH values, specifically at pH levels of 3, 4, 5, 6, and 7. In this experimental setup, five separate Falcon tubes were employed, each containing 1 gram of a distinct adsorbent material. These tubes were filled with pre-measured metal ion solutions. The mixtures underwent continuous agitation for a duration of 120 minutes. Following each pH measurement, the contents of each Falcon tube were subjected to centrifugation and subsequent filtration. The resulting filtrates containing metal ions were examined using AAS.

2.6.3. Variation of contact time

The behavior of adsorption on metal ions was investigated via rice husk, peels of orange, and sugarcane bagasse as adsorbents at varying time intervals of 20, 40, 60, 80, 100, and 120 minutes. 25 ml wastewater sample were used in falcon tubes for the adsorption investigations. Five falcon tubes containing 1g of the adsorbent each were filled with the measured amounts of the metal ion solutions. At pH 6, mixtures were consistently stirred at 27 °C temperature. Each tube’s contents were centrifuged and filtered at the conclusion of each contact period. (AAS) was employed to quantify the levels of metallic ions within the filtrate samples, thereby determining the quantity of these metal ions present.

3. Results and discussion

3.1. Effect of adsorbent dosage

Figure 2 Effect of adsorbents dosage on (a) Cu, (b) Cr, (c) Ni, (d) Cd and (e) Zn
The impact of varying adsorbent dosages of rice husk (RH), orange peels (OP), and sugarcane bagasse (SCB) on the removal of Ni, Cd, Cu, Zn and Cr ions is elucidated through corresponding figure 2. These investigations were conducted under specific experimental conditions, including, pH value of 6, agitation at 250 rpm, temperature of 27°C and contact time of 120 minutes. Notably, at an initial adsorbent dosage of 0.10 grams, the minimal removal percentages for Cu, Cr, Ni, Cd, and Zn were observed, with values of 25.49%, 42.62%, 60.22%, 20.57% and 20.00% for OP, RH, and SCB, respectively. Conversely, the maximal removal percentages for these metal ions, attained at an adsorbent dosage of 1.00 gram, reached 84.90%, 90.45%, 86.21%, 98.00%, and 74.11% for OP, RH, and SCB, respectively. A pivotal aspect in adsorption processes is the quantity of adsorbent employed, as it exerts a profound influence on the adsorption efficacy. With increase in dosage from 0.2 to 1 gram, a notable augmentation in removal efficiency was observed. This phenomenon can be credited to the expanded availability of exterior area for the adsorption of metal ions. However, subsequent to the optimal dosage of 1 gram, the removal efficiency exhibited either a decline or a plateau, owing to the diminishing surface area available for adsorption. Consequently, further augmentations in adsorbent dosage did not confer significant enhancements in removal efficiency. Consequently, 1 gram dosage as judiciously selected as the optimal parameter for the exclusion of Cu, Cr, Ni, Cd, and Zn metal ions, forming the basis for further investigations in this study.

3.2. Effect of pH

pH level exerts a substantial influence on the process of adsorption, as it modulates the functionality of adsorbents by modifying surface characteristics and ionization levels. Notably, pH levels of the metal ion solution affect both the adsorbent material and the metal ions themselves. For Cu ions, the maximum percentage removal efficiency was achieved using OP and SCB at pH 5, yielding removal efficiencies of 81.04% and 82.81%, respectively. RH exhibited its highest efficiency at pH 6, achieving a removal rate of 65.75%. OP and SCB demonstrated their maximum removal efficiencies of Cu at pH 3 (70.15%) and pH 5 (69.50%), respectively, while RH exhibited its highest efficiency at pH 6, achieving a removal rate of 76.80%. Ni ions showed their highest removal efficiency at pH 5, with OP and rice husk RH achieving removal rates of 76.16% and 70.33%, respectively, whereas SCB exhibited its maximum efficiency at pH 6, with a removal rate of 72.75%. Cd ions displayed their highest removal efficiencies at varying pH levels, with OP and RH achieving maximum removal rates of 75.80% and 72.68%, respectively, at pH 6, while SCB exhibited its highest efficiency at pH 7, with a removal rate of 78.46%. Zn ions demonstrated their maximum removal efficiencies at pH 7, with RH and SCB achieving removal rates of 71.05% and 78.59%, respectively, while OP displayed its highest efficiency at pH 6, with a removal rate of 52.82%. The pH equilibrium values indicate a competitive binding scenario between H+ ions and heavy metal cations for external binding sites on the adsorbent materials. This competition outcomes in a notable reduction in adsorption capacity [30]. Additionally, higher pH levels facilitate the formation of metal cation precipitates on the adsorbent surfaces, suggesting that electrostatic interactions may contribute to increased adsorption capacity with rising pH. These findings underscore the substantial impact of pH solution on metal ions speciation and alterations in the functional group protonation consequently [31].

![Figure 3 Effect of pH on (a) Cu, (b) Cr, (c) Ni, (d) Cd and (e) Zn](image-url)
3.3. Effect of contact time

This study sought towards ascertain the optimal steadiness point governing the interaction between adsorbents and adsorbates. The investigation aimed to optimize the exclusion efficiency of copper Cu, Cr, Ni, Cd, and Zn ions from aqueous solutions by systematically varying the contact time over a range spanning from 20 minutes to 120 minutes. The outcomes of this experimentation are visually represented in Figures. According to results, the highest rates elimination on adsorbents for RH, OP, and SCB achieved an equilibrium varies 60-120 minutes for heavy metals impurities. The max percentage removal efficiency of Cu using OP, and RH were 93.45% and 65.25% at the contact time of 120 minutes. In contrast, when utilizing sugarcane bagasse (SCB) as the adsorbent material, a removal efficiency of 80.20% for Cu was attained within a reduced 60 minutes contact time. The maximum removal efficiencies for Cr utilizing OP and RH as adsorbents were found to be 72.06% and 70.92%, respectively, when the contact time was set at 120 minutes. While using SCB it was 93.05% at 60 minutes interaction time. Max. % removal efficiency of Ni using OP, RH and SCB were 70.69%, 73.66% and 77.66% at the contact time of 120, 80 and 120 minutes respectively. The max. percentage removal efficiency of Cd using OP, and SCB were 94.62% and 72.10% at the contact time of 60 minutes. While using RH it was 64.01% at 120 minutes of interaction time. The max. percentage removal efficiency of Zn via OP, and SCB were 78.54% and 84.26% at the contact time of 60 minutes. While using RH it was 85.10% at the contact time of 80 minutes. Initially, Due to the increased surface area exhibited by the adsorbent materials, it is observed that, there was a heightened rate of metal removal. The adsorption efficiency for heavy metals utilizing rice husk, orange peel, and sugarcane bagasse exhibited an upward trend with prolonged contact time until reaching equilibrium.

![Effect of contact time on (a) Cu, (b) Cr, (c) Ni, (d) Cd and (e) Zn](image)

4. Conclusion

The outcomes of this study demonstrate the efficacy of the employed adsorbents in facilitating the removal of Zn, Cu, Cr, Cd and Ni ions. Batch experiments underscore the significant influence of adsorbent dosage, pH, and contact time on the adsorption process for these above-mentioned metal ions. Specifically, the optimal conditions for biosorption of metal ions were observed at an 0.1 grams of dosage, a interaction time of 120 minutes, and a pH range of 5 to 6. The chosen adsorbents, namely orange peels, rice husk, and sugarcane bagasse, exhibit not only cost-effectiveness but also ready availability, rendering them practical choices for the removal of metal ions from wastewater. Furthermore, utilization of these natural adsorbents offers advantages over chemical treatment methods, as it allows for metal recovery and adsorbent regeneration without the need for additional procedures, ultimately reducing the overall price of water/wastewater mitigation. In summary, this investigation establishes that the removal of Zn, Cu, Cr, Cd and Ni ions from effluent can be effectively achieved through the utilization of locally available natural adsorbents. Moreover,
the accessibility, disposal, and low extraction costs associated with these materials further underscore their efficacy in the pre-discharge treatment of wastewater for environmental release.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflicts of interest regarding the publication of this paper.

Statement of ethical approval

The present research work does not contain any studies performed on animals/humans’ subjects by any of the authors.

References


