

Biosorption of Copper from Human Blood Plasma Using *Allium Cepa*

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Abstract – This study investigates the efficacy of *Allium cepa* in removal of Cu²⁺ from human blood plasma *in-vitro* at physiological temperature (38°C). The SEM analysis revealed physical disintegration in the surface morphology of *Allium cepa* biomass after adsorption. Biosorption of Cu²⁺ was dependent on the pH, metal ion concentration, amount of *Allium cepa* biomass used and contact time. The biosorption of the Cu²⁺ was found to be equilibrium at pH 6, metal ion concentration 50 mgL⁻¹ and biosorbent dose 0.60g. Equilibrium sorption occurred at 80 mins with 99.316 %. The adsorption data obtained for Cu²⁺ best fits Temkin isotherm with correlation value (R²) = 0.901 at low binding energy (A_T) = 1.340 Lg⁻¹. The result also revealed that physisorption and chemisorption occurred between the metal ion and binding site on the *Allium cepa* biomass as Intraparticle diffusion proved not to be the only rate controlling step.

Keywords – *Allium cepa*, Biosorption, Freundlich Isotherm, Heavy Metals, SEM and Temkin Isotherm.

I. INTRODUCTION

Chemicals have become an essential part of human life, sustaining activities and development, preventing and controlling many diseases and increasing agricultural yield [1]. Despite their benefits, they can cause adverse effects on human health especially when misused or inappropriately disposed. Heavy metals are among the major constituents of these chemicals. They are harmful because added to their non-biodegradable nature and ability to bioaccumulate in different body parts [2]. When heavy metals enter the human system, they are transported to various parts of the body through the blood plasma which is a medium for excretory product transportation [2].

Biosorption is a method that utilizes biological materials to eliminate heavy metals from aqueous solution. Its advantages over conventional treatment method include low

cost, regeneration of biosorbent, possible metal recovery and high efficiency amongst others [1]. Several studies have reported the potential of biological material to bind heavy metals. Amongst these biomaterial is *Allium cepa* (Onion) which is a vegetable product largely consumed for its potential therapeutic importance [3]. It contains active groups such as carboxylic, sulfate, amino, amide and hydroxyl groups that plays important role in biosorption process [3]. However, lots of biosorption studies have been carried out. For instance Sargassum seaweed as biosorbent for heavy metals [4]; A comparative study on heavy metals biosorption characteristics of some algae [5]; Adsorption of metals by biomaterials derived from the *Ecklonia maxima* [6]; Biosorption of cadmium by brown, green and red seaweeds [7]; Biosorption of lead and nickel by biomass of marine algae [8]; Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils [9];

Chromium (IV) biosorption from aqueous solution using *Cicer arietinum* [10]; Biosorption of copper (II) and cobalt (II) from aqueous solution by crab shell particles [11] amongst others.

Copper are inorganic pollutants that are non-biodegradable. When released into the environment, they cause adverse effect on human beings and animals when ingested. [9]. Exposure to these metals even at low concentration has adverse effect on human and animal health [2]. This study seeks to investigate the biosorption potential of *Allium cepa* on Cu^{2+} removal from the human blood plasma solution. The effect of pH, biosorbent dosage and metal ion concentration will be optimized and used to study the rate of biosorption. The data obtained will be fitted into Freundlich isotherm, Temkin Isotherm and Intraparticle diffusion model.

II. MATERIALS AND METHODS

A. Sample Collection and Preparation

The human blood sample was obtained from the Department of Hematology, Ahmadu Bello University Teaching Hospital, Zaria, Kaduna State, Nigeria. The human blood Plasma was extracted from the human blood sample by centrifugation. The *Allium cepa* was obtained from samara market, Kaduna state, Nigeria. The *Allium cepa* bulb was carefully wash with distilled water and rewashed with de-ionized water, sliced and air dried for a period of 7 days. The dried sample was repeatedly washed with de-ionized water and oven dried for 72 hrs at 60°C to a constant mass, pulverized using agate mortar and sieved with a 0.25-0.50 mm mesh sieve and stored in an air tight plastic container prior to analysis [12].

B. Scanning Electron Microscope (SEM) analysis of *Allium cepa*

The surface morphology was determined before and after biosorption using SEM. The adsorbent was glued to 10mm diameter metal mounts and coated with gold under vacuum in an argon atmosphere. The data was recorded over a selected area of the surface of the sample and a two dimensional image was generated as described by [13].

C. Assessment of Cu^{2+} in Samples

The samples (Human blood plasma and *Allium cepa* biomass) were digested respectively using conventional wet acid digestion as described by [12] and the their filtrates analyzed for Cu^{2+} using Agilent model 3510 Atomic Adsorption Spectrophotometer (AAS).

D. Biosorption Data Evaluation

The percentage sorption of Cu^{2+} was determined using equation 1

$$\text{Biosorption (\%)} = \frac{C_0 - C_e}{C_e} \times 100 \quad (1)$$

Where C_0 and C_e are the initial and equilibrium Cu^{2+} concentrations in human blood plasma respectively. The amount of Cu^{2+} removed from the human blood plasma was calculated using equation 2.

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

Where q_e is the amount of Cu^{2+} bind onto the biosorbent (mgg^{-1}) at equilibrium, C_i and C_e are the initial and final concentration of the metal ion in the human blood plasma (mgL^{-1}), V is the volume of the human blood plasma (cm^3) and m is the amount (g) of biosorbent used.

i. Effect of pH

The effect of pH was studied over a pH range of 2 to 10. The study was carried out by introducing 0.60g of biosorbent into 250 cm^3 conical flasks containing 20 cm^3 human blood plasma solution spiked with 50 mgL^{-1} Cu^{2+} solution. The pH of the mixture was adjusted to pH 2 with 0.1M HNO_3 . The mixture was agitated for 100 mins at 200rpm using a rotary shaker as described by [3]. The adsorbent was separated from the mixture with Whatman No 11 filter paper. The filtrate was digested and analyzed for residual Cu^{2+} using AAS. An equilibrium pH 6 was obtained for further study.

ii. Effect of Metal ion concentration

Equilibrium metal ion concentration was studied by introducing 0.60 g biosorbent into 250 cm^3 conical flask containing 20 cm^3 human blood plasma spiked 20 mgL^{-1} Cu^{2+} solution. The mixture was adjusted to an equilibrium pH 6 using 0.1M HNO_3 and agitated for 100 mins at 200 rpm. The adsorbent was separated from the mixture with Whatman No 11 filter paper. The filtrate was digested and analyzed for residual Cu^{2+} using AAS. This procedure was repeated for Cu^{2+} concentrations of 30 mgL^{-1} , 40 mgL^{-1} , 50 mgL^{-1} , 60 mgL^{-1} and 70 mgL^{-1} respectively. An equilibrium concentration of 50 mgL^{-1} was obtained.

iii. Effect of Biosorbent dosage

Equilibrium biosorbent dosage was studied by introducing 0.20 g of biosorbent into 250 cm^3 conical flask containing 20 cm^3 human blood plasma spiked with equilibrium copper concentration (50 mgL^{-1}). The mixture was adjusted to equilibrium pH 6 and agitated for 100 mins at 200 rpm. The adsorbent was separated from the mixture

with Whatman No 11 filter paper. The filtrate was digested and analyzed for residual copper using AAS. This procedure was repeated for biosorbent dosage of 0.40 g, 0.60g, 0.80g and 1.00 g. An equilibrium biosorbent dose of 0.60 g was obtained.

iv. Rate of biosorption

Equilibrium sorption rate was investigated by introducing 0.60 g of biosorbent into 250 cm³ conical flask containing 20 cm³ human blood plasma spiked with equilibrium Cu²⁺ concentration (50 mgL⁻¹), adjusted to equilibrium pH 6 using 0.1HNO₃ and agitated for 10 mins at 200 rpm with a rotary shaker [14]. The procedure was repeated for 30 mins, 40 mins, 50 mins 60 mins, 70 mins, 80 mins 90 mins 100 mins, 110 mins and 120 min.

III. RESULT AND DISCUSSION

A. Scanning Electron Microscope (SEM)

SEM micrograph of the native and heavy metal (Copper) treated biosorbent are presented in Figs. 1 and 2. The result revealed an uneven surface texture with a lot of irregularities in the surface morphology for the native biosorbent. The SEM micrograph Cu²⁺ treated biosorbent showed remarkable physical disintegration resulting to emergence of protrusions and rough surface area been adduced to the high surface interaction between the binding sites on the surface of the *Allium cepa* biomass and Cu²⁺ [15].

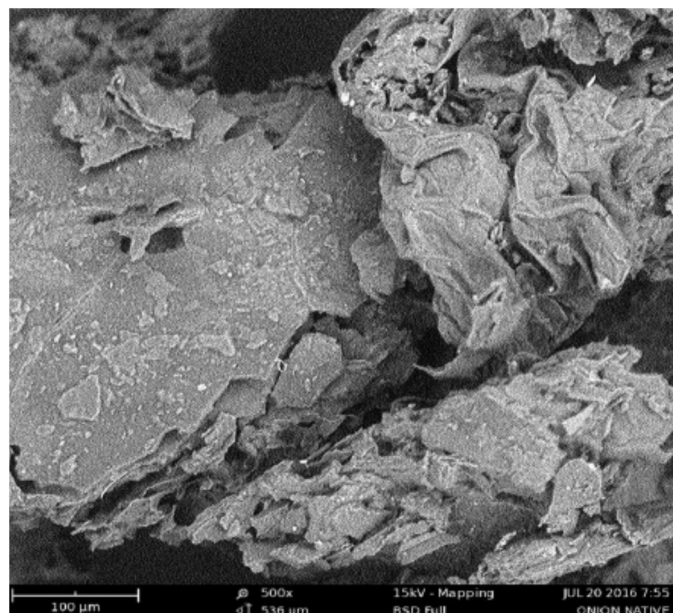


Fig 1: SEM micrograph of *Allium cepa* Biomass

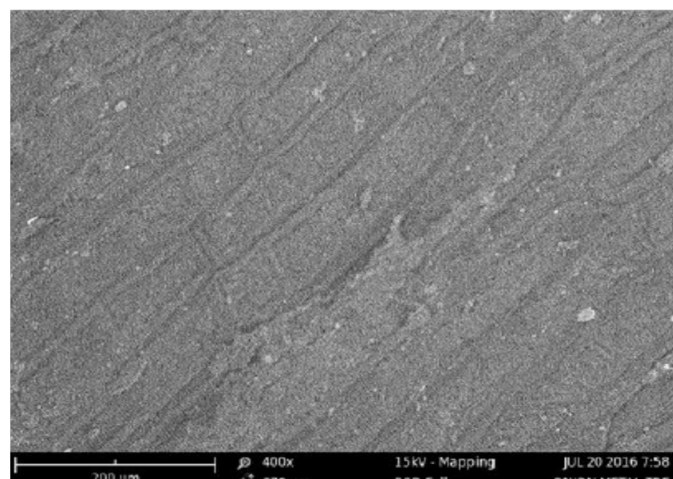


Fig 2: SEM micrograph for Cu²⁺ treated biosorbent

B. Equilibrium Adsorption pH

Effect of pH on Cu²⁺ sorption is presented in Fig. 3. The result revealed an increase in percentage removal of Cu²⁺. The equilibrium sorption was observed at pH 6. After equilibrium pH for the metal ion was attained, desorption occurred with further increase in pH of the solution which indicates high level of interaction between the metal ions and binding sites on the *Allium cepa* biomass as the solution tends towards acidic medium.

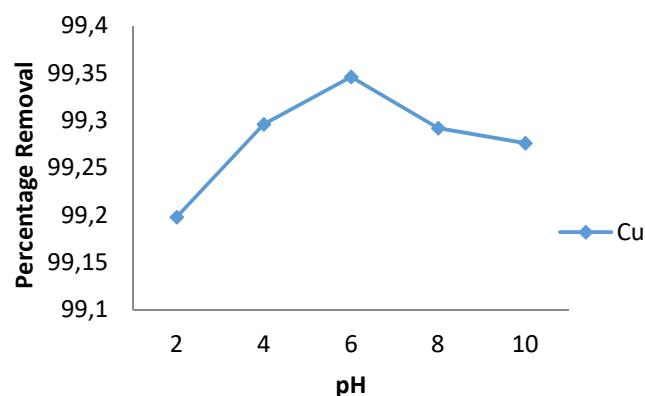


Fig 3: Percentage removal of Cu²⁺ as a function of pH

C. Equilibrium Metal ion concentration

The effect of concentration on Cu²⁺ sorption is presented in Fig 4. The result showed an increase in percentage removal from 20 mgL⁻¹ to 50 mgL⁻¹. The equilibrium concentration for Cu²⁺ sorption occurred at 50 mgL⁻¹ with percentage removal of 99.19 %. The data obtained showed a high interaction between the metal ions and the biosorbent [14].

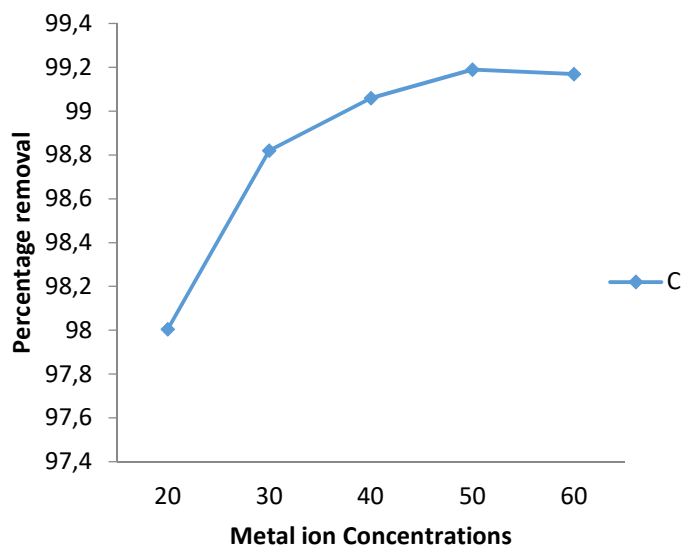


Fig. 4: Percentage removal of Cu^{2+} as a function of concentration

D. Equilibrium Biosorbent dosage

The result in Fig. 5 revealed that maximum sorption of Cu^{2+} occurred at 0.60 g with percentage sorption of 99.34 %. The result showed that at high biosorbent dosage the available metal ions are insufficient to cover the entire exchangeable site on the biosorbent therefore resulting to low metal sorption [11].

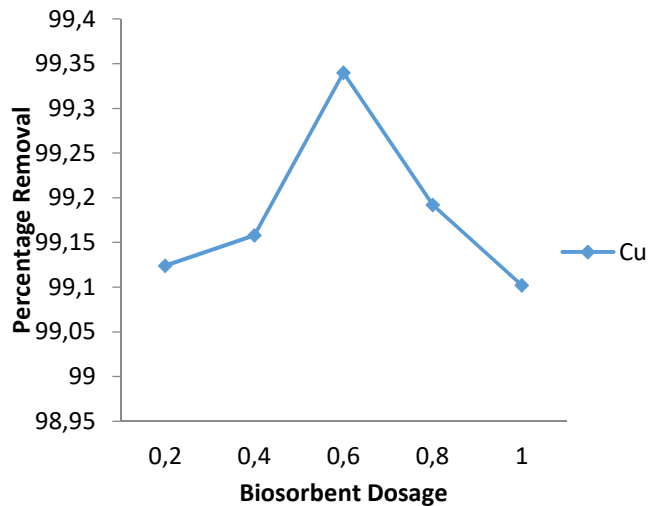


Fig. 6: Percentage removal of Cu^{2+} as a function of Biosorbent dosage

E. Rate of Biosorption

The effect of contact time on Cu^{2+} sorption is presented in Fig. 6. The result showed a significant increase in Cu^{2+} sorption with equilibrium sorption at 80 mins with 99.316 %

removal. Further increase in contact time resulted to release of the adsorbate (Desorption), been adduced to unavailability of free binding sites for metal ion uptake [16].

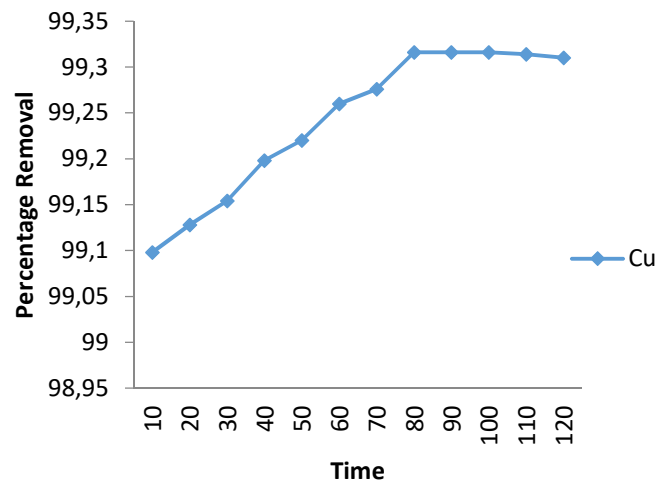


Fig. 6: Percentage removal as a function of Time

F. Biosorption Isotherm

The biosorption isotherm reveals the relationship between equilibrium concentration of adsorbate in the solution and the biosorbent at constant temperature [2]. The data obtained from the percentage removal of Cu^{2+} with contact time was fitted into Freundlich and Temkin isotherms respectively.

i. Freundlich Isotherm

This isotherm model describes non ideal sorption onto heterogeneous surface involving multilayer sorption [15]. The isotherm model is expressed in equation 3

$$q_e = K_f C_e^{1/n} \quad (3)$$

The linearized form is expressed in equation 4

$$\log Q_e = \log K_f + 1/n \log C_e \quad (4)$$

Where Q_e is the amount of adsorbate adsorbed per unit mass of biosorbent, K_f is the freundlich constant measuring adsorption capacity (L/mg), C_e is equilibrium concentration of the adsorbent in solution (mg/L), n is constant related to adsorption efficiency and adsorption intensity of the biosorbent. K_f is dependent on the units upon which Q_e and C_e are expressed [16].

The Freundlich isotherm for Cu^{2+} sorption is presented in Fig. 7. The result revealed that the experimental data obtained for Cu^{2+} sorption doesn't conform to Freundlich isotherm as indicated by the correlation coefficient value $R^2 = (0.217)$. The values of $k_f = 0.3908$ L/mg indicates a low adsorption of Cu^{2+} onto the biosorbent surface. The value of $n = 5.714$

indicates a favourable Cu^{2+} sorption since favourable sorption occurs at $1/n < 1$ [16].

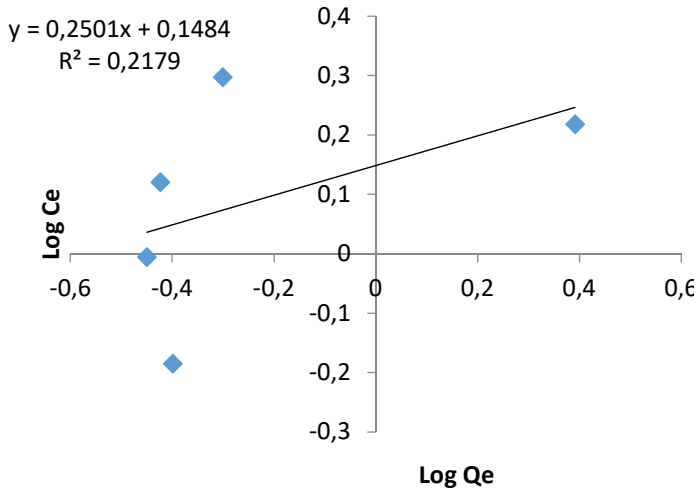


Fig. 7: Freundlich isotherm for Cu^{2+} sorption

ii. *Tempkin Isotherm*

Temkin isotherm takes into cognizance the occupation of the more energetic adsorption sites [17]. Besides the low and large magnitude of concentrations, the model assumes that heat of adsorption by all molecules in a layer would decrease linearly rather than logarithmically with coverage [18].

This is as expressed in equation 5

$$q_e = RT/b_T \ln(AC_e) \quad (5)$$

The linearised Temkin isotherm is presented in equation 6

$$q_e = B \ln A_T + B \ln C_e \quad (6)$$

where $RT/b_T = B$, $T(K)$ is the temperature, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), $A(\text{L/g})$ is the equilibrium binding energy, $B(\text{J/mol})$ is a constant related to heat of sorption and b_T is the Temkin isotherm constant. The linear plot of q_e verse $\ln C_e$ is the Temkin isotherm for the biosorption data presented in Fig. 8 for sorption of Cu^{2+} . From the result obtained $b_T = 86.22$ for Cu^{2+} sorption suggest a high heat of adsorption [19]. Equilibrium binding energy $A_T = 1.340 \text{ Lg}^{-1}$ indicates low binding energy between the metal ions and the active site on the biosorbent [20]. The correlation coefficient $R^2 = 0.901$, indicating conformity to Temkin isotherm.

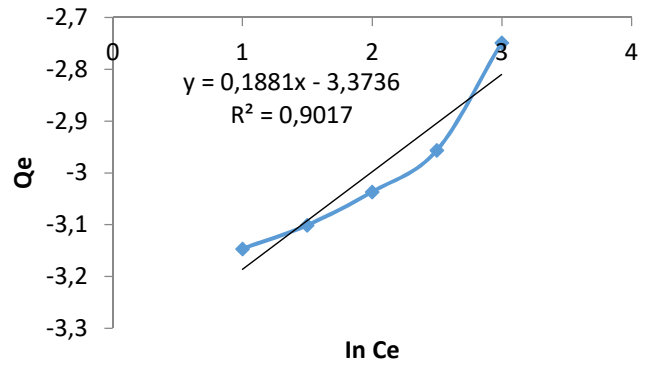


Fig. 8: Temkin Isotherm for Cu^{2+} sorption

G. *Kinetic Study*

i. *Intraparticle Diffusion*

Intraparticle diffusion is employed to identify diffusion mechanism and rate controlling steps that affect the adsorption process [21]. The rate of Intraparticle diffusion is calculated as expressed in equation 7.

$$qt = k_{id}t^{1/2} + C_{ID} \quad 7$$

where, C_{ID} is the intercept and K_{ID} is the Intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$). A plot of uptake (qt) verse ($t^{1/2}$) should be linear if Intraparticle diffusion is take place in the adsorption process and if the line passes through the origin then Intraparticle diffusion is the rate determining step [22]. The experimental data obtained for Intraparticle diffusion of Cu^{2+} sorption is presented in Fig. 9. The result revealed that a plot of qt verse $t^{1/2}$ did not pass through the origin suggesting that Intraparticle diffusion is not the rate determining step [23]. However the data obtained conforms to Intraparticle diffusion as indicated by correlation coefficient value $R^2 = 0.900$. The positive intercept $C_{id} = 1.649$, indicates some degree of boundary layer control [24].

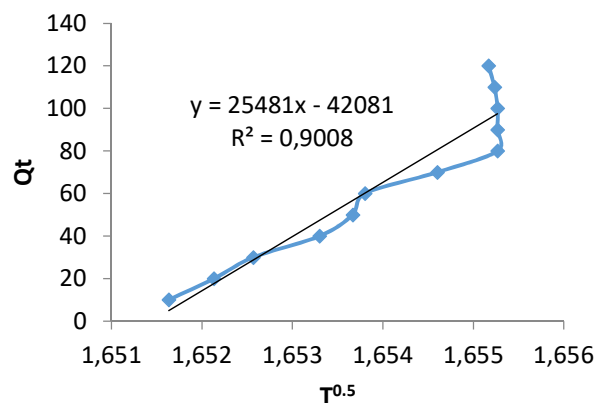


Fig. 9: Intraparticle diffusion model for Cu^{2+} sorption

Table. 1: Isotherm and Kinetic Parameters for Biosorption of Cu^{2+}

Models	Parameters	Values
		Cu^{2+}
Freundlich	K_f	0.3908
	N	5.714
	R^2	0.217
Temkin	b_T	86.220
	A_T	1.340
	R^2	0.901
Intraparticle diffusion	K_i	0.000
	C_{id}	1.649
	R^2	0.900

IV. CONCLUSION

This study has revealed that *Allium cepa* biomass has favourable properties for removal of Cu^{2+} from the human blood plasma in-vitro. The information obtained can be useful in heavy metal removal from the human body in-vivo using natural products. However there is need for further study to investigate the effectiveness of *Allium cepa* biomass in removing copper from human blood plasma in-vivo.

V. CONFLICT OF INTEREST

The author declares that there is no conflict of interest

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