FACTORS AFFECTING COPPER REMOVAL FROM SIMULATED WASTEWATER USING RICE HUSK ASH AS AN ADSORBENT

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ABSTRACT

The present study entails the effect of various factors affecting removal of copper from simulated wastewater by using rice husk ash as an adsorbent. Various standard solutions of copper nitrate were prepared and treated with rice husk ash (RHA) to investigate adsorption on the adsorbent under different conditions of pH, temperature, time and adsorbate dose. Maximum removal of Cu2+ was observed at its low concentration of 10 ppm at 50 °C and 90 minutes contact time. The percentage adsorption decreased with increase in concentration of Cu2+. The removal of 30 ppm and 40 ppm Cu2+ solutions was maximum at pH 6 and 8, respectively. It was concluded that RHA can be used for Cu2+ removal from wastewater containing copper ions by suitably optimizing the conditions.

Keywords:
Copper, Adsorbent, Rice husk ash, Simulated wastewater.

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1. INTRODUCTION

Copper is a heavy metal and when it exceeds permissible limits it may harm to human health (Shukla et al., 2002). The copper contamination, its toxicity and its removal from drinking water using different adsorbents were investigated (Naseem et al. 2014). The low cost adsorbents which can be used for copper removal are saw dust, pine fruit and activated carbon. Yates et al. (1998) performed experiments to study the copper uptake by colloidal SiO2 in aqueous solutions. These solutions were merged with CuCl2 solutions. The solutions were equilibrated for 24 hours. Formation of copper silicates like chrysocolla occurs under acid conditions in supergene copper deposits. The removal of heavy metals through adsorption technique was found to be a practical purification technique which has been used commonly in various industries especially for wastewater treatments (Naeem et al., 2010). Percentage adsorption for RHA-Copper solution system was calculated.
Larous et al. (2003) investigated the copper removal from aqueous solutions using saw dust as an adsorbent. The mechanism of Cu$^{2+}$ adsorption on pine fruit as solid adsorbent was studied and it was found that this adsorbent removes 96-97% copper (Tariq et al., 2009).

The effects of various parameters, such as pH of solution, contact time, temperature and adsorbate concentration were studied. It was observed that adsorption of copper increased with increasing time, temperature, pH and decreased with increasing adsorbate concentration (Naeem et al., 2010).

The adsorption method was found to be profitable due to use of low cost adsorbents, ease of use, accessibility of adsorbents and low operational cost. The adsorption technique is environment friendly, time saving and simple and involves use of simple equipment and apparatus. Similarly, rice husk ash is low cost adsorbent (Zahra et al., 2009; Zahra 2009; Zahra et al., 2009 and Zahra 2010).

The present study aims to study the effects of various factors affecting adsorption of copper from the simulated wastewater using rice husk ash as an adsorbent.

2. MATERIALS AND METHODS

The reagents used in the present study were of analytical grade received from (MERCK)™. Copper nitrate solutions used in this work were prepared in de-ionized water. Rice husk ash (RHA) obtained from PCSIR Laboratories Complex, Lahore was prepared by igniting at 750$^\circ$C. It was then ground to -200 mesh and was used without any chemical treatment for the present experimental work. Atomic absorption spectrometer “Perkin Elmer A Analyst AAS” was used to determine the concentration of copper in each filtrate. The hollow-cathode lamp of copper metal was used. Simulated wastewater was prepared by dissolving 2.95 g of Cu(NO$_3$)$_2$ in a volumetric flask (1000 mL) and increasing the volume upto the mark. 1000 ppm of Cu(NO$_3$)$_2$ solution was used as stock solution. The concentrations of Cu$^{2+}$ after treatment of the standard solutions with RHA under various conditions of pH, temperature, adsorbate dose and time were determined by AAS. Percentage adsorption was calculated by using the following formula.

\[
\% \text{ adsorption} = 100 \left( \frac{(C_i - C_f)}{C_i} \right)
\]

Where; $C_i$ and $C_f$ are final concentrations of Cu$^{2+}$ before and after the treatment with RHA.

3. RESULTS AND DISCUSSION

EFFECT OF ADSORBATE DOSE ON ADSORPTION

Effect of concentration of copper ions on adsorption on rice husk ash was studied by varying the initial concentration of Cu$^{2+}$ solutions (10 ppm - 80 ppm). The results are given in Table 1.
Table 1: Effect of adsorbate dose on adsorption of Cu2+ by RHA (5g), at pH 7, for contact time 30 min at 32 °C

| Sr. No. | Initial concentration of Cu2+ (ppm) | Final concentration of Cu2+ (ppm) | %age adsorption |
|---------|-----------------------------------|----------------------------------|-----------------|
| 1       | 10                                | 0.00                             | 100.0           |
| 2       | 20                                | 0.94                             | 95.3            |
| 3       | 30                                | 4.80                             | 84.0            |
| 4       | 40                                | 10.19                            | 74.5            |
| 5       | 50                                | 15.89                            | 68.2            |
| 6       | 60                                | 21.35                            | 64.4            |
| 7       | 70                                | 26.80                            | 61.7            |
| 8       | 80                                | 34.00                            | 57.5            |

A graph was plotted between the initial concentration of adsorbate (Cu) and % adsorption. For this purpose, different copper standards ranging from 10-80 ppm were taken along the horizontal axis while the % adsorption was along the vertical axis.

Figure 1: Effect of adsorbate dose on adsorption on RHA

Effect of adsorbate dose on adsorption of Cu2+ on rice husk ash was studied by varying the initial concentration of copper solutions. The process of adsorption has an inverse relationship with the adsorbate dose. As figure 1 shows, maximum adsorption was observed when the initial conc. of Cu2+ was the lowest. It was concluded that the decrease in adsorption of ion with the increase of
their concentration may be attributed the phenomenon of ion exchange as has been suggested by Rameshwar et al. (1996). In addition less favorable lattice positions or exchange sites become involved with increasing metal concentration.

**EFFECT OF TIME ON ADSORPTION**

The effects of contact time on the amount of metal ions on adsorbent surface are shown in Table 2. Cu$^{2+}$ solution of 40 ppm was used in order to study the effect of time for copper adsorption.

*Table 2:* Effect of time on adsorption of Cu$^{2+}$ by RHA (5g), pH 7, at 32 °C

| Sr. No. | Initial concentration of Cu$^{2+}$ (ppm) | Time (minutes) given for adsorption | Final concentration of Cu$^{2+}$ (ppm) | % age adsorption |
|---------|----------------------------------------|-----------------------------------|--------------------------------------|----------------|
| 1       | 40                                     | 15                                | 9.94                                 | 75.15          |
| 2       | 40                                     | 30                                | 8.43                                 | 78.9           |
| 3       | 40                                     | 60                                | 9.06                                 | 82.3           |
| 4       | 40                                     | 90                                | 5.74                                 | 85.6           |
| 5       | 40                                     | 120                               | 8.67                                 | 78.3           |

A graph was plotted between the various time intervals and % adsorption. For this purpose, the % adsorptions of copper standard (40 ppm) at various time intervals were taken along horizontal axis while the % adsorption was plotted along the vertical axis.

*Figure 2:* Effect of time on adsorption of copper
Effect of time on adsorption of Cu$^{2+}$ (40 ppm) on rice husk ash was studied by varying the time intervals taken for adsorption. Adsorption of copper was varied by varying the time for adsorption. As figure 2 show, maximum adsorption was at 90 minute. As the time passes the adsorption increases. But after 2 hours, desorption of copper was observed.

**EFFECT OF TEMPERATURE ON ADSORPTION**

Effect of temperature on copper adsorption was observed. Three concentrations of copper solution (20, 30, 40 ppm) were studied at five different temperature ranges (15, 32, 50, 65 and 80 °C).

**Table 3.1:** Effect of temperature on adsorption of Cu$^{2+}$ by RHA (5g), pH 7, for contact time 30 min at 15 °C

| Sr. No. | Initial concentration of Cu$^{2+}$ (ppm) | Final concentration of Cu$^{2+}$ (ppm) | %age adsorption |
|---------|--------------------------------------|--------------------------------------|---------------|
| 1       | 20                                    | 2.74                                  | 86.3          |
| 2       | 30                                    | 7.50                                  | 75.0          |
| 3       | 40                                    | 11.53                                 | 68.2          |

**Table 3.2:** Effect of temperature on adsorption of Cu$^{2+}$ by RHA (5g), pH 7, for contact time 30 min at 32 °C

| Sr. No. | Initial concentration of Cu$^{2+}$ (ppm) | Final conc. of Cu$^{2+}$ (ppm) | %age adsorption |
|---------|----------------------------------------|---------------------------------|---------------|
| 1       | 20                                     | 3.40                            | 89.2          |
| 2       | 30                                     | 6.54                            | 78.2          |
| 3       | 40                                     | 12.0                            | 70.0          |

**Table 3.3:** Effect of temperature on adsorption of Cu$^{2+}$ by RHA (5g), pH 7, for contact time 30 min at 50 °C

| Sr. No. | Initial concentration of Cu$^{2+}$ (ppm) | Final concentration of Cu$^{2+}$ (ppm) | %age adsorption |
|---------|----------------------------------------|----------------------------------------|---------------|
| 1       | 20                                     | 1.45                                   | 92.7          |
| 2       | 30                                     | 5.50                                   | 81.7          |
| 3       | 40                                     | 11.06                                 | 72.3          |
Table 3.4: Effect of temperature on adsorption of Cu^{2+} by RHA (5g), pH 7, for contact time 30 min at 65 °C

| Sr. No. | Initial concentration of Cu^{2+} (ppm) | Final concentration of Cu^{2+} (ppm) | %age adsorption |
|---------|--------------------------------------|--------------------------------------|-----------------|
| 1       | 20                                   | 2.56                                 | 87.2            |
| 2       | 30                                   | 6.39                                 | 78.7            |
| 3       | 40                                   | 14.07                                | 64.8            |

Table 3.5: Effect of temperature on adsorption of Cu^{2+} by RHA (5g), pH 7, for contact time 30 min at 80 °C

| Sr. No. | Initial concentration of Cu^{2+} (ppm) | Final concentration of Cu^{2+} (ppm) | %age adsorption |
|---------|--------------------------------------|--------------------------------------|-----------------|
| 1       | 20                                   | 1.58                                 | 84.5            |
| 2       | 30                                   | 4.30                                 | 77.6            |
| 3       | 40                                   | 13.13                                | 63.1            |

A graph was plotted between the various temperature ranges and % adsorption. For this purpose, the % adsorption of different copper standards (20 ppm 30 ppm, 40 ppm) at various temperature ranges were taken. Various temperature ranges were taken along horizontal axis while the % adsorption was plotted along the vertical axis.

Figure 3.1: Effect of temperature on adsorption of copper for 20 ppm
Effect of temperature on Cu$^{2+}$ adsorption on rice husk ash was studied at various temperature ranges. Effect of temperature on 20 ppm, 30 ppm and 40 ppm copper standards was studied. In case of each of copper standards (20 ppm, 30 ppm, 40 ppm), the maximum adsorption was noted at 50 °C. However as the temperature increase beyond 50 °C, desorption of Cu$^{2+}$ was observed. Therefore, an increase in temperature after certain limit, decreased the adsorption of Cu$^{2+}$ and favored desorption from rice husk ash. (Fig.3.1, 3.2, and 3.3)

**EFFECT OF pH ON ADSORPTION**

As the solution is acidic, so it is very necessary to control the heavy metals uptake. pH strongly affect % copper removal and its uptake.
Table 4.1: Effect of pH on adsorption of Cu$^{2+}$ for 30 ppm by RHA (5g), for contact time 30 min at 32 °C

| Sr. No. | Initial concentration of Cu$^{2+}$ (ppm) | pH | Final Concentration of Cu$^{2+}$ (ppm) | % age adsorption |
|---------|-----------------------------------------|----|---------------------------------------|-----------------|
| 1       | 30                                      | 02 | 21.54                                 | 28.2            |
| 2       | 30                                      | 04 | 15.25                                 | 49.2            |
| 3       | 30                                      | 06 | 1.47                                  | 95.1            |
| 4       | 30                                      | 08 | 4.86                                  | 83.8            |
| 5       | 30                                      | 10 | 9.74                                  | 67.5            |
| 6       | 30                                      | 12 | 11.84                                 | 60.5            |

Table 4.2: Effect of pH on adsorption of Cu$^{2+}$ for 40 ppm by RHA (5g), for contact time 30 min at 32 °C

| Sr. No. | Initial Concentration of Cu$^{2+}$ (ppm) | pH | Final concentration of Cu$^{2+}$ (ppm) | % age adsorption |
|---------|------------------------------------------|----|----------------------------------------|-----------------|
| 1       | 40                                       | 02 | 27.04                                  | 32.4            |
| 2       | 40                                       | 04 | 17.50                                  | 56.2            |
| 3       | 40                                       | 06 | 4.53                                   | 88.7            |
| 4       | 40                                       | 08 | 0.03                                   | 99.9            |
| 5       | 40                                       | 10 | 6.29                                   | 84.3            |
| 6       | 40                                       | 12 | 12.65                                  | 68.4            |

A graph was plotted between the various pH ranges and % adsorption. For this purpose, the % adsorption of different copper standards (30 ppm, 40 ppm) at various pH ranges were taken. Various pH ranges were taken along horizontal axis while the % adsorption was plotted along the vertical axis.
Adsorption of Cu$^{2+}$ on RHA was analyzed at different pH ranges (2 to 12). Standard used for this were 30 ppm and 40 ppm. pH for each solution of copper(II) standards was studied at 2, 4, 6, 8, 10, and 12. In the solutions of both the concentrations, the adsorption of Cu$^{2+}$ was maximum at pH 6 & 8. With increase in pH, adsorption increases. Adsorption was maximum in slightly acidic solutions (Fig.4.1, 4.2). The minimum adsorption was observed at pH 2. It may be due to the higher concentration and higher mobility of H$^+$ ions present. At lower pH value, the adsorbent surface is surrounded by H$^+$ ions, thereby blocking the metal ions to approach the binding sites of adsorbent (Wong et al. 2003). With pH increase, more negatively charged surface becomes available which help in copper removal. Adsorption of metal cations increases with increasing pH because the metal ionic species become less stable in the solution.

**Figure 4.1:** Effect of pH on adsorption of copper for 30 ppm

**Figure 4.2:** Effect of pH on adsorption of copper for 40 ppm
4. CONCLUSION

From the above study, it was concluded that removal of copper from wastewater depend on different factors which may be controlled and adjusted for the removal of copper using rice husk ash. It can also be noted that rice husk ash is good adsorbent as 100% removal was possible using adsorption technique.

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