Moringa stenopetala Seed Cake Powder as Biosorbent for Wastewater Treatment and Its Adsorption Isotherm and Thermodynamic Study

Sisay Tadesse, Ermias Haile
Department of Chemistry, Hawassa University, P.O. Box 05, Hawassa, Ethiopia

Abstract
The aim of this work was to study the effectiveness of a coagulant that removes different pollutants. Adsorbent dose, contact time, and temperature in different turbidity were evaluated. The adsorbent dose were varied from 20–160 mg/l. The time were varied from 10 min– 310 min. The optimal conditions of adsorption obtained were 100 mg/l of adsorbent dose and 45 min contact time for high turbid (361 to 465 NTU) water and 40 mg/l for low turbid (36.8 to 39.9 NTU) water. *Moringa stenopet*ala is effective for high turbidity (98.5%). From 0.1 mg/l initial concentration of the metals, the highest removal efficiency of 82.9% was found for Pb and the lowest for Cr (53.18%). The results showed better fit by the Freundlich models, describing a multilayer adsorption. The thermodynamic studies suggested that a high temperature favors for the adsorption of heavy metals on *M. stenopetala*, indicating a spontaneous adsorption process.
Keywords: *M.stenopetala*, Wastewater Treatment, Adsorption isotherm, Thermodynamic study

Introduction

Environmental issues are a critical factor for today's industry competitiveness. Indeed, the society and the individual consumers could set a common framework for companies' commitment and engagement regarding environment protection. Redesign the process, recover by-products or reuse effluents are some of the possible actions towards an ecoefficient strategy. Nevertheless, a point remains crucial in such mission: the ability to defend natural ecosystems from polluted wastewaters. For such purpose, a wastewater treatment plant that maximizes removal efficiency and minimizes investment and operation costs is a key factor [1].

As one of the key water purification processes, coagulation binds the colloidal particles and bacteria, allowing an electrostatic precipitation of contaminates from solution, the cost-effective consideration of which is distinct in developing countries, such as Malawi. The seeds of *Moringa oleifera*, which is a tropical tree commonly found in parts of Africa, India, Malaysia, Sir Lanka and America, has been widely used as a coagulant in terms of the powder extract [2, 3]

Several coagulants of plant origin have been traditionally used to clean water. Of special interest are the *M. stenopetala* seeds which increasingly are being recognized as a substitute for wastewater treatment due to its effectiveness as a water purifier. *Moringa stenopetala* seed cake powder has coagulating properties that bind and agglomerate to negatively charged particulates which constitute any wastewater. However, there is still paucity of information on efficiency of the Ethiopian endemic plant *M. stenopetala* and the best amount (dose) of coagulant that removes the different pollutants from the effluent. [3].

Therefore, the major objective of the study was to assess the degree of wastewater treatment efficiency using *M. stenopetala* seed cake powder. The specific objectives were to analyse physico-chemical (Turbidity, TDS, NO_3-N, PO_4^{3-}, F, NO_2, SO_4^{2-}) , bacteriological analysis (Total Coliform and Fecal Coliform), to perform Heavy metal analysis (Cu, Cd, Pb, Ni, Zn, Cr) of treated and untreated water with *M. stenopetala* seed cake powder, to see thermodynamic property, to choose the best amount of coagulant that removes the different parameters from the effluent and to check the adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of adsorbent were estimated by Langmuir and Freundlich isotherms.

Materials and Methods

Description of the Study area and study design

The *M. stenopetala* seed used for this study was collected from Arbamench and Hawassa, in South Nations, Nationalities and peoples Regional State (SNNPR) Ethiopia and transported to Hawassa University Chemistry Department Laboratory [4]. The dry *M. stenopetala* pods were split open to obtain the seed kernels, which were allowed to air-dry, crushed using mortar and pestle and again dried. Finally it was milled by analytical mill to produce kilogram of powder, sieved with 150μm to 250μm mesh size and then packed for the trial.

Water Sampling and Transportation

The water sample collected from some factories (Hawassa Textile Share Company and Hawassa Tabor Ceramics). They are discharge waste waters into the nearby shallow swamp that drains into *Tikur Wuha* River, the only constant in flow to Lake Hawassa, and yet the chemical composition of the waste water is unknown [5].

Composite sampling technique according to the procedure was followed [6]. Generally, procedures followed the recommendations of Standard Methods for the Examination of Water and Wastewater [7].

Instrument and Apparatus
Digital analytical balance (ADAM, Model AFP-110L, England), Flame atomic absorption spectroscopy (Buck Scientific, Model 210VGP AAS, USA), Drying oven (Digit heat, J. P. Selecta, Spain), Analytical mill (IKA®, Model A11 basic, IRA), Palintest® Photometer 5000 (Wagtech, Thatcham. Berkshire, UK) series and Round Test Tubes, Portable pH meter (Model HI9024, HANNA Instrument) were used for measurement.

Chemicals and reagents
The chemicals used were 68% HNO_3 (Spectrosol®, BDH, England), 37% HCl (Aldrich, A.C.S. Reagent, Germany), Palintest® Photometer tablet (Wagtech, Thatcham. Berkshire, UK), pH buffers (4.0, 7.0 and 10.01), and 30% H_2O_2 (Spectrosol®, BDH, England). Stock standard solutions (Buck Scientific purographics calibration standards, USA) containing 1000 mg/l of the metals were used. Deionized water was used for rinsing apparatus prior to analysis.

Batch Studies
Study of Adsorbent Dosages
The jar test was conducted for measuring coagulation activity and to find the optimum dose and contact time. Jar test, turbidimeter was used for turbidity measurements. The turbidity for water samples were 36.8 - 39.9 and 361- 465 for low and high turbidity, respectively.

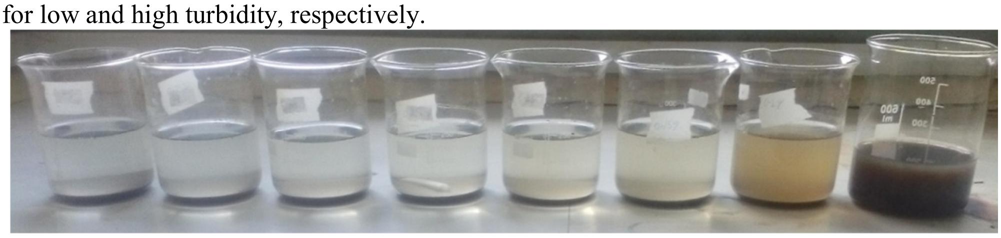

Figure 2: Waste water before and after treatment with different dose seed powder.

This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation. Waste water sample of 250 ml each was kept with the *M. stenopetala* as an adsorbent, in jar test. optimum dose of 100 mg/l(Figure 2) and 40 mg/l for high and low turbidity respectively in the beaker contents were mixed rapidly for 10 sec at 250 rpm; this was followed by 15 min of slowly mixing at 20 rpm to aid in floc formation at room temperature. The flocculated suspensions were allowed to stand without disturbance for 45 min (optimum) to simulate settling. The supernatant thus formed were sampled and measured for turbidity and TDS before and after treatment.

Effect of Contact Time
The effect of contact time on adsorption was examined with different time 10 min to 310 min as indicated in the Figure 4 for high and low turbidity with the optimized dose the powder in 250 ml waste water sample.

Adsorption Isotherms
The adsorption experiments were carried out by batch method. Percentage removal of turbidity and metal ion calculated by following equation:

$$\text{Re}moval\% = \left(\frac{C_o - C}{C_o}\right) \times 100 \quad (1)$$

where C_0 is the initial concentration of metal ions (mg l^{-1}) in the wastewater sample and C is the final concentration of metal ions (mg l^{-1}). The amount of heavy metal adsorbed onto biosorbent (qe, mg g^{-1}) was calculated using the Equation 2. These data were evaluated by Langmuir and Freundlich adsorption isotherm equations, two equilibrium isotherm models usually used to interpret the efficiency of metal sorption

$$q_e(mg.g^{-1}) = (C_o - C) \times \frac{V}{M} \quad (2)$$

Where V is the volume of solution (l) in contact with the biosorbent and M is the mass (g) of the biosorbent. The equilibrium of the biosorption process is often described by fitting the experimental points with models usually used for the representation of isotherm adsorption equilibrium.

Digestion of waste water and preparation for FAAS
The sample preparation of the wastewater was done by using the standard method [8, 9].The digested sample

solutions kept in refrigerator for further analysis by flame atomic absorption spectroscopy.

Measurement of Physico-chemical and Bacteriological parameters

The pH of the sample was measured with a portable pH meter (Model HI9024, HANNA Instrument) calibrated with pH 4.0, 7.0 and 10.01 standard buffer solutions. Total dissolved solid (TDS) was analyzed. Turbidity of sample was measured with portable turbidity meter (model 0839, cole-parmer) calibrated with 0.5, 10 and 20 NTU standards. Each sample was analysed for NH_3, NO_3^-, F^-, Cl^-, SO_4 and PO_4^{3-} using procedures outlined in the Palintest Photometer Method for the examination of water. Faecal coliform and total coliform count were carried out using Paqualab™ incubator (Paqualab Standard System 50, ELE International Limited, U.K.). The membrane filter technique was used to determine the number of colony forming units per 100 ml (cfu/100 ml) of fecal coliforms and total coliform in water.

Statistical Analysis of Data

Statistical analysis was made to check whether there was a significant difference in concentration between low and high turbidity wastewater upon treating with *M. stenopetala* . t-test was used to check whether there was a significant difference or not and the calculation was made using Microsoft Excel and Origin Pro 8 SR0, 2007.

Results and Discussion

Optimum condition of *Moringa stenopetala* powder

The result of this study (Table 2) showed that use of *Moringa stenopetala* seed powder not only diminishes water pollution, but also harmful bacteria. The seed powder joins with the solids in the water and sinks to the bottom.

100 mg/l powder showed maximum reduction of turbidity (98.5%) after 45 min optimum settling time for high, and 40 mg/l powder showed maximum reduction of turbidity (77.8%) and after 60 min optimum settling time for low turbidity respectively. At the 0.05 level, the percent removal of turbidity is significantly different. The concentrations of total dissolved solids in the water is also a rough indicator of mineral content [10].

Table 2: Average Percentage Removal Efficiency of *Moringa stenopetala* seed cake powder for different parameters (heavy metals, anions, Turbidity, TDS and CF).

Parameters	Low turbidity (31.6 to 36.2 NTU)			High turbidity (361 to 465 NTU)		
	Untreated	Treated	Efficiency, %	Untreated	Treated	Efficiency, %
Cu, mg/l	0.016 ±0.001	0.005±0.0001	68.75	0.018±0.001	0.004±0.001	77.77
Cd, mg/l	0.010±0.0002	0.004±0.001	60.0	0.007±0.0001	0.003±0.0003	57.14
Pb, mg/l	0.042±0.0001	0.034±0.002	19.047	0.030±0.002	0.021±0.001	30.0
Ni, mg/l	0.029±0.0001	0.015±0.001	48.27	0.066±0.0005	0.022±0.0007	66.67
Zn, mg/l	0.297±0.0047	0.080±0.003	73.06	0.185±0.008	0.061±0.001	67.03
Cr, mg/l	0.018±0.0002	0.010±0.0001	44.44	0.016±0.0017	0.007±0.0001	56.25
Turb, NTU	31.6±0.085	7.4±0.148	77.84	353±5.080	5.1±0.271	98.5
TDS, mg/l	751±2.064	475±4.961	36.75	983±9.537	725±3.810	26.24
NO_3, mg/l	15.2±0.057	6.4±0.170	57.89	13±0.422	7.8±0.137	40.0
PO_4^{3-}, mg/l	2.4±0.091	1.2±0.022	50.0	4.6±0.021	2.9±0.0209	36.95
F, mg/l	1.2±0.004	0.7±0.001	41.66	0.9±0.073	0.5±0.0038	44.44
SO_4^{2-}, mg/l	5.4±0.008	4.1±0.002	24.07	8.2±0.044	4.3±0.071	47.56
NO_2,mg/l	4.8±0.003	2.7±0.001	43.75	3.6±0.081	2.7±0.0093	25.0
Cl^-, mg/l	14.6±0.041	8.9±0.003	39.04	24.5±0.106	11.9±0.004	51.42
TC (Cfu)	67±3.821	42±4.846	37.31	94±2.150	38±6.204	59.57
FC (Cfu)	32±5.672	19±3.910	40.62	71±6.201	44±3.007	38.03

Effect of Adsorbent Dose

Figure 3 shows that the % removal increased as dose increased from 20 to 160 mg/l and becomes constant at higher doses for Turbidity, and TDS. This is because at higher dose of adsorbent, due to increased surface area, more adsorption sites are available causing higher removal [11]. Further increase in adsorbent dose, did not cause any significant increase in removal of metal ion. Because the metal ions reached equilibrium status between solid and solution phase.

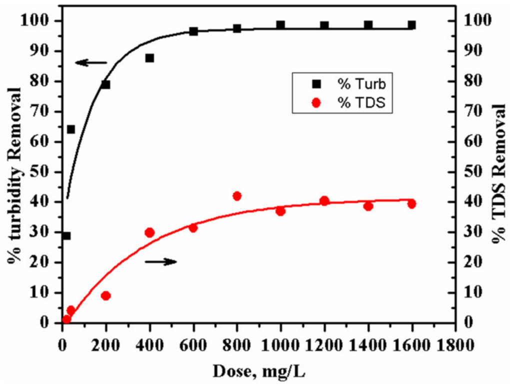

Figure 3: Effect of adsorbent dose of *M. stenopetala* on adsorption of Turbidity and TDS

Effect of Contact Time

Influence of contact time on adsorption of Turbidity on *M. stenopetala* was investigated in the range of 10 min to 310 min for the optimized doses (Figure 4). Maximum rate of removal occurred within around 60 min of settling time. There after removal rate became slow was observed to be constant because the system has reached equilibrium.

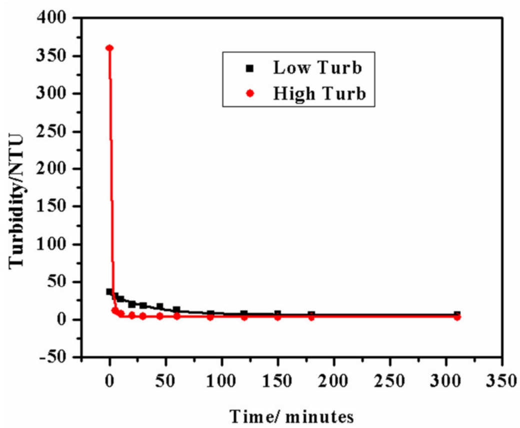

Figure 4: Effect of contact time on adsorption of low and high Turbidity on *M. stenopetala*

Effect of initial concentration of heavy metals

Individual metal of known concentrations were prepared with deionized water. The initial concentrations for Pb, Ni, Cu, Cr, Zn and Cd of the synthetic groundwater samples were varied 0.1, 0.5, 1, 1.5, 2 and 2.5 mg/l for each metal at fixed dosages of 100 mg/l (Table 3). The removal efficiency became below 50% when the concentration exceeds 1.5 mg/l.

Table 3: The relationship between removal efficiency of *M. stenopetala* and initial concentrations of heavy metals

Initial concentration of the metals (mg/L)	0.1	0.5	1.0	1.5	2.0	2.5
% Removal efficiency of Pb	82.9	52.82	43.21	41.98	37.66	31.59
% Removal efficiency of Cd	57.48	56.16	54.93	48.73	45.01	36.23
% Removal efficiency of Ni	78.60	56.8	48.80	39.77	36.20	35.93
% Removal efficiency of Cr	53.18	52.28	43.17	38.64	33.85	33.67
% Removal efficiency of Cu	63.30	51.42	32.81	31.97	32.06	19.46
% Removal efficiency of Zn	78.54	75.28	64.31	48.75	49.30	48.34

Adsorption isotherm

Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure [12, 13]. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. The adsorption curves were applied to both the Langmuir and Freundlich equations. The Freundlich isotherm model, assumes that the adsorption occurs on heterogeneous surfaces, it is used in the case of a possible formation of more than monolayer of adsorption on the surface, and the sites are heterogeneous with different energies of fixation, is often expressed as;

$$q_e = K_F (C_e)^{\frac{1}{n}} \quad (3)$$

This equation can be linearized as follows:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln(C_e) \quad (4)$$

where K_f is Freundlich isotherm constant (l/g) and n is Freundlich isotherm exponent(dimensionless). Values of K_f and n were calculated from the intercept and slope of plots lnqe vs lnCe and a straight line indicates the confirmation of the Freundlich isotherm for adsorption (Figure 6a and Table 4). The value of n should be greater than one confirming good adsorption of heavy metals onto the adsorbent (Table 4) otherwise desorption becomes predominant. According to [14], if a value of n = 1, the adsorption is linear, for n < 1, the adsorption is chemisorption, and for n > 1 the adsorption is a favorable physical adsorption.

Langmuir isotherm, which assumes that a monolayer of heavy metals is formed on a relatively regular adsorbent surface, using the partially protonated groups of the adsorbent. The Langmuir isotherm has been successfully applied to many real sorption processes and is expressed as follows:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (5)$$

where q_e is the amount adsorbed at equilibrium (mg/ g), C_e the equilibrium concentration (mg/ l), b a constant related to the energy or net enthalpy of adsorption (l/ mg), and Q_0 the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/ g). Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with heavy metals and allows the comparison of adsorption performance, particularly in the cases where the adsorbent did not reach its full saturation in experiments. The Langmuir equation can be described by the linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (6)$$

A plot of (Ce/qe) versus Ce gives a straight line with slope $1/Q^0$ and intercept $1/Q^0b$. Q^0 and b can be determined from this plot (Figure7(b) and Table 3). The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

Table 4: Freundlich and Langmuir adsorption isotherm constants

Metals (mg/l)	Langmuir constants				Freundlich constants		
	Q^o(mg/g)	R_L	b(l/ mg)	R^2	K_F (l/mg)	n	R^2
Cu	0.6178	0.9180	0.8923	0.8910	0.443	1.822689	0.9254
Cd	1.5431	0.8346	0.3962	0.9254	0.826	1.261893	0.9611
Pb	0.9924	0.6701	0.4924	0.8926	0.619	1.973515	0.9873
Ni	1.0619	0.5963	0.4513	0.9398	0.6634	1.808187	0.9966
Zn	1.4282	0.7040	0.2102	0.8774	1.0405	1.602538	0.9540
Cr	1.3176	0.3868	0.6339	0.8863	0.61192	1.329946	0.9774

where b is the Langmuir constant and C_0 the initial heavy metals concentration (mg/L). R_L value indicates the type of isotherm. According to [15], R_L value indicates the adsorption nature to be either unfavorable if R_L>1), linear if R_L =1, favourable if 0< R_L<1 and irreversible if R_L=0. From the data calculated in Table 3, R_L values between 0 and 1 indicating that Langmuir isotherm is favourable (Table 3). R^2(correlation coefficient) values approaching to one, clearly suggest that Langmuir isotherm holds good to explain adsorption of metals on *M. stenopetala* (Table 3).

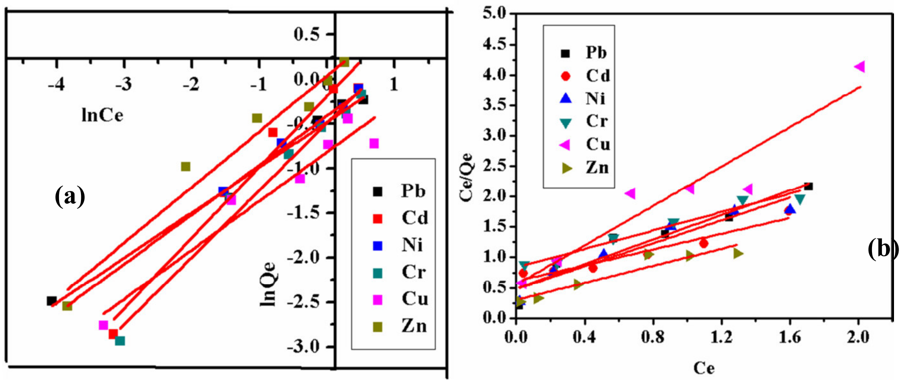

Figure 6: Adsorption isotherms at 298 ˚K (a)Freundlich and (b)Langmuir.

Effect of Temperature and Thermodynamic Parameters

The effect of temperature on the adsorption of heavy metals on *M. stenopetala* seed powder was investigated by conducting experiments for 0.1 mg/L of initial metals ion concentrations at 293, 298, 303, 308 and 313 K. It was observed that by increasing the temperature percentage removal of heavy metals increased. This showed that the adsorption process was endothermic in nature. The thermodynamic parameters: Gibb's free energy (ΔG°), enthalpy (ΔH) and entropy (ΔS°) were calculated using the following equations:

$$\ln\left(\frac{q_e m}{C_e}\right)=\left(\frac{\Delta S^0}{R}\right)+\left(\frac{-\Delta H^0}{RT}\right) \tag{8}$$

$$\Delta G^0=\Delta H^0-T\Delta S^0 \tag{9}$$

where m is the adsorbent dose (g/ l), Ce is concentration of metals ion (mg/ l), qe is the amount of metals ion at equilibrium in unit mass of adsorbent (mg/ g), qe/ Ce is called the adsorption affinity. ΔH, ΔS° and ΔG° are change in enthalpy (kJ/ mol), entropy (J/ mol.K) and free energy (kJ/ mol), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K). The values of ΔH and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of ln (q_em/ Ce) vs. 1/ T, respectively, thereafter ΔG° values were determined from Eq. (9). The values of thermodynamic parameters are presented in Table 5.

Table 5: Thermodynamic parameters for adsorption of heavy metalson *M.stenopetala*.

Parameters	ΔH° (kJ/mol)	ΔS° (Jmol/K)	ΔG° (kJ/mol)				
			293 °K	298 °K	303 °K	308 °K	313 °K
Pb	6.44×10^{-03}	0.0380	-11.2	-11.3408	-11.531	-11.721	-11.912
Cd	4.70×10^{-03}	0.0295	-8.64	-8.79068	-8.938	-9.085	-9.233
Ni	3.84×10^{-03}	0.0330	-9.69	-9.85689	-10.022	-10.187	-10.353
Cr	4.84×10^{-03}	0.0288	-8.45	-8.59233	-8.736	-8.8808	-9.025
Cu	4.80×10^{-03}	0.0306	-8.98	-9.13744	-9.2908	-9.4442	-9.597
Zn	1.05×10^{-03}	0.0295	-8.67	-8.81910	-8.9670	-9.1150	-9.263

The results showed that the ΔG° values are negative and increased in their absolute values with temperature[16]. This result suggested that a high temperature is favored for the adsorption of heavy metals on *M.stenopetala*, indicated a spontaneous adsorption process. The values of heat of adsorption, ΔH is positive for metals ion, indicated that the adsorption process of heavy metals on *M.stenopetala* was endothermic. A positive ΔS suggested that heavy metals were not stable on the adsorption sites of *M.stenopetala* probably due to the increase in translational energy of metal ions.

Conclusions

The present work explores the development in the field of purification of water through minimal energy input and low investment. Adsorption tends to increase with contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Thus it can be concluded that seeds of *M. stenopetala* can be used for the removal of heavy metals and improves the physicochchemical and bacteriological parameters of the waste water. On this study *M. stenopetala* coagulant has been found to have high coagulation activity only for high turbidity water and the activity is low for low turbid water. It was also seen that the efficiency of removal of heavy metal concentration is greater with high turbidity. The data for heavy metals fit well with Freundlich isotherm model whereas adsorption by *M. Stenopetala* can be modeled by both Freundlich and Langmuir isotherms.

Conflicts of Interest
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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