**Article**

# Adsorption characteristics of Cu(II) metal ions in aqueous solutions using phaseolus*aureus* low-cost materials

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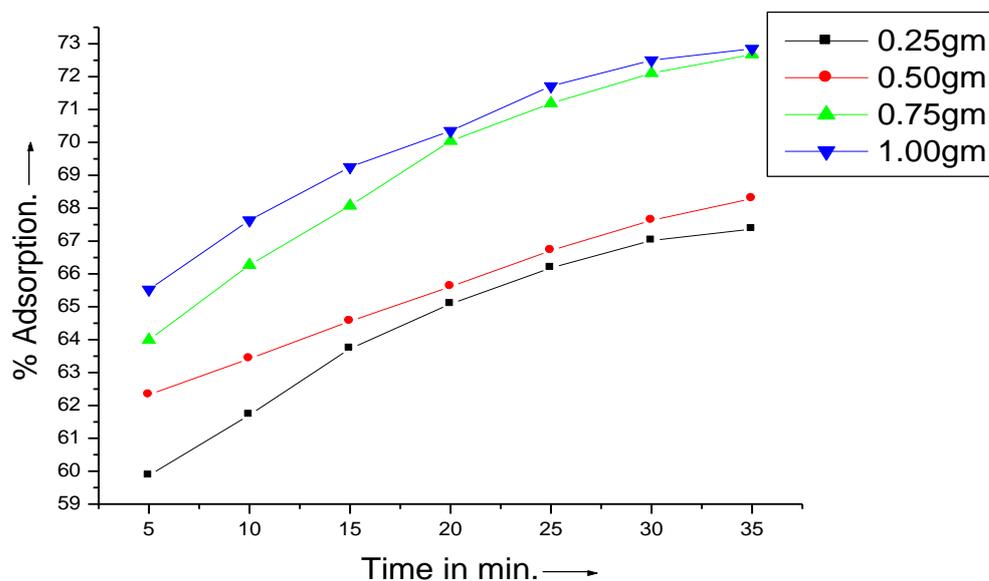
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- **Novelty and Highlights:**

  1 – Phaseolus*aureus* low cost biomaterial is investigated for adsorption of Cu(II).

  2 –Maximum adsorption was found to be 400 mg/g at optimum pH 5.10



Percentage of adsorption efficiency against time for fixed concentration (100 mg/L), and varied GGSH adsorption dose.

# Adsorption characteristics of Cu (II) metal ions in aqueous solutions using *phaseolusaureus* low-cost materials

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**Abstract:**  Adsorption of Cu (II) metal ions into non-conventional *phaseolusaureus* adsorbents developed from seed husk of *phaseolusaureus* was investigated in batch adsorption technique. The aim of the present investigation is to study the potential of green gram seeds (GGSH) for Cu (II) ion adsorption and optimize the parameters like contact time, adsorbent dosage, initial metal ion concentration, initial pH and temperature of solution were varied in order to evaluate their influence on the adsorption process. The results obtained indicate that the adsorption of Cu (II) metal ion by GGSH is better at higher metal ion concentration and higher adsorbent dose. The maximum adsorption capacity was found to be 400.00 mg/g which was obtained at 100 mg/L metal ion concentration and 0.5 gm of GGSH dose. pH 5.10 was chosen as the optimum pH and better adsorption occurred at lower solution temperature. The equilibrium adsorption data were fitted to Langmuir adsorption model and model parameters were evaluated. We can conclude that Langmuir adsorption model is suited to the experimental equilibrium data for GGSH because value of $R^2$ was found to be 0.999. The result shows that GGSH powder has scope for modification to use as low cost adsorbent for adsorption of Cu (II) from aqueous solution.

## Introduction

Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. Many industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non-degradable into toxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise these could pose threats to public health and affects the aesthetic quality of potable water. According to WHO the metals of most immediate concern are copper, zinc, iron, mercury, chromium and lead [1].

Generally, metals could be divided into four distinguished categories which are toxic metals, strategic metals, precious metals and radionuclides. Among these toxic metals are the ones associated for causing serious environmental threats, making its removal from the aquatic environment essential. From the various types of toxic metals present in wastewater, copper was chosen for the adsorption studies with regards to its wide use in industry and potential pollution impact. Copper is listed as one of the pollutants found in wastewater by the United State Environmental Protection Agency (USEPA) in 1978 [2]. In industrial waste, copper mainly appears to be in the form of the bivalent Cu (II). According to Ultman's encyclopaedia Cu (II) is more toxic than the metal itself. This is because it is soluble in water in its ionic form and can easily absorb into living organisms. High dosage of Cu in the aquatic environment generate toxicological concerns

as it can deposit into the brain, liver, pancreas and myocardium [3].Thus Cu (II) metal ion concentration of wastewater should be reduced to value of at least 1.0 to 1.5 mg/L.

The increasing stringent environmental regulation and enforcement of discharge limits require effective decontamination and purification methods. From the analytical point of view, it is known that solid phase extraction (adsorption) is an attractive technique based on the use of the adsorbent that retains analytes. The adsorption process provided its advantage over the other processes because of its cost effectiveness and the high quality of the treated effluent it produces. Different cheap adsorbents such as rice husk [4], sawdust [5], wheat shell [6], cashew nut shell [7], teak leaves [8], seed and seed shell of mango [9], gram seed husk [10], bajra powder [11], etc. were used to remove dyes and heavy metal ions from wastewater. The present study was under taken to evaluate the efficiency of GGSH for adsorption of Cu (II) metal ions in aqueous solution in addition to estimate the optimum adsorption condition and the suitable adsorption isotherms with their related conditions.

## Experimental

### Preparation of adsorbent:

The mature and fresh green gram seeds (GGSH) were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, the green gram seeds are soaked into distilled water up to 24 hours. Then their skin was removing from their pulses and washed with distilled water. It is dried in shadow. After drying the husk was ground by grinder to constant size of 60 $\mu m$ fine powders. The dried fine powder adsorbent was kept in an air tight glass bottle ready for further experiments.

### Preparation of adsorbate:

The copper stock solution (1000mg/L) was prepared using analytical grades of $CuSO_4.5H_2O$, which was purchased from SD Fine Chemicals Pvt. Ltd. Mumbai. Necessary dilutions were done to obtain 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L of copper solution. Standard concentrations were also prepared for calibration processes. The concentrations of Cu (II) metal ion was measured at the wavelength of their maximum absorbance ($\lambda$ max) that was determined by UV-Visible single beam Spectrophotometer (BioEra:CalNo.BI/CI/SP/SB-S-03). The pH of the Cu (II) metal ion solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution and measurement was done by digital pH-meter (Elico: LI 615).

### Adsorption experiments:

The adsorption of Cu (II) metal ions from aqueous solution was investigated in batch adsorption techniques. The GGSH with different adsorbent dose (0.25, 0.50, 0.75 and 1.0 gm) were added in each separate conical flask containing 50 mL of 100 mg/L Cu (II) solution. After adsorption time solution was filtered and 10 ml of sample solution was transferred to 100 ml beaker; and 5 ml of 25 % aqueous citric acid solution was added to it. The solution were made slightly alkaline by the addition of dilute ammonia solution then boiled to remove excess of ammonia. A 15 ml of 4% EDTA solution was added and cooled to room temperature and transferred to a separating funnel. A 10 ml of 0.2 % aqueous sodium diethyl dithiocarbamate solution was added with constant shaking for 45 seconds. A yellow brown colour was developed into the solution.

A 20 ml of butyl acetate (ethanoate) was added into the funnel and the solution was shaken for 30 seconds. The organic layer acquires yellow coloration. The content was further agitated for 15 seconds then the phases obtained were allowed to separate. The lower aqueous layer was removed. A 20 ml of 5 % sulphuric acid (v/v) was added

with constant shaking for 15 seconds, it was cooled thus organic phase was separated. The absorbance was determined at 560 nm against blank. The operating parameters for each set of experiment are summarized in Table 1.

Table 1: Variation of experimental operating parameters.

| Parameters | Values Investigated |
|---|---|
| Contact time in min. | 5, 10, 15, 20, 25, 30, 35 and 24hrs. |
| Amount of adsorbent gm/50ml | 0.25, 0.50, 0.75, 1.0 |
| Initial concentration of Cu (II) solution (mg/L) | 25, 50, 75, 100 |
| Adsorption temperature (K) | 304.2, 309.2. 314.2, 319.2, 324.2 |
| pH | 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 |

The amount of Cu (II) metal ions adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm [12], and then the kinetic adsorption parameters were calculated by;

$$q = \frac{V(Co - Ct)}{M} \qquad (1)$$

Where, $q$ is the amount of Cu (II) metal ions adsorbed from the solution $(mg/g)$, $Co$ is the concentration before adsorption $(mg/L)$, and $Ct$ is concentration after adsorption. $V$ is the volume of adsorbate $(L)$ and $M$ is the weight of the adsorbent $(gm)$.

The percentage adsorption of Cu (II) metal ions was calculated by following equation;

Percentage adsorption $= \frac{(C_0 - C_e)}{C_0} * 100 \qquad (2)$

Where, $C_0$ and $C_e$ are the initial and equilibrium concentrations respectively.

*Equilibrium studies:*

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Classical adsorption models, Langmuir

and Freundlich were used to describe the equilibrium between Cu (II) metal ions on the GGSH at constant temperature. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites.

The linear form of the equation is given by

$$\frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e} \qquad (3)$$

Where, $C_e$ $(mg/L)$ is the equilibrium concentration of the adsorbate, $q_e$ $(mg/gm)$ is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, $Q_0$ $(mg/gm)$ and $b$ $(L/mg)$ are Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption respectively. The values of $Q_0$ and $b$ are calculated from the slope and intercept of plot of $\frac{1}{q_e}$ against $\frac{1}{C_e}$ respectively [13, 14]. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_L$ which is a dimensionless constant referred to as separation factor or equilibrium parameter [15].

$$R_L = \frac{1}{1 + bC_0} \qquad (4)$$

Where, $C_0$ is initial concentration in ppm and $b$ is Langmuir constant related to the energy of adsorption. $R_L$ Value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [16].

The Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is also expressed as

$$\frac{x}{m} = K_f C_e^{1/n} \qquad (5)$$

Where $C_e$ is the equilibrium concentration of adsorbate $(mg/L)$. The constants $K_f$ and $n$ can be obtained by taking *log* on both sides of equation (5) as follows,

$$\log \frac{x}{m} = \frac{1}{n} \log C_e + \log K_f \qquad (6)$$

The constant $K_f$ is an approximate indicator of adsorption capacity, while $\frac{1}{n}$ is a function of the strength of adsorption

in the adsorption process [17]. If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption [18]. A plot of $\log \frac{x}{m}$ against $\log C_e$ gives a straight line with an intercept on the ordinate axis. The value of $n$ and $K_f$ can be obtained from the slope and the intercept of the linear plot. The value of $n$ is greater than unity, (1<$n$<10), that means favourable adsorption [19]

## Results and discussion

*Effect of contact time and initial concentration:*

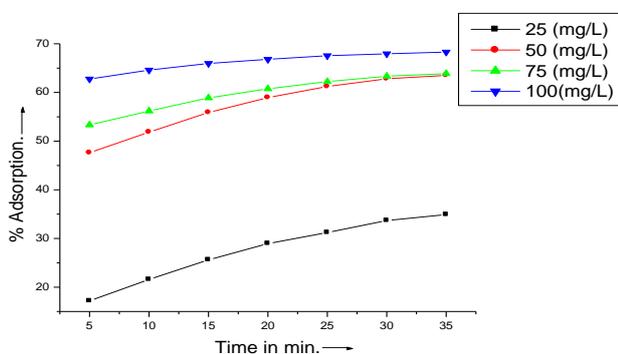The effect of contact time was studied at different initial Cu (II) metal ion concentrations and GGSH dosage.



**Fig. 1:** Percentage adsorption efficiency against time for fixed (0.5 gm/50 ml) GGSH dose and varied Cu (II) ion conc.

Fig. 1 shows the plot of percentage adsorption against time for a fixed GGSH dose of 0.5 gm/50 ml, and varied Cu (II) metal ion concentration. It can be clearly observed that the percentage adsorption increased rapidly until time reached 35 min. After this time, there was drop in percentage adsorption. The highest percentage adsorption was found to be 34.91, 63.51, 63.86, and 68.29 for concentration of 25 mg/L, 50 mg/L, 75 mg/L, and 100 mg/L respectively. From the concentration experiments, 100 mg/L of Cu (II)

metal ion was found to be optimal for the dose of GGSH used.

*Effect of adsorbent dose:*

The relation of percentage adsorption efficiency with time at varied GGSH dosages is depicted in **Fig 2.**
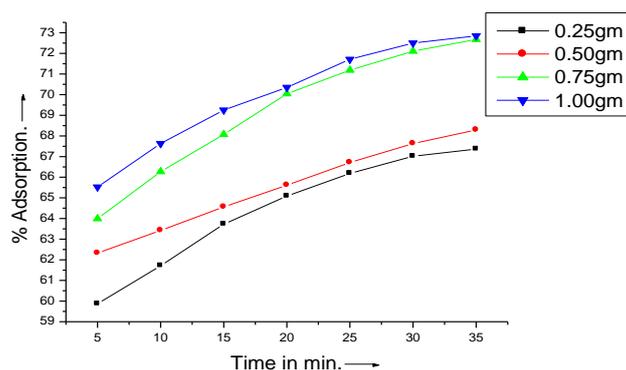


Fig. 2 Percentage adsorption efficiency against time for fixed concentration (100 mg/L), and varied GGSH adsorption dose

Fig. 2 shows the plot of percentage adsorption against time for a fixed Cu (II) metal ion concentration (100 mg/L), and varied adsorption dose of GGSH. It can be clearly observed that the percentage adsorption is higher at beginning time for the all dosage used. This is due to the large surface area of GGSH available during the initial time. As the surface adsorption sites become exhausted, the adsorption rate is slow. The highest percentage adsorption was found to be 67.37, 68.29, 72.67, and 72.85 for GGSH dose of 0.25gm, 0.50 gm, 0.75 gm, and 1.0 gm respectively. From the adsorption dose of GGSH experiments, 1.0 gm. was found to be optimal dose for the 100 mg/L concentration of Cu (II) metal ion used.

*Effect of pH:*

The pH of the adsorbate solution is considered one of the most important factors affecting the adsorption process. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of

the largest metal in terms of hydrolysis, complexation by inorganic ligands and redox potential [20]. In the present investigation, the pH was adjusted in the range of 2.0 – 11.0 by using 0.1 M HCl or 0.1 M NaOH solution. The experiments were carried out at 100 mg/L of initial metal ion concentration with 0.5 gm adsorbent dose at 29.5 $^0$C. Adsorption could not be carried out beyond pH 6 due to the precipitation of Cu (OH)$_2$. This is supported by several other studies [21-23]. Solution with pH lower than 2.0 was also not suitable as for this solution, the surface active sites of the adsorbent would be protonated, resulting in a competition of Cu (II) and H$^+$ ions for the same surface active sites which would result in a low copper adsorption.
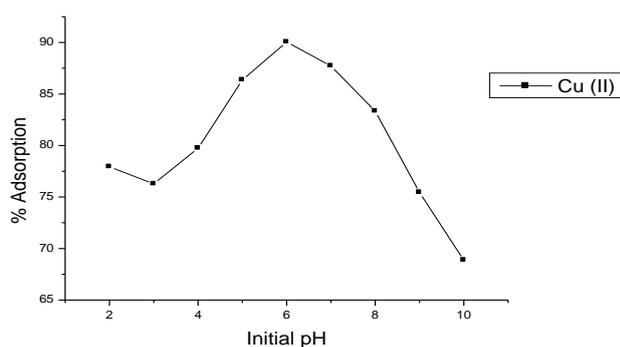


Fig. 3 Percentage adsorption against initial pH at 100 mg/L.Cu (II) conc, and 0.5 gm of GGSH dose at 29.5 $^0$C.

Fig 3 shows that the adsorption is highest for pH 6.0. This result was also presented in many previous studies which involved a maximum adsorption from pH 4.5 –5.5 [24, 25]. The competition of Cu (II) and H$^+$ ions for appropriate sites on the adsorbent sites on the adsorbent surface lowers the adsorption of Cu (II) ions. However, as the pH of the solution increases, this competition weakens, where Cu (II) ions replace H$^+$ ions bounds to the adsorbent since increasing number of protons are dissociated from functional groups on the cell wall. In addition, at higher pH, there will be a change in the dominant functional groups responsible for binding on the cell wall, with carboxylate groups and di-amine groups being the most

important ones for pH< 5 and pH 6 respectively. More negative groups were then made available on the adsorbent surface as pH increases.

The negatively charged adsorbent surface increased the electrostatic attraction between positively charged adsorbate and negatively charged adsorbent particles therefore leading to an increase in the adsorption of Cu (II) ions. However, further increase in the pH will cause the metals to forms precipitates.

*Effect of temperature:*

In order to examine the effect of temperature on Cu (II) metal ion adsorption five different temperatures were selected. Experiments were carried out at 304.2, 309.2, 314.2, 319.2, and 324.2 $^0$K.
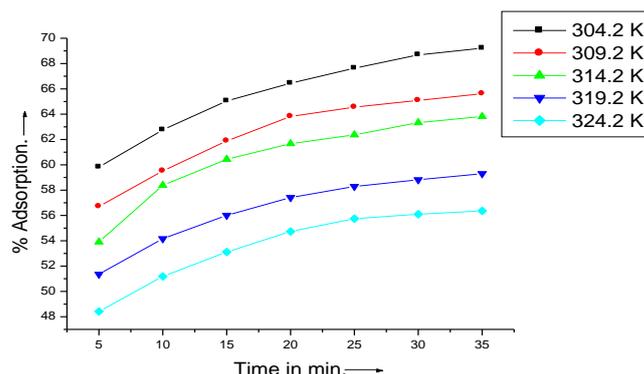


Fig. 4 Percentage adsorption against time at 100 mg/L Cu (II) conc., and 0.5 gm of GSH dose at different temperature.

Fig 4 shows that the percentage adsorption increases when the temperature decreased. This is more significant at low temperature (304.2 K) at 100 mg/L concentration, the highest increase in percentage adsorption efficiency. The increase of percentage adsorption at low temperature signifies that the exothermic nature of the adsorption process.

Thermodynamic Parameters such as Gibb's free energy change$\Delta G^0$, enthalpy change $\Delta H^0$and entropy change $\Delta S^0$ were determined using the following equations [26-29].

$$K_c = \frac{c_{ad}}{c_e} \qquad (7)$$

$$\Delta G^0 = -RT \ln K_c \qquad (8)$$

Where,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (9)$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \qquad (10)$$

Where, $K_c$ is the equilibrium constant, $C_{ad}$ is the amount of metal ion adsorbed per litre of the solution at the equilibrium, $C_e$ is the equilibrium concentration (*mg/L*) of the metal in the solution, $T$ is the temperature in Kelvin and $R$ is the gas constant (*8.314 J/mole*).The values of $\Delta H^0$ and $\Delta S^0$ were determined from the slopes and intercepts of the plot of $\log K_c$ against $\frac{1}{T}$ respectively. Thermodynamic parameter values are shown in Table 2.

Table 2: Thermodynamic parameter values with Copper metal ion solution.

| Temp (K) | ΔG° KJ/mole | ΔH° KJ/mole | ΔS° J/mole |
|---|---|---|---|
| 304.2 | -6.500 | - 36.022 | - 97.048 |
| 309.2 | -6.015 | - | - |
| 314.2 | -5.530 | - | - |
| 319.2 | -5.044 | - | - |
| 324.2 | -4.559 | - | - |

The negative value of $\Delta G^0$ (Table 2) confirms that the feasibility of the reaction and spontaneous nature of the adsorption. The $\Delta G^0$ values obtained in this study for the Cu (II) metal ions are < -10 KJ/mole, which indicate that physical adsorption was the predominant mechanism in the adsorption process. The negative value of $\Delta H^0$ suggests that the adsorption to be in agreement with the exothermic

Freundlich adsorption isotherm gives the relationship between the equilibrium liquid. Since $R_L$ values lies between 0 to 1 for Cu (II) metal ion studies indicates that the adsorption of Cu (II) metal ion is favorable. The data in Table 3 reveal that the Langmuir model yields better fit than the Freundlich model. The values of $n$ suggests that deviation from linearity, if $n = 1$ the adsorption is homogenous and there is no interaction between adsorbed

nature of interaction [30, 31]. The negative value of $\Delta S^0$ suggests the decreased disorder and randomness at the solid solution interface with some structural changes in the Cu (II) ion and the adsorbent.

*Adsorption isotherms:*

Many models have been proposed to explain adsorption equilibrium, but the most important factor is to have applicability over the entire range of process conditions. The most widely used isotherms for solid-liquid adsorption are the Langmuir and Freundlich adsorption isotherms [32]. Both of these isotherms relate the adsorption density, $q_e$ to equilibrium adsorbate concentration in the bulk fluid phase $C_e$ [33]. Langmuir isotherm model is valid for monolayer adsorption on to surface containing a finite number of identical sites. The essential features of a Langmuir isotherms can be expressed in terms of dimensionless constant or separation factor $R_L$. The amount of Cu (II) metal ion adsorbed *(qe)*, Langmuir constants (capacity *(Q0)* and energy *(b)* of adsorption).

Table 3: Isotherm parameter values with Copper [Cu (II)] metal ions.

| Adsorbent | Langmuir constants | | | | Freundlich constants | | |
|---|---|---|---|---|---|---|---|
| | $Q_0$ (mg/gm) | b*10^{-6} (L/gm) | $R_L$ | $R^2$ | n | $K_f$ (mg/gm(L/gm))^{1/n} | $R^2$ |
| GGSH | 400.000 | 2.925 | 0.999 | 0.957 | 1.04 | 17.636 | 0.971 |

species. The values of *n* is greater than unity, *(1< n <10),* that means favourable adsorption [34].

## Conclusion:

The following conclusions can be drawn based on the investigation of Cu (II) metal ion adsorption by GGSH.

i. The optimum contact time for the maximum adsorption capacity of Cu (II) metal ion adsorption on GGSH was 35 minutes.

ii. The percentage adsorption of Cu (II) metal ion on GGSH increased with increasing GGSH adsorption dose and with increase in concentration of Cu(II) ion solution

iii. The maximum percentage adsorption capacity of Cu (II) metal ion on GGSH was 400.00 mg/g at a pH of 5.10

iv. Higher percentage adsorption capacity of Cu (II) metal ion on GGSH was observed at lower temperature.

v. The negative value of $\Delta G^0$ confirms that the feasibility of the reaction and spontaneous nature of the adsorption.

vi. The negative value of $\Delta H^0$ suggests that the adsorption to be in agreement with the exothermic nature of interaction.

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