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CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 9, Issue, 5(C), pp. 26688-26692, May, 2018

ISSN: 0976-3031

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

SORPTION OF COPPER ON RICE HUSK AND COCONUT HUSK: A STATISTICAL OPTIMIZATION APPROACH

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DOI: http://dx.doi.org/10.24327/ijrsr.2018.0905.2104

ARTICLE INFO

Article History:

Received 17th February, 2018
Received in revised form 21st March, 2018
Accepted 05th April, 2018
Published online 28th May, 2018

Key Words:

Agro waste, Response surface, methodology, Box-Behnken design, Copper

ABSTRACT

Copper is one of the most important heavy metal used in various industries. Nevertheless, it is one of the main pollutants in the environmental. As it poses toxicity to an ecosystem, it is a matter of concern. Hence we attempt to conduct adsorption studies to remove the copper from a synthetic media. Coconut husk and rice husk were deployed and their efficiency as adsorbent was studied. The experiments were investigated by adopting Response Surface Methodology (RSM) using Box-Behnken Design. The influences of physical and chemical parameters (initial adsorbate concentration, adsorbent dosage and contact time) were studied. As predicated by the model, a maximum of 82.4% and 94.7% were adsorbed by rice husk and coconut husk respectively. The regression co-efficient of 87.5% and 97.6% were displayed by rice husk and coconut husk. The results infer that coconut husk could be a choice as an adsorbent over a rice husk.

INTRODUCTION

Over the last few decades, the toxic waste generated from industries such as mining, electroplating, tannery, agro-chemicals has created tremendous impact on environment by causing heavy metal pollution. Wastewater contaminated with heavy metal is responsible for various chronic diseases in humans as it enters the human body through a process of bio-accumulation [1,2].

Copper is considered as one of the toxic heavy metals majorly generated by mining as well as electroplating industry. Overabundance admission of copper in human causes "Wilson's illness", sickness, regurgitating, stomach spasms, higher concentration of copper causes liver, brain damage and kidney issues [3]. As per EPA the drinking water should not surpass 1.3 mg/land measure of copper that industry is permitted to discharge is additionally given in EPA. According to World Health Organization (WHO) toxic limit of Cu^{+2}concentration in drinking water should not exceed 1.5mg/lit [4].

Several techniques have been tried for the abatement of heavy metals. Recently Jayalatha and Veena-Kumara-Adi [5] conducted column studies in soil and showed that biosurfactant could effectively and efficiently restore the lost physicochemical properties due to Zinc contamination. Adsorption method for metal removal has gained much attention for its efficient treatment of wastewater through low cost adsorbent; it is flexible in designing and operating. Biological sources are considered as an important biosorbent for the removal of heavy metal, due to its easy availability, renewable nature and cost effectiveness [6]. Agricultural wastes are easily available, affordable, eco-friendly, have high capacity for the adsorption of heavy metals[7]. Agro by products such as, coconut husk for adsorption of Cu, Pb, Fe, Cr and Cd; rice husk and groundnut shell for adsorption of copper; sawdust for copper removal; peanut husk for Cu^{+2} Zn^{+2} and Mn^{+2} removal, pigeon pea pod for removing nickel, tea waste for removal ofCu^{+2} Zn^{+2} and Ni^{+2} etc are used in the past investigation.

Rice husk is a horticultural waste material produced in rice delivering nation. The yearly world rice creation is around 500

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million metric tons, of which it contains 10–20% rice husk. Dry rice husk contains 70–85% of natural matter (lignin, cellulose, sugars, and so forth) and silica, which is available in the cell film. Rice husk is economical and easily available [8].Modified rice husk is used in many investigations for adsorption of heavy metals.

The utilization of coconut husk as a biosorption material presents solid potential because of its high substance of lignin of around 35-45% and cellulose of around 23-43% coconut shell powder is seems to be an alluring and economical alternative for the biosorption expulsion of broke up metals [9].

Optimization of process parameters is one the crucial step to achieve maximum response. Traditional optimization methods such as one factor at a time involves great number of experiments and are time consuming and also it overlooks the interaction effect between the variables. Over last few years, statistical methods was preferred by many researchers as it possess their advantages such as reducing the number of experiments and interpretation of possible interactions among the factors and thus reducing error in an economical manner. Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes [10,11,12].

The intention of this investigation is to learn the adsorption behavior of some low cost adsorbents such as coconut husk and rice husk on the heavy metal removal of copper. Box Behnken design was used for the optimizing the conditions of the copper metal removal from the waste water (synthetically prepared). Parameter such as time, initial concentration of Cu^{+2} , adsorbent dosage was studied and to know the efficiency of heavy metal removal from the rice husk and coconut husk.

MATERIAL AND METHODS

Preparation of adsorbent

Rice husk: Rice husk was collected from nearby rice mill in the Davangere, Karnataka, India. It was pre-treated as per standard protocol [13]. Rice husk was sieved to obtain particle size of 0.6 mm. The sieved adsorbent was washed with distilled water several times and open air dried further treated with 2% of tartaric acid in 100ml of distilled water wash the treated husk and dried.

Coconut husk: Coconut husk initially was pre-treated as per standard protocol [14]. Coconut husk was collected from the farm, grounded into a fine particles, washed with distilled water several times and open air dried. Later the husk was treated with 0.1N HCl and washed with water later kept in the oven with 105^0c for 24 hrs.

Preparation of adsorbate

Cupric sulphate ($CuSo_4.5H_2O$) was used to prepare stock solution (15). The Cu^{+2} stock solution (1000 mg/lit) was prepared by dissolving 3.927gms of $CuSo_4.5H_2O$ in 1000 ml distilled water. Synthetic samples of different concentration of Cu^{+2} (10,100,55ppm) were prepared.

Batch biosorption studies

The removal of $Cu^{+2}$from aqueous solution using the Rice and coconut husk was examined in a batch mode operation. The batch sorption studies were carried out in a 250 ml conical flask containing 200 mlCu^{+2}solution of various concentrations as mentioned in Table 2. The suspension was maintained under agitation on a reciprocal shaker at 150 RPM at various time intervals. Later the Cu^{+2}solution were subjected to filtration using cellulose filter membrane (0.45 μm). The concentrations of the Cu^{+2}ions in the filtrate was analyzed using Atomic absorption spectroscopy (AAS).

Metal analysis: Atomic absorption spectroscopy was adopted to estimate copper using nitric acid digestion method [16] and later samples were injected to the AAS.

The % Copper removal, R (%), was calculated after each run as follows:

Metal removal (%) at any instant of time was determined by the following equation:

$$Heavy\ metal\ removal(\%) = \frac{(C_i - C_f)}{C_i} * 100 \quad (1)$$

Where, $C_i$and C_f represent initial and final metal concentration (mg/L) at any instant of time, respectively.

Design of experiment

Optimization of Process variables by Box-Behnken Design

In order to maximize the Cu^{+2} removal efficiency a Box-Behnken factorial design consisting of three factors and three levels was employed. Effect of biosorbent dosage (A), Initial Cu^{+2} concentration (B), and incubation time (C) on % Cu^{+2} absorption efficiency was evaluated. The levels of each variable are shown in Table 1. Fifteen experiments were performed in triplicates to evaluate the pure error. The total number of experiments were calculated from the equation 2.

$$N = 2K(K = 2) + C_0 \quad (2)$$

Where, K is number of factors and C_0 is the number of central point.

The low and high level of the variables with the experimental data for both rice and coconut husk were prepared as in Table 2. The second order equation describing the interaction between the process variables and the response variable is described in the equation 3

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} x_i x_j + \sum \beta_{ii} x_i^2 \quad (3)$$

Where, Y was the measured response variable; β_0, β_i, β_{ij}, β_{ii} were constant and regression coefficients of the model, and x_i, x_j represent the independent variables in coded values. The coding was done by the equation 4

$$x_i = \frac{X_i - \bar{X}_i}{eX_i} \quad (4)$$

Where, x_i was the coded value of an independent variable, *Xi,* was the real value of an independent variable, $\bar{X}_i$was the real value of an independent variable at the centre point, and ΔXi was the step change value .The optimum conditions were confirmed by accomplishing a validation experiments. Monitored Responses and outputs are compared with predicted model. The fitted polynomial equations were expressed as response plots by using the MINITAB (version 16) software program that allows to visualise the relation between the response and experimental levels of every factor and to deduce the optimum condition.

RESULTS AND DISCUSSION

The main significance of this work was utilization of agro wastes viz., rice husk and cocnut husk which otherwise would go waste causing short term and long term effects on eco system.

Effect of process parameters on Cu^{+2} adsorption efficiency

Rice Husk

The design matrix and corresponding response of Rice husk as biosorbent was mentioned in Table 2. It was observed the absorption capacity was varied from 29.8 to 84.4 %, which shows the significance of the optimization. Multiple regression analysis was carried out to evaluate the adequacy of the model. The second order polynomial was fitted in the equation 5

$$Y = 56.4 - 3.8\,A + 0.286\,B - 1.74\,C + 1.4\,A^2 - 0.00481B^2 + 0.0441C^2 - 0.104AB + 1.639\,AC + 0.00087\,BC \quad (5)$$

Where A= Dosage of Rice husk, B= Initial Conc of Cu^{+2}, C= Incubation time.

The results were analysed with the aid of ANOVA and results were shown in (Table 3). According to ANOVA, the quadratic model proved to be highly significant with the Fisher F test (mean square regression: mean square residual is 3.89) with a very low probability value ($P_{model} > 0.05$). The goodness of fit for the model was determined through co-efficient of determination value and it was evident that the model is highly significant with R^2 of 0.875. This shows that the model is capable of explaining 87.5 % of the variation in response. The student's t distribution and the corresponding P values, along with the parameter estimate are shown in Table 4. It was evident from the Table 4, that except Initial Cu^{+2} concentration in both linear and square terms all other factors seems to be insignificant. The % Removal of Cu^{+2} ions was depicted via 3D Plots, where the response was plotted on Z-axis against two independent variable while keeping other variable at mid-level fig 1(a-c), Fig 1a depicts that with increase in Initial Cu^{+2}concentration reduction in absorption efficiency was observed, but it was observed that with increase in time the absorption was increased. Fig 1(b) depicts that with higher rice husk dosage and time higher removal efficiency was observed, while at higher rice husk dosage and lower initial Cu^{+2}concentration higher % Cu^{+2}removal was observed Fig 1(c).

Coconut Husk

The design matrix and corresponding response of coconut husk as biosorbent was mentioned in Table 2.It was observed the absorption capacity was varied from 44.8 to 94.7 %, which shows the significance of the optimization. Multiple regression analysis was carried out to evaluate the adequacy of the model. The second order polynomial was fitted in the equation 6

$$Y = 78.24 - 63.0\,A - 1.073\,B + 1.057\,C - 35.61A^2 + 0.004407B^2 - 0.0164C^2 + 0.381AB - 1.443\,AC + 0.00346\,BC \quad (6)$$

Where A= Dosage of Coconut husk, B= Initial Conc of Cu^{+2}, C= Incubation time.

The results were analysed with the aid of ANOVA and results were shown in (Table 3). According to ANOVA, the quadratic model proved to be highly significant with the Fisher F test (mean square regression: mean square residual is 22.85) with a very low probability value ($P_{model} > 0.05$). The goodness of fit for the model was determined through co-efficient of determination value and it was evident that the model is highly significant with R^2 of 0.976. This shows that the model is capable of explaining 97.63 % of the variation in response .The student's t distribution and the corresponding P values, along with the parameter estimate are shown in Table 4. It was evident from the Table 4, in case of coconut husk biosorption; it was observed that incubation time was insignificant in linear, square as well interaction term with Initial Cu^{+2} concentrations. All other parameters showed significance, hence showing better metal removal capacity compared to rice husk. The % Removal of Cu^{+2} ions was depicted via 3D Plots, where the response was plotted on Z-axis against two independent variable while keeping other variable at mid-level fig 2(a-c). Figure 2a shows positive interaction between coconut husk dosage and time, with the increase in coconut husk % removal of Cu^{+2} was increasing and the adsorption time is very less compared to that of rice husk this is because of the availability of the surface area. Fig 2b depicts the interaction between Initial Cu^{+2} concentration and time, it was observed that at lower metal concentration maximum adsorption was witnessed and time didn't showed any significant impact on the response. Similarly fig 2c shows that with higher biosorbent concentration and lower metal concentration above 90% metal removal efficiency can be achieved.

Validation

Table 1 Experimental Design Factors Level in Response Surface Methodology

Variables	Units	Factor code	Levels	
			Low(-1)	High (+1)
Adsorbent dosage	Grams	A	0.2	1
Initial conc of Cu^{+2}	ppm	B	10	100
Time	Hours	C	2	24

Table 2 Box-Behnken Design Table (Randomized) For Independent Variables

Run	Adsorbent dosage (A)		Initial Conc of Cu (B)		Time (C)		Rice husk (% Cu^{+2} Removal)		Coconut husk (% Cu^{+2} Removal)	
	Code	Value (grams)	Code	Value (ppm)	Code	Value (hours)	Expt	Predt	Expt	Predt
1	0	0.6	1	100	-1	2	31.06	27.75	67.47	63.85
2	1	1	-1	10	0	13	56.07	61.56	92.55	91.84
3	0	0.6	-1	10	1	24	60.53	63.85	87.59	91.20
4	-1	0.2	-1	10	0	13	48.40	47.09	91.39	87.56
5	-1	0.2	1	100	0	13	29.88	24.39	44.80	45.51
6	1	1	0	55	-1	2	47.51	49.51	80.66	80.45
7	-1	0.2	0	55	1	24	50.43	48.43	61.26	61.47
8	0	0.6	0	55	0	13	50.63	50.63	72.31	72.31
9	1	1	0	55	1	24	82.40	73.59	69.66	66.76
10	0	0.6	0	55	0	13	50.63	50.63	72.31	72.31
11	-1	0.2	0	55	-1	2	44.39	53.20	46.88	49.77
12	0	0.6	-1	10	-1	2	62.53	55.04	94.70	95.62
13	0	0.6	1	100	1	24	30.78	38.27	67.20	66.28
14	0	0.6	0	55	0	13	50.63	50.63	72.31	72.31
15	1	1	1	100	0	13	30.08	31.39	73.38	77.20

*All experiments were performed in duplicates and the average values were present

Table 3 Analysis of Variance (ANOVA) Table for Rice Husk and Coconut Husk

	Rice husk					Coconut Husk				
Source	DF	Adj SS	Adj MS	F-Value	P-Value	DF	Adj SS	AdjMS	F-Value	P-Value
Model	9	2526.45	280.72	3.89	0.08	9	3080.69	342.3	22.85	0.00
Linear	3	1814.81	604.94	8.38	0.02	3	2255.86	751.95	50.19	0.00
A	1	230.61	230.61	3.19	0.13	1	646.78	646.78	43.17	0.00
B	1	1397.54	1397.54	19.35	0.01	1	1607.08	1607.08	107.26	0.00
C	1	186.66	186.66	2.58	0.17	1	2	2	0.13	0.73
Square	3	488.97	162.99	2.26	0.20	3	463.93	154.64	10.32	0.01
A*A	1	0.18	0.18	0	0.96	1	119.99	119.99	8.01	0.04
B*B	1	350.22	350.22	4.85	0.08	1	294.02	294.02	19.62	0.01
C*C	1	105.26	105.26	1.46	0.28	1	14.6	14.6	0.97	0.37
2-Way Interaction	3	222.68	74.23	1.03	0.46	3	360.9	120.3	8.03	0.02
A*B	1	13.95	13.95	0.19	0.68	1	187.96	187.96	12.55	0.02
A*C	1	207.99	207.99	2.88	0.15	1	161.21	161.21	10.76	0.02
B*C	1	0.73	0.73	0.01	0.92	1	11.72	11.72	0.78	0.42
Error	5	361.07	72.21			5	74.91	14.98		
Lack-of-Fit	3	361.07	120.36			3	74.91	24.97	*	*
Pure Error	2	0	0			2	0	0		
Total	14	2887.52				14	3155.6			

Table 4 Model coefficient estimated by multiple linear regressions

	Rice Husk					Coconut Husk			
Term	Coef	SE Coef	T-Value	P-Value	Effect	Coef	SECoef	T-Value	P-Value
Constant	50.63	4.91	10.32	0		72.31	2.23	32.35	0
A	5.37	3	1.79	0.134	17.98	8.99	1.37	6.57	0.001
B	-13.22	3	-4.4	0.007	-28.35	-14.17	1.37	-10.36	0
C	4.83	3	1.61	0.169	-1	-0.5	1.37	-0.36	0.730 1.00
A*A	0.22	4.42	0.05	0.962	-11.4	-5.7	2.01	-2.83	0.037 1.01
B*B	-9.74	4.42	-2.2	0.079	17.85	8.92	2.01	4.43	0.007
C*C	5.34	4.42	1.21	0.281	-3.98	-1.99	2.01	-0.99	0.369 1.01
A*B	-1.87	4.25	-0.44	0.679	13.71	6.86	1.94	3.54	0.017
A*C	7.21	4.25	1.7	0.15	-12.7	-6.35	1.94	-3.28	0.022 1.00
B*C	0.43	4.25	0.1	0.924	3.42	1.71	1.94	0.88	0.417

Surface plots for Rice husk

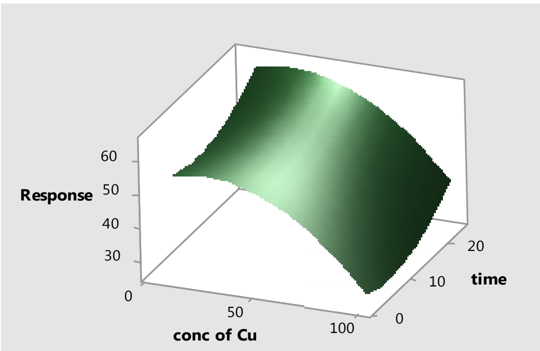

Figure 1(a) Surface Plot for The Interaction between Concentration of Copper and Time while Holding the Dosage of Ricehusk at 0.6 gms.

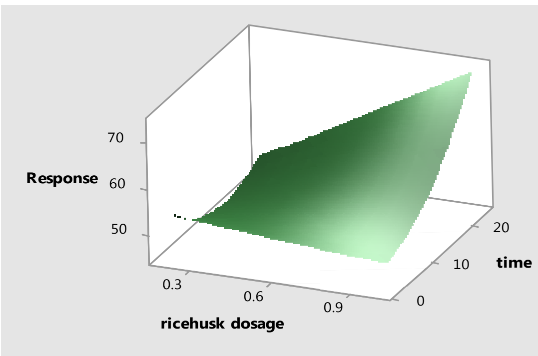

Figure 1(b) Surface Plot for the Effect of Interaction between Time and the Dosage of Rice Husk While Holding the Initial Concentration of Copper at 55ppm.

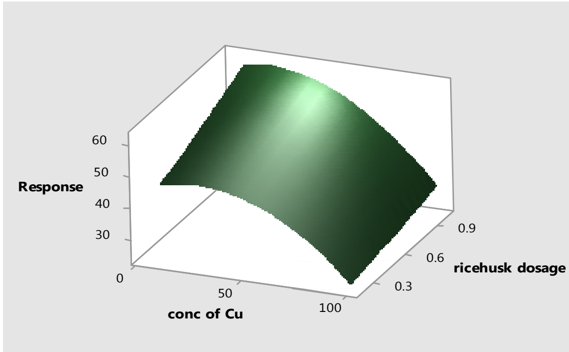

Figure 1(c) Surface Plot for the Effect of Interaction between Initial Concentration of Copper and Dosage of Ricehusk while Holding the Time at 13hrs.

Surface plots for Coconut husk

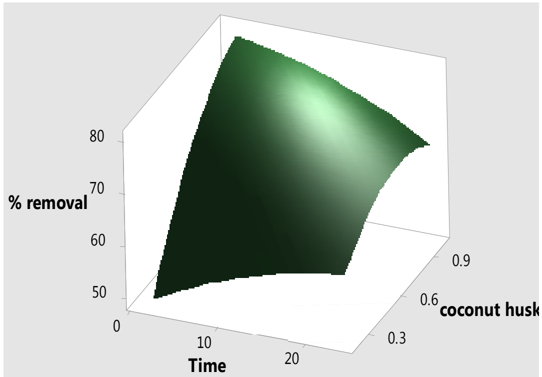

Figure 2(a) Surface Plot for the Effect of Interaction between Time and the Dosage of Coconut Husk while Holding the Initial Concentration of Copper at 55ppm

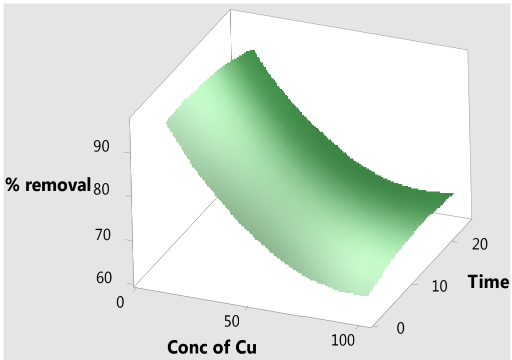

Figure 2(b) Surface Plot for the Effect of Interaction between Initial Concentration of Copper and the Time While Holding the Dosage of Coconut Husk at 0.6grams

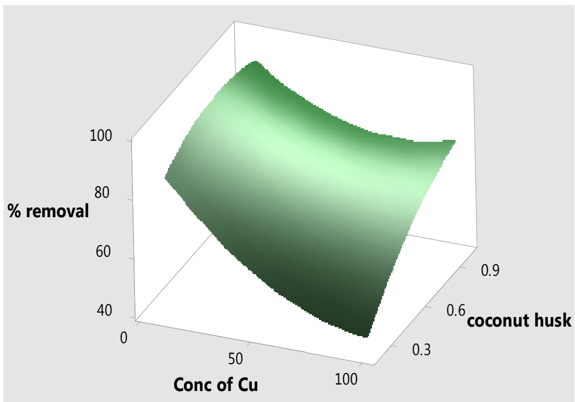

Figure 2(C) Surface Plot for the Effect of Interaction between Initial Concentration of Copper and the Dosage of Coconut Husk while Holding the Time at 13hrs.

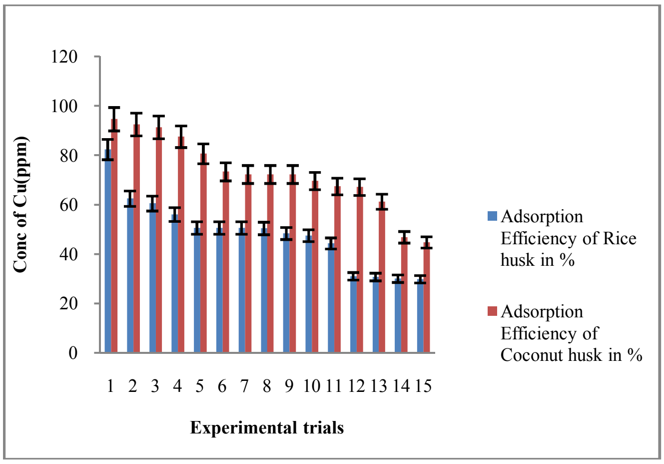

Figure 3 Comparison of Rice Husk and Coconut Husk

The results show that the percentage removal of copper is high in coconut husk when compared to the rice husk in Figure 3. The maximum efficiency obtained by the coconut husk is 94.7033% at 10ppm initial conc, 0.6gm of adsorbent dosage and 2hr of time. The maximum efficiency obtained by rice husk is 82.40% at 55ppm, 1gm of rice husk and 24hrs of time. And in each trial we can see coconut husk gives the maximum efficiency in removal of copper then the rice husk. Hence the coconut husk is more efficient as it is having greater surface area for adsorption of copper when compared with the rice husk

CONCLUSION

There is proper co ordination between expected and predicted values so Box Behnken design can be adopted. All the three variables played a significant role for the adsorption. Coconut husk seems to be better adsorbent compared to rice husk in the experimental design set levels of variables. Around 95% of copper was quickly adsorbed at lower conc.

Acknowledgment

Authors wish to thank The HOD, Civil Department; Co-Ordinator, PG Department of Environmental Engineering; the Management, Bapuji Institute of Engineering and Technology, Davangere, for facilitating the work.

Conflict of interest

All authors of the paper have read and agreed to submission to your journal. The authors declare that they have no conflict of interests. This paper is not published elsewhere and it is not been submitted for publication elsewhere.

Ethical approval

This article does not contain any studies with human participants or animals.

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