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# Thermodynamic of Adsorption: Studying the effect of temperature on adsorption of the metal ions from aqueous Solutions using Non-conventional adsorbents

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**ABSTRACT**

Early studies on the adsorption and ion exchange potential of coconut coir dust (*Cocos nucifera L.*) has great proficiency for removal of trace metal ions from waste water and industrial effluents. Several factors influence the process of waste water detoxification by agricultural biomass. In this paper the effect of temperature on the extent of adsorption of this metals by unconventional adsorbent is being monitored for Cu(II), Pb(II), Zn(II) and Ni(II) in aqueous solutions. The results show increase percentage adsorption with increase in temperature for all the metal ions indicating an endothermic reaction. It was also observed that the average enthalpy adsorption $\Delta H^0$ and $K_0$ increased with increase in temperature for all the adsorption of metal ions on the adsorbents indicating an endothermic process. The values of $\Delta H^0$ were greater than +20kj/g/mols for most of the adsorption which supports chemisorption reaction. It was observed that the effect of temperature was more pronounced on the adsorption of the metal ions on the modified coir extract viz; CTR and STR, than the unmodified coir dust. This shows that the CTR, and STR adsorbents were more efficient at higher temperatures than the coir dust.



## Introduction

. The temperature of an adsorption reaction strongly influence not only the site dissociation of the adsorbent/resin surface but also the solution chemistry of the metal ions. The surface charge of the adsorbent/ion-exchanger and degree of dissociation is determined by the temperature of the system.

Over the years enhanced industrial activities has led to the discharge of unprecedented volumes of waste waters and effluents into the environment. The various activities associated with environmental pollution are mining operations, ore-processing and smelting, urbanization, metal-plating, tanneries and agriculture-related processes (Okieiman et al, 1991; Raji et al, 1997). These metal contaminants are not biodegrable but accumulate in living organisms becoming a permanent burden on the ecosystem (Balasubramaniam and Ahamen, 1998). Their presence in the environment even at low concentration has therefore the potential of becoming a cause of toxicity to humans and other forms of life (Langmiur, 1918). Industrial effluents and drinking water loaded with metals is thus a serious public health problem (Faisal and Hasmain, 2004). Over-abundance of the essential trace elements and particularly their substitution by non-essential ones, such as Cd, Ni, Ag can also cause toxicity symptoms.

From the ecotoxicological point of view, metals such as Cd, Hg and Pb, the so-called family of "big three", are highly toxic and are included in the 'Red List' of priority pollutants published by the Department of the Environment, United Kingdom and in List 1 of European Economic Commission (EEC) Dangerous substances directive (Sekar et al, 2004). The same directive lists Cu, Ni, Sn and Cr in "List II", which contains pollutants of less toxicity. These metals, nevertheless, create environmental pollution problems since, although not necessarily toxic at low concentrations, can accumulate in the food chain and upon entry into human body are not excreted. Hence, from environmental and human safety point of view, it is of the utmost importance that metal contaminants are removed from industrial wastewaters before their release into the environment.

Several efforts targeted at reducing and/or removing these harmful substances demands harnessing the temperature of the system in order to achieve optimum result hence the burden of this research.

## Materials and Method

Coir dust $(500mg)$, Csrboxylated Coir extract resin (CTR) and Sulphonated Coir extract resin(II) of different particle sizes $50-600(m$ were taken separately in conical flasks containing $50ml$ of $\frac{10mg}{l}$ of the Cu(II), Pb(II), Ni(II) and Zn(II) solution and were shaken for 3 hours on orbital shaker at agitation speed of $140rpm$ at $30°C$. The process was repeated for 40°C and 60°C respectively. At the end of this period the samples were filtered and adsorbate concentrations were determined using Atomic Absorption Spectrophotometer.

## Result and Discussion

The effect of temperature on the adsorption of the metal ions Cu(II), Pb(II), Zn(II), and Ni(II), are shown in tables 1 – 4 respectively. The results show increase percentage adsorption with increase in temperature for all the metal ions indicating an endothermic reaction. The plots of percentage adsorption versus initial concentration of Cu(II), Pb(II), Zn(II) and Ni(II) on the CD, CTR, STR at temperatures of 30° C,

To further account for the effect of temperature on the equilibrium sorption of metal ions on these adsorbents, the

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thermodynamic equilibrium constant $K_o$, the average standard enthalpy change, $\Delta H^0$, $\Delta G^0$, the standard free energy of spontaneity and standard enthropy $\Delta S^0$, were determined and presented in Tables 5 – 7.

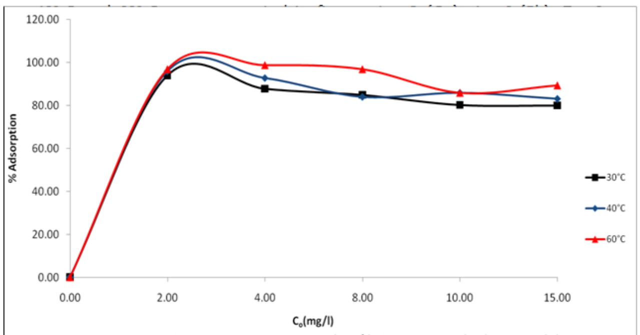


***Fig. 1*** **- Plot of % adsorption versus $C_o$(mg/l) for Coir Dust (CD) with Cu(II) at 30°C, 40°C, 60°C**

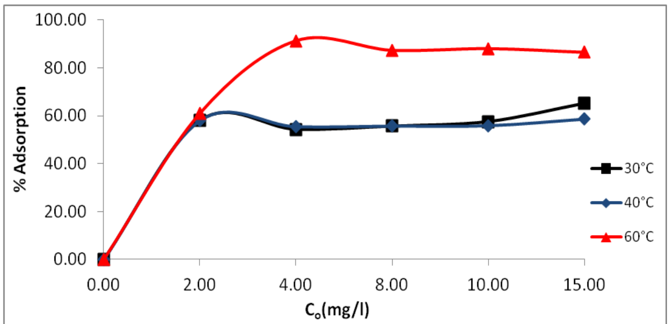


***Fig. 2*** - Plot of % adsorption versus $C_o$(mg/l) for carboxylated coir extract resin (CTR) with Cu(II) at 30°C, 40°C, 60°C

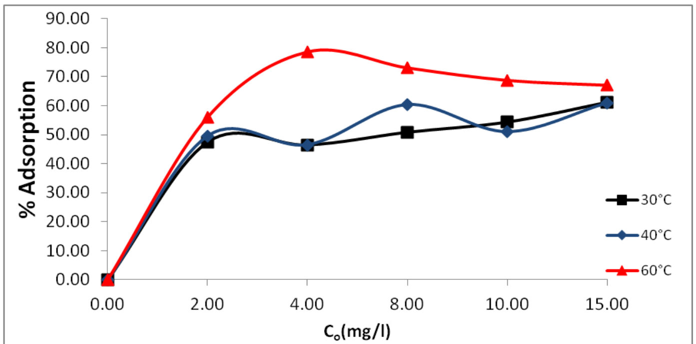


***Fig. 3*** - Plot of % Adsorption versus $C_o$(mg/l) for sulphonated coir extract resin (STR) with Cu(II) at 30°C, 40°C, 60°C

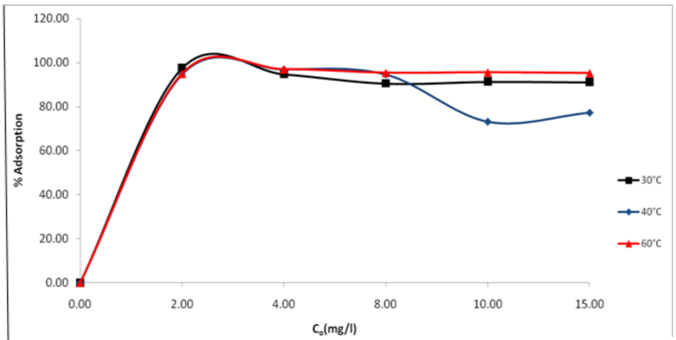


***Fig. 4*** **- Plot of % adsorption versus $C_o$(mg/l) for Coir Dust (CD) with Pb(II) at 30°C, 40°C, 60°C**

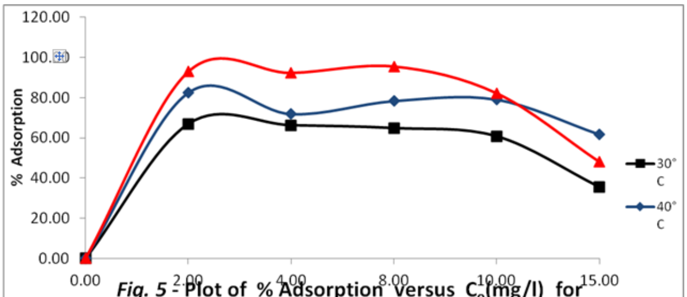


***Fig. 5*** **- Plot of % Adsorption versus $C_o$(mg/l) for carboxylated coir extract resin (CTR) with Pb(II) at 30°C, 40°C, 60°C**

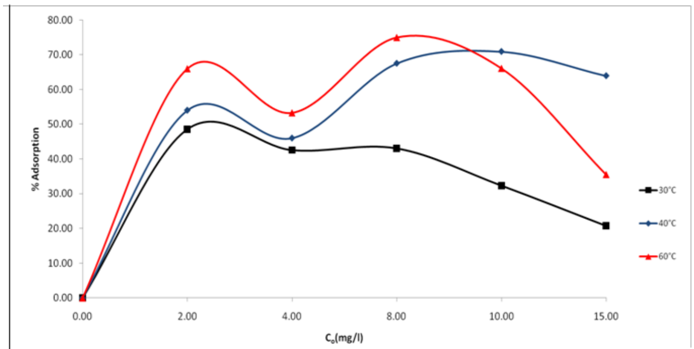


***Fig. 6*** **- Plot of % Adsorption versus $C_o$(mg/l) for Sulphonated coir extract resin (STR) with Pb(II) at 30°C, 40°C, 60°**

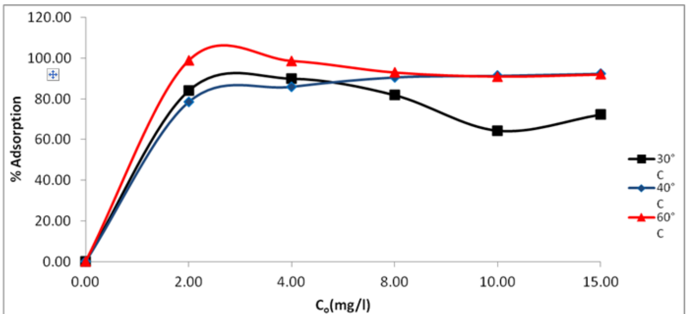


***Fig. 7*** - Plot of % Adsorption versus $C_o$(mg/l) for coir dust (CD) with Zn(II) at 30°C, 40°C, 60°C

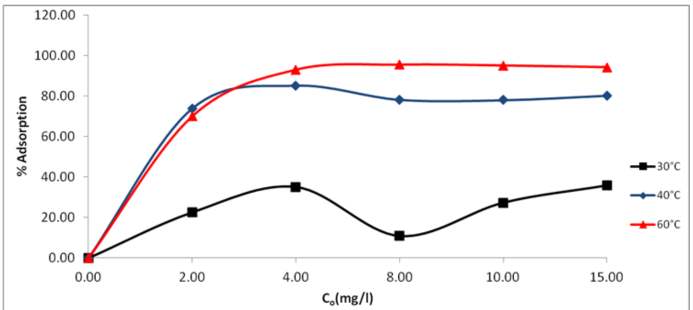


***Fig. 8*** - Plot of % Adsorption versus $C_o$(mg/l) for carboxylated coir extract resin (CTR) with Zn(II) at 30°C, 40°C, 60°C

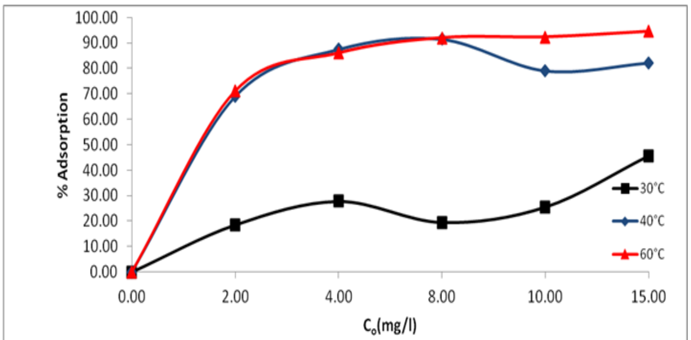


***Fig. 9*** - Plot of % Adsorption versus $C_o$(mg/l) for sulphonated coir extract resin (STR) with Zn(II) at 30°C, 40°C, 60°C

**Table 1: Percentage Uptake of Pb(II) on Adsorbents at Different Temperature**

| **Pb(II)** | **CD** | | | **CTR** | | | **STR** | | |
|---|---|---|---|---|---|---|---|---|---|
| Initial Conc Co(mg/l) | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 |
| 2 | 97.50 | 94.50 | 95.0 | 67.0 | 82.50 | 93.0 | 48.50 | 54.0 | 66.0 |
| 4 | 94.75 | 96.80 | 97.0 | 66.30 | 71.80 | 92.30 | 42.50 | 46.0 | 53.30 |
| 8 | 90.50 | 94.50 | 95.40 | 64.88 | 78.30 | 95.50 | 43.0 | 67.50 | 75.0 |
| 10 | 91.30 | 73.10 | 95.60 | 60.80 | 79.0 | 82.20 | 32.20 | 70.90 | 66.10 |
| 15 | 91.07 | 77.20 | 95.27 | 35.53 | 61.67 | 48.0 | 20.73 | 63.93 | 35.53 |

**Table 2: Percentage Uptake of Cu(II) on Adsorbents at Different Temperature**

| **Cu(II)** | **CD** | | | **CTR** | | | **STR** | | |
|---|---|---|---|---|---|---|---|---|---|
| Initial Conc Co(mg/l) | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 |
| 2 | 94.0 | 96.0 | 97.0 | 58.0 | 58.0 | 61.0 | 47.40 | 49.50 | 56.0 |
| 4 | 87.75 | 92.80 | 98.90 | 54.30 | 55.50 | 91.30 | 46.50 | 46.50 | 75.50 |
| 8 | 84.88 | 84.00 | 97.0 | 55.63 | 55.75 | 57.30 | 56.88 | 60.30 | 73.0 |
| 10 | 80.20 | 85.90 | 86.00 | 57.50 | 55.90 | 88.0 | 54.40 | 51.0 | 68.70 |
| 15 | 79.93 | 83.13 | 89.47 | 65.10 | 58.67 | 86.47 | 61.20 | 60.87 | 67.0 |

**Table 3: Percentage Uptake of Zn(II) on Adsorbents at Different Temperature**

| **Zn(II)** | **CD** | | | **CTR** | | | **STR** | | |
|---|---|---|---|---|---|---|---|---|---|
| Initial Conc Co(mg/l) | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 |
| 2 | 84.0 | 78.50 | 98.90 | 22.50 | 74.0 | 70.0 | 18.50 | 69.0 | 71.0 |
| 4 | 90.00 | 86.0 | 98.70 | 35.0 | 85.30 | 93.0 | 27.75 | 87.50 | 86.0 |
| 8 | 81.88 | 90.63 | 93.0 | 10.88 | 78.30 | 95.50 | 19.50 | 91.50 | 92.0 |
| 10 | 64.40 | 91.40 | 91.0 | 27.30 | 78.10 | 95.10 | 25.50 | 79.10 | 92.30 |
| 15 | 72.29 | 92.40 | 92.0 | 35.80 | 80.33 | 94.27 | 45.60 | 82.20 | 94.47 |

**Table 4: Percentage Uptake of Ni(II) on Adsorbents at Different Temperature**

| **Ni(II)** | **CD** | | | **CTR** | | | **STR** | | |
|---|---|---|---|---|---|---|---|---|---|
| Initial Conc Co(mg/l) | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 | ($^o$K) 303 | ($^o$K) 313 | ($^o$K) 333 |
| 2 | 93.50 | 91.0 | 95.35 | 54.0 | 35.0 | 33.0 | 6.50 | 33.0 | 32.0 |
| 4 | 92.30 | 91.75 | 96.80 | 56.75 | 43.50 | 46.0 | 3.0 | 40.75 | 37.75 |
| 8 | 86.00 | 93.88 | 95.0 | 64.38 | 34.50 | 42.63 | 2.60 | 36.88 | 42.75 |
| 10 | 87.60 | 90.40 | 95.10 | 42.80 | 36.40 | 47.50 | 7.40 | 36.70 | 44.0 |
| 15 | 79.47 | 89.33 | 93.60 | 54.27 | 41.93 | 23.13 | 35.13 | 33.07 | 45.20 |

**Table 5: Thermodynamic Parameter for Adsorption of Metal Ions on Coir Dust**

| **Metal** | **Temp ($^o$K)** | **$K_O$** | **$\Delta G^o$ KJ/mol** | **$\Delta H^o$ KJ/mol** | **$\Delta S^o$ KJ/mol** |
|---|---|---|---|---|---|
| Cu | 303 | 2.84 | -2.63 | +4.195 | +2.166 |
| | 333 | 3.29 | -3.29 | | +2.38 |
| | 303 | 3.66 | -3.27 | +14.51 | -5.65 |
| Pb | 333 | 6.13 | -5.03 | | +6.20 |
| | 303 | 2.93 | -2.98 | | -1.84 |
| Zn | 333 | 1.27 | -0.60 | | -5.60 |
| | 333 | | -2.400 | | -5.10 |
| Ni | 303 | 0.21 | +3.91 | | |
| | | | | +33.80 | -1.24 |
| | 333 | 0.71 | +0.95 | | -1.13 |

**Table 6: Thermodynamic Parameter for Adsrption of Metal Ions on Carboxylated Resin**

| **Metal** | **Temp ($^o$K)** | **$K_O$** | **$\Delta G^o$ KJ/mol** | **$\Delta H^o$ KJ/mol** | **$\Delta S^o$ KJ/mol** |
|---|---|---|---|---|---|
| Cu | 303 | 3.31 | -3.02 | +83.86 | +27.58 |
| | 333 | 1.65 | -4.99 | | +28.21 |
| Pb | 303 | 1.22 | -0.501 | +24.50 | +7.94 |
| | 333 | 2.93 | -2.98 | | -18.72 |
| Zn | 303 | 1.27 | -0.60 | +17.56 | +5.77 |
| | 333 | 2.38 | -2.40 | | +5.70 |
| Ni | 303 | 0.21 | +3.93 | -19.16 | -7.33 |
| | 333 | 0.71 | +0.95 | | -6.38 |

**Table 7: Thermodynamic Parameter for Adsorption of Metal Ions on Sulphonated Resin**

| Metal | Temp ($^o$K) | $K_O$ | $\Delta G^o$ KJ/mol | $\Delta H^o$ KJ/mol | $\Delta S^o$ KJ/mol |
|---|---|---|---|---|---|
| Cu | 303 | 3.31 | -3.02 | +83.86 | +27.58 |
| | 333 | 0.17 | +4.99 | | +28.20 |
| Pb | 303 | 0.36 | +2.57 | +58.63 | -19.43 |
| | 333 | 2.93 | -2.98 | | -19.56 |
| Zn | 333 | 1.27 | -0.60 | +17.57 | +5.77 |
| | 303 | 2.38 | -2.40 | | +6.34 |
| Ni | 303 | 0.21 | +3.91 | +33.80 | +11.97 |
| | 333 | 0.71 | +0.93 | | +11.03 |

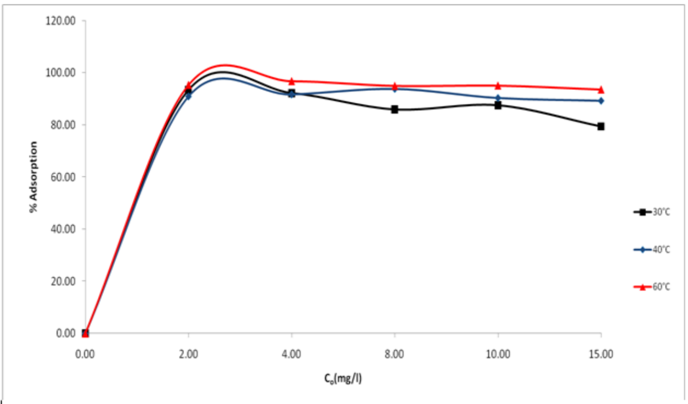


***Fig. 10*** **- Plot of % Adsorption versus $C_o$(mg/l) for coir Dust (CD) with Ni(II) at 30°C, 40°C, 60°C**

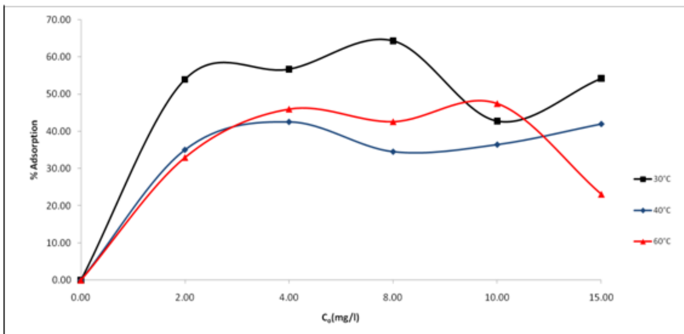


***Fig. 11*** **- Plot of % Adsorption versus $C_o$(mg/l) for carboxylated coir extract resin (CTR) with Ni(II) at 30°C, 40°C, 60°C**

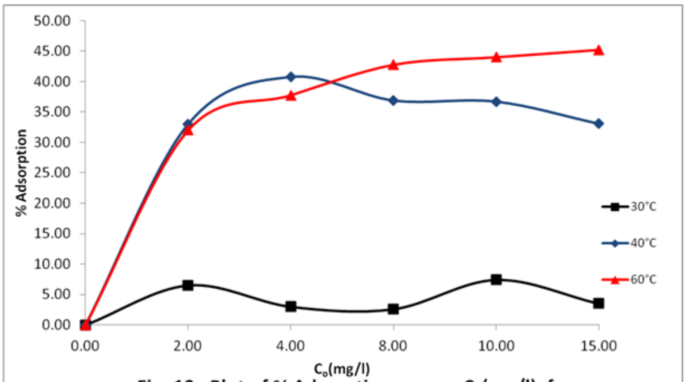


***Fig. 12*** **- Plot of % Adsorption versus $C_o$(mg/l) for sulphonated coir extract resin (STR) with Ni(II) at 30°C, 40°C, 60°C**

It was observed that the average enthalpy adsorption $\Delta H^0$ and $K_0$ increased with increase in temperature for all the adsorption of metal ions on the adsorbents indicating an endothermic process. The negative values of $\Delta G^0$ indicates the spontaneous nature of adsorption of metal ions by the adsorbent. Most of the values of $\Delta G^0$ were negative while some were positive, the more negative $\Delta G^0$ means that reaction reaches the equilibrium with more products and less reactants but with more positive $\Delta G^0$, the reverse is the case. (Eligwe, et. al, 1999). The values of $\Delta H^0$ were greater than +20kj/g/mols for most of the adsorption which supports chemisorption reaction. It was observed that the effect of temperature was more pronounced on the adsorption of the metal ions on the modified coir extract viz; CTR and STR, than the unmodified coir dust. (Figures 2, 3, 5, 6, 8, 9, 11, 12). This shows that the CTR, and STR adsorbents were more efficient at higher temperatures than the coir dust. This is an advantage using these resins to remove metal pollutants from industrial effluents which usually are discharged at high temperatures . Many other researchers have reported endothermic reactions for the adsorption of Cu(II) on adsorbents (Stylianou et al., 2007 and Israel et al., 2010). Endothermic adsorption of Pb(II) on adsorbents have also been reported (Sekar et al., 2004, Adebowale et al., 2008, Hashem, 2008). Sharma and Singh, 2008, and Ma et. al., 2011 also reported endothermic adsorption of Zinc on rice husk and chitosan – aluminium oxide composite material. Endothermic process for the adsorption of Ni(II), by orange peel and hazel nuts activated carbon have been reported (Ajmal et al., 2000, and Demibras et al., 2000).

**Conclusion**

The effect of temperature change on adsorption of Pb(II), Zn(II), Cu(II) and Ni(II) was investigated using CD, CTR and STR as unconventional adsorbents. The adsorption was found to be more effective at higher temperature confprming the reaction as endothermic process

The values of $\Delta H^0$ were greater than +20kj/g/mols for most of the adsorption which supports chemisorption reaction. It was observed that the effect of temperature was more pronounced on the adsorption of the metal ions on the modified coir extract viz; CTR and STR, than the unmodified coir dust. This shows that the CTR, and STR adsorbents were more efficient at higher temperatures than the coir dust.

It can be shown that Coconut Coir dust and its modified resins can be effective in adsorption of metal ions from aqueous solution and can be enhance at elevated temperature.

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