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Research Article

Application of *Aspergillus fumigatus* biomass for the removal of copper and nickel ions from aqueous solution

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Biosorption, *Aspergillus fumigatus*, Langmuir isotherm, Freundlich isotherm.

Abstract

Fungi, like other microorganisms, have the ability to remove heavy metals from solutions as many studies have shown. This study focused on the biosorption capacity of immobilized *Aspergillus fumigatus* biomass for Cu(II) and Ni(II) ions in solution. The dependence of the biosorption efficiency on various parameters, such as biosorbent weight, solution pH, contact time and initial metal ion concentration was investigated. The maximum Cu(II) removal efficiency of 98.08 % was recorded at pH 5.0 and contact time of 2 h. For Ni(II) ions, the maximum efficiency of 98.53 % was recorded at pH 5.0 and a contact time of 2 h also. The data from the batch experiments had a good fit well to both the Langmuir and Freundlich isotherms. The R^2 values for the Langmuir isotherm for Cu(II) and Ni(II) ions were 0.9879 and 0.9900, respectively. The maximum biosorption capacity (Q^o), for Cu(II) and Ni(II), were 3.86 and 10.59 mg/g, respectively. The R^2 values obtained from the plots were 0.9376 for Cu(II) and 0.9074 for Ni(II). The kinetic data had a better fit for the pseudo–second order kinetic model than the pseudo-first order model indicating that chemisorption is a possible mechanism for the biosorption process. Therefore, it can be inferred from these results that the biomass of *Aspergillus fumigatus* immobilized in calcium alginate is a low – cost, readily available biosorbent for the removal of copper and nickel ions from wastewaters.

1. Introduction

Large amounts of wastewater heavy metals are released daily into the environment. These heavy metals are discharged as by-products of various industrial activities. These metals are non-biodegradable and persistent. They have the ability to bioaccumulate in the soil and may eventually enter the food chain [1]. This poses a serious threat to humans and organisms since they are highly toxic and have been implicated in many chronic diseases, including those of the liver, kidney and skin [2]. Copper and nickel contamination arise mainly from mining and electroplating industries. They are both considered as some of the essential elements required in trace amounts for plant and animal growth and development but at high concentrations they become toxic. Various physical and chemical methods are currently employed to remove heavy metals from industrial wastewater. These methods include chemical precipitation, filtration, the use of membranes and the use of activated carbon, among others [3]. These processes have the setbacks of being highly expensive and in some cases produce other toxic by-products whose disposal poses a different challenge [4]. Biosorption, which involves the use of microorganisms as bio-sorbents for the removal of heavy metals, has been shown to be a potential alternative to existing methods [5]. These microorganisms have the ability to remove heavy metals from contaminated wastewater because of the nature of their biological surfaces. These surfaces contain different functional groups which can form complexes with metal ions. Fungi are especially more effective because of the nature of their cell walls. Fungal cell walls are rich in polysaccharides and glycoproteins. These contain various metal-binding groups, like amines, phosphates, carboxyls and hydroxyls [1]. Metal uptake by the cell wall is broadly based on two mechanisms [6]. The first mechanism involves uptake directed by functional groups, such as phosphate, carboxyl, amine and phosphate diester species of these compounds [7]. The second uptake mechanism involves physiochemical inorganic interactions directed by adsorption phenomena [6]. Biosorption has many advantages over the methods currently being deployed to remove heavy metals, including low cost, high efficiency, minimal sludge production and simplicity of operation [8]. The main objective of this study was to screen of the fungal species Aspergillus fumigatus to determine its potential to remove the ions of heavy metals copper and nickel from the solution of their salts and to investigate the conditions under which the biosorption process will be most effective.

2. Materials and methods

2.1. Preparation of biosorbent

Stock solutions containing 1000 mg/L of both metal ions were prepared by dissolving 2.953 g of $Cu(NO_3)_2$ and 4.0503 g of $NiCl_2.6H_2O$ in 1 dm^3 volumetric flasks containing water. After shaking, distilled water was added to each flask to reach the mark. Identified and purified *Aspergillus fumigatus* sample was obtained from the fungal collection of the Nigerian Institute for Leather Science and Technology (NILEST), Zaria. The culturing and cultivation of the biomass were performed in the Research and Development Laboratory of the same institution. The fungal biomass was cultivated on Potato Dextrose Agar (PDA) plates using the method reported by [9]. The immobilization of biomass was carried out by the method described by Mishra et al., [10]. A 100 cm^3 solution of 4 % (w/v) sodium alginate was added to the same volume of a 2 % (w/v) solution of fungal biomass in a conical flask. The mixture was shaken vigorously for 1 hour at 30 ^{0}C to ensure proper mixing. The mixture after it became homogenous was then released through a 10 cm^3 syringe into a 2 % (w/v) $CaCl_2$ solution. The beads which resulted from the mixing process were washed with distilled water.

2.2. Batch adsorption experiments

The biosorption efficiency of *Aspergillus fumigatus* for Cu(II) and Ni(II) ions in solution was evaluated under various conditions by varying one parameter at a time while keeping the others constant [11]. The parameters evaluated in this study included biosorbent dose, initial pH of solution, initial concentration of the metal ion and agitation time. The experiments were carried out at a constant temperature of 30 ^{0}C in 100 cm^3 conical flasks containing 50 cm^3 of solution. The effect of biosorbent weight on biosorption efficiency was investigated at 10 - 200 mg biosorbent weight while the other parameters were kept constant (initial metal ion concentration, 10 mg/L; contact time, 120 min and pH, 5.0). To investigate the effect of solution pH, the biosorption efficiency was evaluated at pH values of 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 while the other parameters were kept constant. The dependence of the biosorption efficiency on the initial metal ion concentrations were evaluated at 10, 20, 40, 60, 80 and 100 mg/L, while the other parameters were kept constant. The effects of agitation time on the removal efficiencies were evaluated at 10, 20, 40, 60, 80, 100, 120 and 150 min contact time, while the other parameters were kept constant.

The conical flasks containing the sample solutions were agitated on a conical flask shaker at 150 rpm under the conditions stated above. After the reactions were completed, the samples were filtered into polypropylene sample bottles. The residual concentrations of Cu(II) and Ni(II) ions were determined using an Atomic Absorption Spectrophotometer (AA280AFS, Agilent Technologies, California, USA). The removal or biosorption efficiency was calculated using equation (1)

$$\text{Biosorption Efficiency (\%)} = \frac{(C_o - C_e)}{C_o} x\, 100 \quad (1)$$

The amount of Cu(II) and Ni(II) ions removed (mg/g)

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was calculated using equation (2):

$$q_e = \frac{V(C_o - C_e)}{M} \quad (2)$$

where C_o and C_e are the initial and the final concentrations of the metal ions in solution (mg/L) respectively, q_e is the amount adsorbed in mg/g of the adsorbate at equilibrium, V is the volume in litres of the solution used during the experiment and M is the mass of the biosorbent in grams [12].

3. Results and discussion

3.1. Effect of biosorbent dose on biosorption efficiency

Fig. 1 shows the effect of biosorbent dose on the biosorption of Cu(II) and Ni(II) ions from the solution by the biomass. The figure shows that the removal efficiency increased with an increase in the biosorbent weight. The copper removal rate increased from 86.07 % at 10 mg biosorbent weight to 97.83 % at 200 mg. The removal efficiency of Ni(II) increased from 56.37 % at 10 mg biosorbent weight to 92.41 % at 200 mg of biosorbent weight. The increase in the percentage removal of the ions with an increase in biomass weight is due to the fact that with an increase in biomass weight, more and more surface becomes available for solutes to adsorb and this increases the rate of biosorption [13].

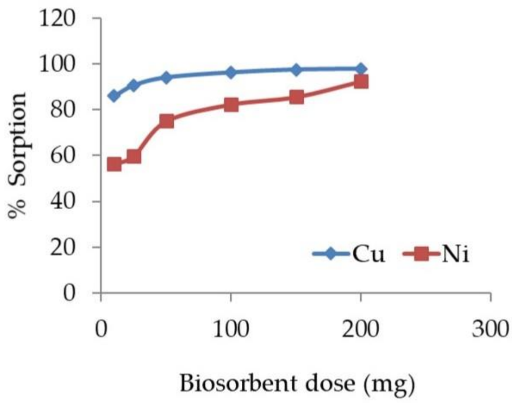

Figure 1. Effect of biosorbent dose on biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

3.2. Effect of initial solution pH on biosorption efficiency.

Fig. 2 shows the variation in the removal efficiency with the initial solution pH. The removal efficiency for Cu(II) increased from 18.60 % at pH 3.0 to 97.09 % at pH 6.0 while the result for Ni(II) increased from 38.96 % at pH 3.0 to 97.08 % at pH 8.0. At low pH, the biosorption efficiency was quite low because the binding sites were highly protonated. For this reason, there was competition between the hydroxonium ions and the metal ions for the occupation of the binding sites. At higher pH values, however, the cell surfaces became more negatively charged, which led to a greater attraction for the metal ions and hence an increase in biosorption efficiency [14].

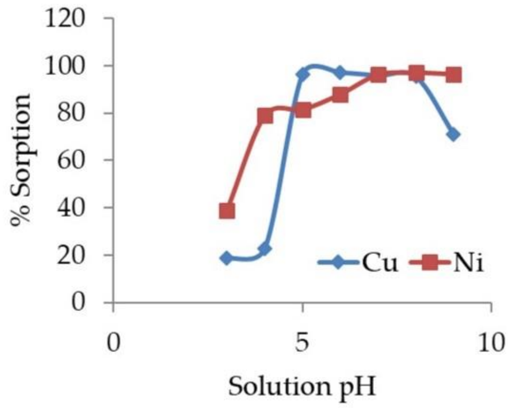

Figure 2. Effect of solution pH on biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

3.3. Effect of agitation time on removal efficiency

The variation in the removal efficiency with the contact time between Cu(II) and Ni(II) ions and the fungal biomass is presented in Fig. 3.

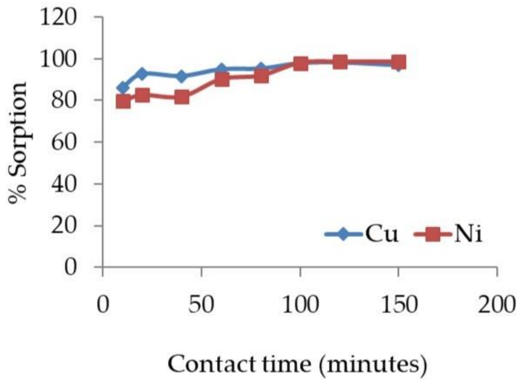

Figure 3. Effect of contact time on biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

The results indicated that the biosorption efficiency of the fungal biomass for the Cu(II) ions increased from 86.22 % at 10 min to a maximum of 98.08 % at 120 min. The efficiency of the removal of Ni(II) ions by the biosorbent increased from 79.67 % at 10 min contact time to 98.53 % at 120 min. The initial sudden increase

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in removal efficiency at the initial stage can be explained in terms of the high driving force, which decreases with time due to the exhaustion of binding sites [15].

3.4. Effect of initial metal ion concentration on biosorption efficiency

The effect of the initial metal ion concentration on the removal efficiency of the biosorbent for Cu(II) and Ni(II) ions is shown in Fig. 4. The results show that the removal efficiency of Cu(II) ions decreased from 94.14 % at 10 mg/L to 25.31 % at 100 mg/L. For Ni(II) ions, the removal efficiency decreased from 97.32 % at 10 mg/L to 24.70 % at 100 mg/L metal ion concentration. The higher biosorption efficiency at low metal concentrations is due to the complete interaction of ions with the available binding sites, which results in higher efficiency [1]. At higher concentrations, the number of metals remaining unbound in the solution due to the saturation of available binding sites increases hence the lower biosorption efficiency at higher metal ion concentrations [16].

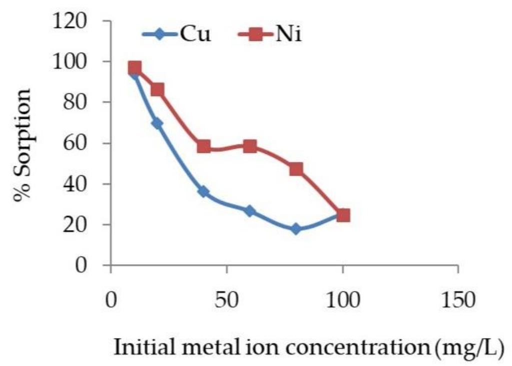

Figure 4. Effect of initial metal ion concentration on biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

3.5. Adsorption isotherms

Adsorption isotherms are useful for describing the interactions that take place between the adsorbent and adsorbate in solution [14]. They are useful in explaining the relationships between the adsorbent and the adsorbate and the mass of the adsorbed species per unit mass of the adsorbent in the medium under a given set of conditions [17]. The data obtained from the adsorption experiments were analyzed using the Langmuir and Freundlich isotherms. The Langmuir isotherm is based on the assumption that adsorption takes place in a single–layer and that there is no interaction between the adsorbate molecules. The Freundlich isotherm is based on the assumption that adsorption process takes place on heterogeneous surfaces and in multilayers.

The Langmuir isotherm in its linear form is shown in equation (3) [15].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \quad (3)$$

Where C_e is the residual concentration of the ions, qe is the adsorption capacity at equilibrium, K_L (L/g) is the Langmuir constant and Q^o (mg/g) is the maximum biosorption capacity. From a plot of C_e/q_e against C_e, the values of K_L (L/g) and Q^o (mg/g) were obtained from the slope and intercept, respectively.

The Langmuir isotherm plots for the two metal ions are shown in Fig. 5.

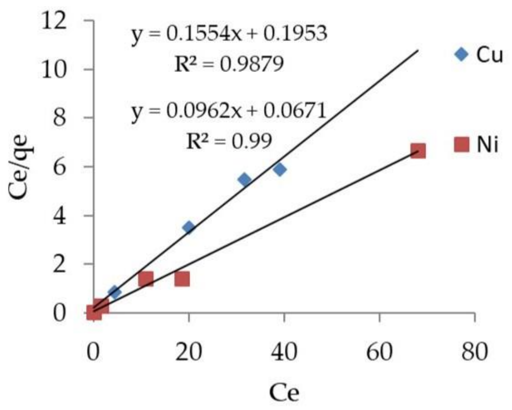

Figure 5. Langmuir isotherm for the biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

The R^2 values from the Langmuir plots for Cu(II) and Ni(II) were 0.9815 and 0.9900 respectively. The high R^2 values for both ions show that they are well suited to the Langmuir model, which indicatesmonolayer adsorption. The maximum biosorption capacity Q^o (mg/g) for Cu(II) and Ni(II) as calculated from the plots were 6.43 and 10.59 mg/g, respectively. The reported values of Q^o for nickel and copper by other fungi include 47.8 mg/g for *Trichoderma viride* [14], 1.683 mg/g for *Saccharomyces cerevisiae* [18] and 60.13 mg/g for *Mucor racemosus* [19]. The Langmuir constant

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K_L indicates the stability of the combination between the adsorbate and adsorbent surface [20]. Generally, a low value of K_L, such as those obtained in this study, indicates that the adsorbate has a high affinity for the adsorbent [20].

The adsorption equilibrium data were also analyzed using the Freundlich isotherm. The linearized form of the Freundlich equation is shown in equation (4) [17].

$$log q_e = \quad log K_f + \frac{1}{n} log C_e \qquad (4)$$

Where q_e (mg/g) is the equilibrium adsorption capacity, C_e is the residual concentration of metal ion in solution at equilibrium (mg/L), K_f is the metal uptake capacity and n is a measure of adsorption intensity. A plot of *1og Ce* against *1og qe* yielded the value of 1og K_f as the intercept and the value of *1*/n as the slope. The Freundlich isotherm plots for Cu(II) and Ni(II) in Fig. 6.

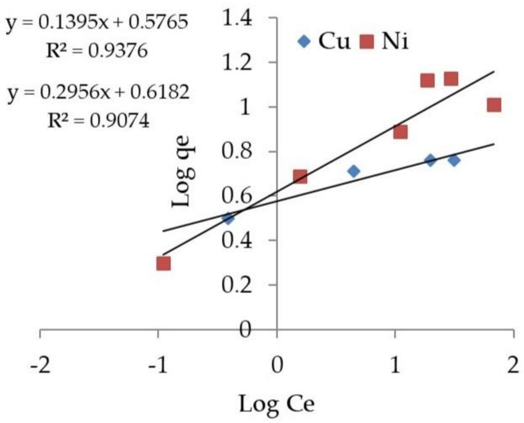

Figure 6. Freundlich isotherm for the biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

The R^2 values for the metal ions obtained from the plots were 0.9376 and 0.9074 for Cu(II) and Ni(II), respectively which shows that the biosorption process can be described by the Freundlich isotherm. The values of K_f and n are presented in Table 1.

The values of n for the two metal ions were 7.17 and 3.38 respectively. Values of n ($1 < n < 10$) or $1/n$ ($0 < 1/n < 1$) indicate beneficial adsorption [21]. In addition to the good K_f and n values, high correlation coefficients were found for both the Langmuir and Freundlich models, implying that both of them could be used to describe the adsorption process of Cu(II) and Ni(II) onto the *Aspergillus fumigatus* biomass.

Table 1. Adsorption isotherm parameters for the biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

Isotherm	Metal ions		
	Constants	Cu (II)	Ni (II)
Langmuir	Q^o (mgg^{-1})	3.86	10.59
	K_L (Lmg^{-1})	0.79	1.43
	R^2	0.9879	0.9900
Freundlich	K_f (mgg^{-1})	3.77	4.15
	n (Lmg^{-1})	7.17	3.38
	R^2	0.9376	0.9074

3.6 Adsorption kinetics

To determine the mechanism of the biosorption process, a kinetic study of the reaction was undertaken using the pseudo-first order and pseudo-second order kinetic models to analyze the results obtained from the batch adsorption experiments described in section 2.2 above. This is also necessary for selecting the optimum operating conditions for the full-scale batch process.

The pseudo - first order kinetic equation is written in equation 5 [22].

$$Log(q_e - q_t) = Log\, q_e - \frac{k_1}{2.303} t \qquad (5)$$

Where q_e (mg/L) and q_t (mg/L) are the adsorption capacities at equilibrium and at time t respectively. k_1 (L/min) is the rate constant for the pseudo –first order adsorption. A plot of log $(q_e - q_t)$ against t gave a straight line from which k_1 (L/min) and *qe* (mg/L) were determined from the slope and intercept of the plot, respectively.

Fig. 7 shows the pseudo – first order kinetic plots for the adsorption of Cu(II) and Ni(II) onto the biosorbent. The correlation coefficient, R^2, for the pseudo – first order kinetic plot for the ions are 0.6784 and 0.7096, respectively. The values of *qe* and k_1 obtained from the plots are listed in Table 2. From the table, it can be seen that there is a significant disparity between the calculated and theoretical values of *qe*. These results suggest that the biosorption of Cu(II) and Ni(II) onto the biosorbent does not fit the pseudo – first order kinetic model.

The linear form of the pseudo – second order kinetic equation is given by equation 6.

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Table 2. Kinetic parameters for the biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

Metal ions	Pseudo – first order constants				Pseudo – second order constants		
Ion	*qe* (*Expt.*)*	R^2	k_1	*qe*(*Calc.*)*	R^2	k_2	*qe*(*Calc.*)*
Cu(II)	1.53	0.6784	0.020	0.326	0.9996	0.359	1.537
Ni (II)	2.69	0.7096	0.049	0.796	0.9974	0.058	2.792

**Expt.* = experimental; *Calc.* = calculated

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e (mg/L) and q_t (mg/L) are the adsorption capacities at equilibrium and at time t respectively and k_2 (g/mgmin) is the rate constant for pseudo – second order adsorption. A plot of t/q_t against t gave a linear plot from which q_e and k_2 were determined from the slope and intercept, respectively.

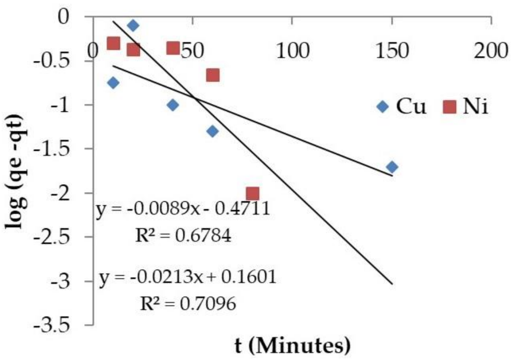

Figure 7. Pseudo – first order kinetic plot for the biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

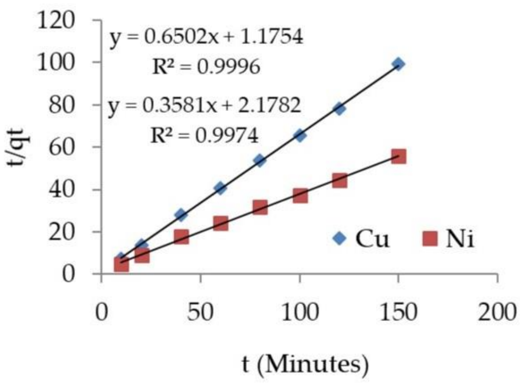

Figure 8. Pseudo – second order kinetic plots for the biosorption of Cu(II) and Ni(II) ions by *Aspergillus fumigatus* biomass.

Fig. 8 shows the pseudo – second order kinetic plots for the adsorption of Cu(II) and Ni(II) onto the biosorbent. The plots gave R^2 values for the Cu(II) and Ni(II) ions of 0.9996 and 0.9974, respectively. The values of *qe* and k_2 obtained from the plots are listed in Table 2. The R^2 values were high and the values of their theoretical *qe* were in good agreement with those obtained experimentally as shown in the table. These results indicate that the biosorption reaction follows the pseudo–second order kinetic model and that chemisorption is the rate-controlling mechanism [23].

4. Conclusions

The present study investigated the biosorption capacity of immobilized *Aspergillus fumigatus* for copper and nickel ions from in aqueous in solution. The results indicated that the biosorption efficiency was dependent on the operating parameters, namely biosorbent weight, initial solution pH, contact time and initial metal ion concentration. Of these, solution pH is the most important because solution chemistry depends on it. The values of Q^o, the maximum biosorption capacity for both ions were obtained as 3.86 mg/g for copper and 10.59 mg/g for nickel ions in solution, respectively. The adsorption isotherm plots for the two ions showed a good fit for both the Langmuir Freundlich isotherm models. This shows that *Aspergillus fumigatus* has the potential for use as a biosorbent for the removal of copper and nickel from metal - bearing wastewaters.

Disclaimer (artificial intelligence)

Author(s) hereby state that no generative AI tools such as Large Language Models (ChatGPT, Copilot, etc.) and text-to-image generators were utilized in the preparation or editing of this manuscript.

Authors' contributions

Conceptualized, research designed, funding of the research the research, drafted and edited the manuscript, D.O.J., A.U.; wrote the first draft of the manuscript, D.O.J.

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Availability of data and materials

The datasets used during the current study are available from the corresponding author on reasonable request.

Conflicts of interest

The authors declare that no conflict of interest/competing interests exists with respect to the submitted work.

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