Comparative Studies of Isotherm and Kinetics on the Adsorption of Cr (VI) and Ni (II) from Aqueous Solutions by Powder of Mosambi Fruit Peelings

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Author's contribution

The only author performed the whole research work. Author RHK developed the project and prepared the manuscript.

ABSTRACT

This study focuses on the use of powder of Mosambi fruit peelings (PMFP) as an inexpensive and efficient adsorbent to remove Cr(VI) and Ni (II) from aqueous solutions. The influence of physico-chemical key parameters such as the initial metal ion concentration, pH, agitation time, particle size and adsorbent dosage has been considered in batch tests. Sorbent ability to adsorb Cr(VI) and Ni (II) ions were examined and the mechanism involved in the process was investigated. The optimum results were determined at an initial chromium ion concentration was $10 mgL^{-1}$, p^H=2, agitation time=60min, an adsorbent dose (150 mg/50ml) and the particle size (0.6mm) Langmuir constants [Q_0=7.51(mg/g) and b=1.69(L/mg)] Freundlich constant (K_f=2.94), Lagergren rate constants (K_{ad} (min^{-1})=5.75 x10-2) for [Cr(VI)] 10 mgL^{-1} and initial nickel ion concentration of 50 (mg L^{-1}), pH=4,agitation time – 90 min, an adsorbent dose (125mg/50ml) and the particle size (0.6mm). The % adsorption, Langmuir constants [Q_0=29.41(mg/g) and b=0.4789(L/mg)], Freundlich constant K_f= 23.92(mg/g) and n=2.24 (L/mg), Lagergren rate constants [K_{ad} (min^{-1}) = 4.37 x 10^{-2}] for [Ni (II)] 50 (mg L^{-1}), were determined for the adsorption system as a function of sorbate concentration. The equilibrium data obtained were tested using Langmuir**,** Freundlich adsorption isotherm

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model and the kinetic data obtained were fitted to pseudo first order model. Heavy metal removal with the above adsorbent appears to be technically feasible, ecofriendly and has high efficacy.

ABBREVIATIONS

DMG: Dimethylglyoxime; PMFP: Powder of Mosambi Fruit Peelings; DPC: Diphenyl Carbazide.

1. INTRODUCTION

Water is central to our lives but it is also the world's most threatened essential resource. Some of the worst industrial pollution is contaminating the world's most vulnerable water resources, Many industries such as metal plating facilities, mining operations and tanneries discharge waste containing heavy metal ions [1]. As pollutants, heavy metals were intensively studied due to their significance from the point of view of persistence and toxicity. These toxic metals can cause accumulative poisoning, cancer and brain damage when found above the tolerance levels [2]. The industrial use of chromium can be of three types, namely metallurgical, refractory material and chemical industries. The metallurgical industries use chromite ores for production of ferrochromes which are used in the manufacture of stainless steel and alloy steels. The refractory industry utilizes chromium for production of chromite bricks, which is used in melting furnace linings. In chemical industries, chromite ores are used in the preparation of sodium and potassium chromate. Chemicals for tanning agents, pigments, catalysts and wood preservatives are obtained from dichromate. Chromate and inorganic chemical manufacturing industries are the main source of chromium pollution [3]. The toxicity of chromium depends on its oxidation state and water quality. Of the tri and hexavalent chromium, Cr(VI) was found to be more toxic and readily pass through the red blood cell membrane. Respiratory effects are the main consequences of occupational exposures. Over exposure to chromium dust and mists cause irritation of skin and respiratory tract, lung carcinoma, intravascular hemolysis, maxillary, sinus cancer and acute renal failure have been reported to result in workers who are exposed to high levels of Cr(VI) from ingestion of potassium dichromate [4-6].Many adsorbents were tested to remove hexavalent chromium from aqueous solutions and wastewaters. Reports on tamarind nut carbon [7], mixture of fly ash and activated carbon [8], pipal bark [9], rice husk ash [10], corncob [11] and Coffee Wastes [12] are a few to mention. One of the important toxic metals, Nickel (II) finds its way into the water bodies through effluents from industries. It is present in the effluents of silver refineries, zinc base casting and storage battery industries. As it resists corrosion even at high temperature, it can also be used in gas turbines, rocket engines and desalination plants. It is also used in coinage and costume jewellery. Skin contact with nickel causes a painful disease called "nickel itch" which is fatal [13]. Heavy metals have a tendency to bioaccumulate and end up as permanent destructive elements in environment [14]. Heavy metals like Zn, Cr, Cu, Ni, and As are known to have toxic effects at very low concentrations [15] as well as very high concentration [16]**.** Nickel is a toxic heavy metal found in the environment as a result of various natural and industrial activities. Nickel has been implicated as an embryotoxin and teratogen [17]. The higher concentration of Ni causes poisoning effects like headache, dizziness, nausea, tightness of

the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis and extreme weakness [18-19].

The removal and rapid decontamination of heavy metals Cr(VI) and Ni(II) become very important for the environmental remediation. Many processes have been used for the removal of heavy metals from waste waters, such as chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange and adsorption .For dilute metal concentrations, ion exchange, reverse osmosis and adsorption can be applied. However, the common use of ion exchange and reverse osmosis is restricted by the high operating cost. As an alternative to chemical precipitation, membrane filtration, or ion exchange, adsorption processes with a wide variety adsorbents have been tested. The adsorbents used should have some specific properties, such as a high ability to reduce the concentration of heavy metals below the acceptable limits, high adsorption capacity and long lifetime [20].Thus, it is a continuing need to identify and develop low-cost and efficient adsorbents for facile and efficient removal process.

In an effort to evolve a useful user-friendly, eco-friendly and economical process, the present study was taken up. This study includes the adsorption studies on Cr(VI) and Ni (II) ions using powder of Mosambi fruit peelings. The efficiency of this adsorbent was studied and maximum adsorption and lowest equilibrium time for this adsorbent was recorded.

2. MATERIALS AND METHODS

2.1 Adsorbent

Easy availability, economical to use and proven potential for other metals, have been the reasons for selection of this adsorbent Powder of Mosambi Fruit Peelings (PMFP) were used to adsorb Cr(VI) and Ni (II) ions.

2.2 Powder of Mosambi Fruit Peelings (PMFP)

Mosambi fruits are very famous in India. They belong to citrus family and are popularly called as sweet limes. It is the first choice of many Indians as fruit juice. The peelings of the fruits were collected from the shops, dried and chopped, cleaned and soaked in distilled water for 24 hrs. The soaked pieces of peelings were sun-dried and powdered. Size of the particles selected for the study was 0.6 mm.

2.3 Measurement of pH of the Adsorbent

Five grams of adsorbent powder was taken into a 1000 ml beaker. To this 150 ml of freshly boiled and cooled water was added and then heated till boiling point. The contents were digested for ten minutes and kept aside for ten minutes. The solution was filtered and pH was measured. The metal ion solutions for standard solutions and further dilutions were prepared following the procedures described [21].

2.4 Preparation of Metal ion Solutions

The Chromium (VI) and Nickel (II) ions were estimated using standard methods. AR grade chemicals and double distilled water were used for all the analyses. The concentrations of the metal ions were estimated using UV-visible spectrophotometer (ELICO SL 150).

Standard Chromium Solution**:** Potassium dichromate AR grade was used to prepared standard chromium(VI) solution, 2.830 g of potassium dichromate was weighed in an electronic balance and taken into 1000 ml volumetric flask. A solution was prepared making it up to 1000 ml.

Standard Nickel Solution**:** Nickel (II) solution was prepared by using AR Grade nickel ammonium sulphate; 6.7280 g of nickel ammonium sulphate was taken into a 1000 ml volumetric flask. 5 ml of 1% HNO3 was added to it immediately. Then the contents were made up to 1000 ml with double distilled water.

2.5 Analysis of Metal Ions

2.5.1 Analysis of chromium (VI)

Chromium (VI) was estimated using UV – visible spectrophotometer (ELICO-SL 150) by Diphenyl Carbazide (DPC) method. Different dilutions of Cr(VI) solutions containing less than 30 mgL^{-1} of chromium concentrations were added with 2.5 ml of Diphenyl Carbazide solution. The diphenyl carbazide solution was prepared by dissolving 200 mg of 1.5 diphenyl carbazide in 100 ml of 95% alcohol. The contents were mixed with an acid solution of 40 ml of concentrated H_2SO_4 and 360 ml of distilled water. The contents were refrigerated for not less than 24 hrs, and to a maximum of one month. The absorbance was measured in the UV – visible spectrophotometer at 540 nm. The reagent blank was also measured following the same procedure.

2.5.2 Analysis of nickel (II)

Spectrophotometric analysis was adopted to estimate Nickel (II), by using dimethylglyoxime (DMG). Different standard solutions containing less than 100 mgL-1 of Nickel (II) were prepared and 2 ml of 20% w/v sodium tartarate solution 10 ml of 4% w/v potassium persulphate 2.5 ml of 5 M sodium hydroxide solutions and 15 ml of (1+30) HCl solutions were added. Again 0.6 ml of 1% DMG solutions were added to this mixture. The contents were made upto 50 ml. The absorbance was measured after 30 minutes using UV–visible spectrophotometer at 465 nm. A reagent blank was also prepared for Nickel (II) solution.The results for a heavy metal concentrations were expressed in mg L^{-1} while those of the concentration equilibrium, equilibrium time, and adsorption capacity etc., were compared with the Langmuir and Freundlich isotherms.

2.6 Batch Equilibrium Method

All experiments were carried out at room temperature (27ºC) in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were carried out by taking 50 ml metal ion sample (AR grade) in a 100 ml Erlenmeyer flask and after pH adjustments; a known quantity of dried adsorbent was added. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker until equilibrium conditions were reached. After shaking, the suspension was allowed to settle. The residual biomass adsorbed with metal ion was filtered using whatman 42 filter paper (Whatman International Ltd., Maid Stone, England), filtrate was collected and subjected for metal ion estimation using UV-visible spectrophotometer (ELICO SL 150). The values of percent metal uptake by the sorbent (Sorption efficiency) and the amount of metal ion adsorbed has been calculated using the following relationships

$$Sorption\ efficiency = \frac{C_i - C_f}{C_i} \times 100$$

$$Amount\ adsorbed\ (q_e) = \frac{C_i - C_f}{m} \times v$$

where,

C_i = Initial concentration of metal ion in the solution (mg L^{-1})
C_f = Final concentration of metal ion in the solution (mg L^{-1})
m = Mass of adsorbent (g L^{-1})
v = Volume of solution (L)
q_e = Amount of metal ion adsorbed per gram of adsorbent.

Control experiments were carried out and the average values of duplicate runs were obtained and analyzed (Error: ±1-2% for percentage removal and ±0.005-0.01 mg g^{-1} for amount adsorbed). The adsorbents selected were very common and eco-friendly. The work mainly helps in bringing sorbent into use to handle the heavy metals.

3. RESULTS AND DISCUSSION

3.1 Characteristics of PMFP

The Characteristics of PMFP is discussed in the Table 1.

Table 1. Characteristics of PMFP

S. No	Parameter	Value
1	Apparent Density (g/ml)	1.5673
2	Moisture Content % (w/w)	70.90%
3	Loss on ignition % (w/w)	95.80
4	p^H	4.69
5	Particle size	0.6mm
6	Calcium as Ca	1.04
7	Lignin Content % (w/w)	7.3
8	Cellulose % (w/w)	2.9

3.2 Effect of pH on % Removal of Metal Ions

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of metal ions, concentration of counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Studies were carried out to obtain optimum pH for the adsorption of Chromium (VI) using 150 mg of PMFP adsorbent in 50ml solution of 10 mgL^{-1} of Cr(VI) concentration adjusted to different pH values from 2.0 to 9.0.The solutions after equilibrium were centrifuged and analyzed for Cr(VI) content. The results obtained were presented in (Fig. 1). It was evident from the (Fig. 1), that maximum removal of 91.28% was achieved at pH 2.0 and the per cent removal was found to be almost constant after pH range 6 to 9. In the absence of adsorbent, precipitation started at pH greater than 6.0 and in the presence it started at 7.0. Since the aim of the work is to study only the adsorption phenomenon, it was decided to maintain pH value at 2.0 for

all further experiments [22].Many reports revealed that maximum adsorption of Cr(VI) are in the pH range of 2-6. The results obtained for the adsorption of Cr(VI) on powder of Mosambi fruit peelings adsorbent are in good agreement with the removal of Cr(VI) by saw dust and pine leaves at pH 2.0 [23]. Where as to find out optimum pH for the removal of Nickel (II), 125 mg of the PMFP adsorbent in 50 ml solution of 50 mgL-1 of nickel(II) concentration are adjusted to different pH values ranging from 2.0 to 9.0. They were equilibrated for 120 minutes and centrifuged. The filtrates were tested for Ni(II)concentrations spectrophotometrically. (Fig. 2) shows the effect of pH on adsorption of Ni (II) ion. Maximum 92.56% removal was observed at pH 4. The percentage of adsorption increased with increase in initial pH and decreased with increase in initial pH up to 6. The adsorption of metal cations depends on the nature of metal ions, adsorbent surface and species of the metals. At lower pH values, Nickel removal was inhibited, possibly because of the competition between hydrogen and nickel ions in the sorption site. With apparent preponderances of hydrogen ions, it restricts the approach of metal cations as a consequence of the repulsive force. At pH > 6 precipitations started and hence, higher pH was not selected for the present study. Biosorption of nickel Ni(II) was maximum at pH=4, as the pH exceeded, the biosorption began to decrease. This is possibly due to the precipitations of Ni (II) ions as a result of hydroxide anions forming nickel hydroxide precipitate. The adsorption of Ni (II) ion is reported to be highly pH dependent. Adsorption of Ni (II) on activated carbon is found to be efficient at pH less than 4.5 [24] and adsorption of Ni (II) on waste tea (*Camellia sinensis*) materials is also found to be efficient at pH less than 5 [25].
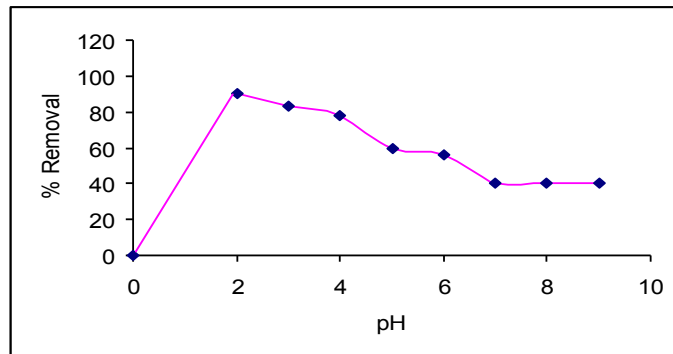

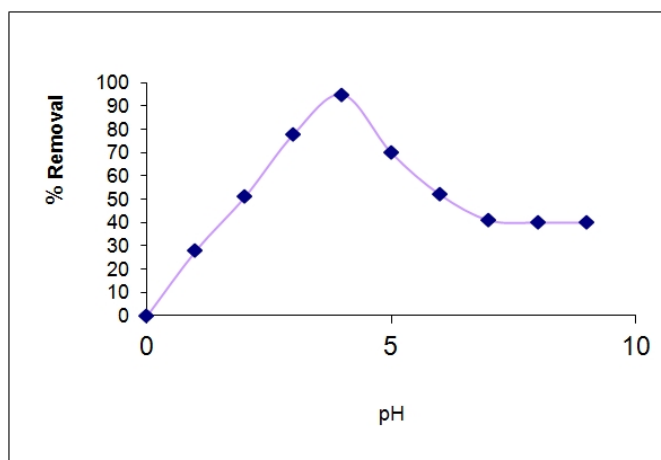**Fig. 1. Effect of pH on % removal of chromium(VI)**

Fig. 2. Effect of pH on % removal of Ni (II)

3.3 Effect of Equilibrium Time and Initial Metal Ion Concentration

Equilibrium experiments were carried out by agitating 50ml of different concentration of Cr(VI) solutions (10-30 mg/l) adjusted to pH 2.0 along with 150 mg of PMFP adsorbent. After equilibrating for different time periods, the solutions were centrifuged and analyzed for chromium (VI) content. The rate of uptake was rapid in the beginning and became slow in the later stages and reached saturation. This is due to the fact that the metal ion occupied the sites in a random manner because of maximum availability of sites, as the time passed, the active sites were blocked and hence the rate decreased. For maximum removal of Chromium(VI) by the adsorbent, the solutions should be equilibrated for 60 min irrespective of the initial concentration. The amounts of chromium(VI) adsorbed were 3.04, 5.03 and 6.62 mg/g for Cr(VI) concentrations of 10, 20 and 30mgL^{-1}, respectively. The formation of monolayer of Cr(VI) ions on the outer surface of the adsorbent is suggested based on the observation that the curves shown in (Fig. 3) were single, smooth and continuous. The equilibrium time observed in this experiment was equal with that observed for chromium adsorption by other adsorbents like activated soya bean hull [26] and rice husk ash [27]. To investigate the optimum equilibrium time, batch experiments were carried out by agitating 50ml of different concentrations of nickel (II) solutions ranging from 50mgL^{-1}, 75mgL^{-1}, 100mgL^{-1} which are maintained at pH = 4.0 and with 125mg of adsorbent. After equilibrating for different time periods from 15-20 min, the solutions were centrifuged and analyzed for Ni (II) content and the percent adsorption in each case was determined. Equilibrium time was found to be 90 min. At this equilibrium time the amounts adsorbed were 18.51; 24.80; and 29.52mg/g for Ni(II) concentrations of 50, 75 and 100 mgL^{-1}, respectively. The increase in initial Ni (II) concentration decreased the percent adsorption and increased the amount of metal uptake per unit mass of the adsorbent mg/g. The per cent adsorption vs time plot in (Fig. 4) was smooth and continuous leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. Similar results have been reported for the adsorbents like treated GAC and carbon aerogel by [28] In case of PMFP per cent removal increased sharply leading to 98% removal of Nickel (II).
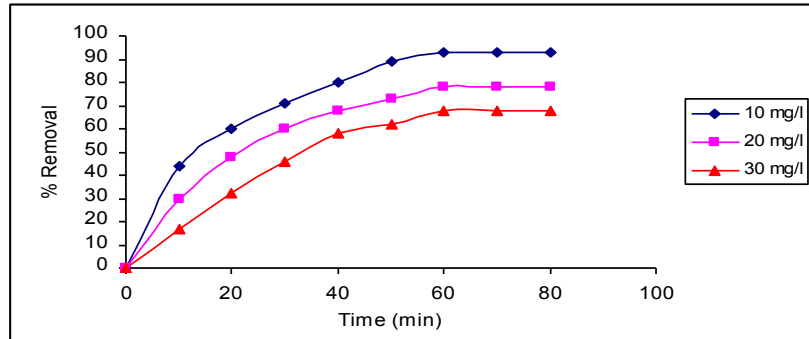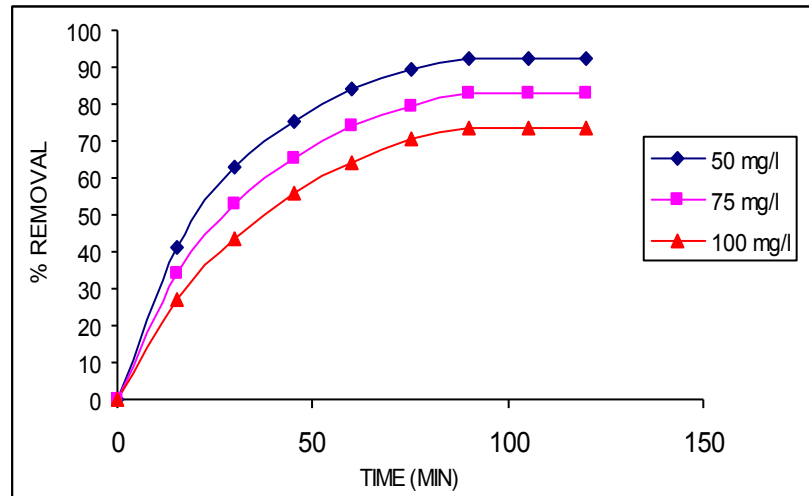
Fig. 3. Effect of time and %removal of chromium (VI)

Fig. 4. Effect of time on the % removal of Ni (II)

3.4 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of Cr(VI) was studied by varying amounts of the adsorbent from 25-200 mg. The adsorbent was added to 50ml of Cr(VI) solutions of concentration 10 mg/l and equilibrated for 60 min, whereas the adsorbent was added to 50 ml of Nickel (II) solution of 50 mg/l concentrations and equilibrated for 90 min After equilibrium time, the solutions were centrifuged and analyzed for Chromium (VI) and Nickel (II) content. The results shown in Table 2 reveal that 100% adsorption was possible with 200mg of adsorbent dose. The results in (Figs. 5 and 6) indicated that adsorption increased with increase in adsorbent dosage. This increase in percent adsorption with the increase in adsorbent dosage was due to the availability of more surface area of the adsorbent [29].
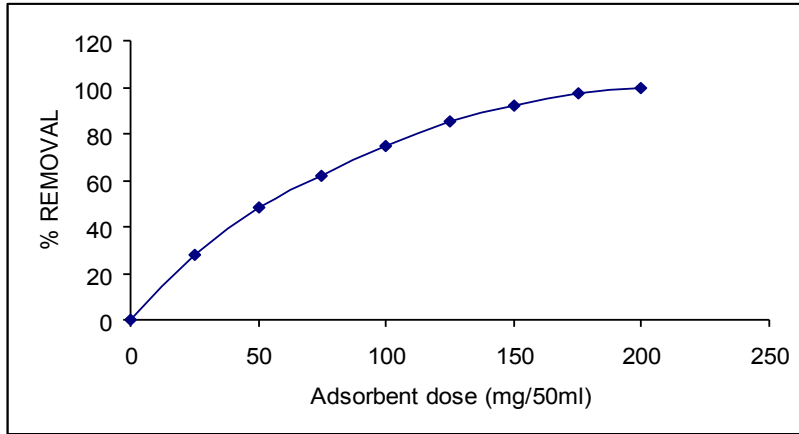
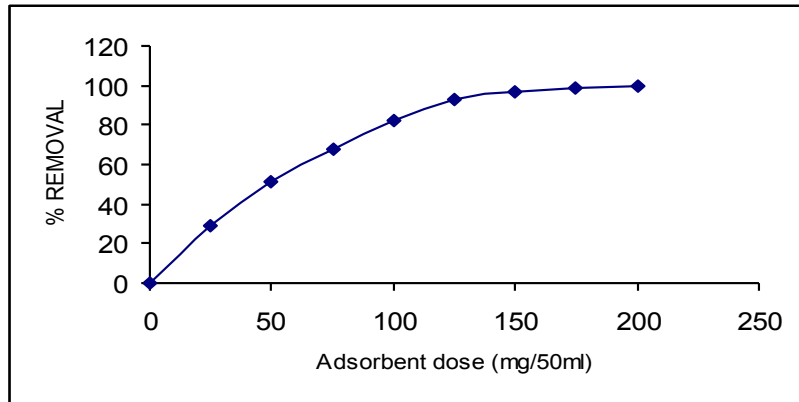**Fig. 5. Effect of adsorbent dose on % removal of Cr(VI)**

Fig. 6. Effect of adsorbent dose % removal of Ni (II)

Table 2. Quantity of Chromium (VI) and Nickel (II) adsorbed and % removal at different doses of adsorbent

Adsorbent dose mg/50ml	% Removal		Equilibrium concentration Ce (mg L^{-1})		Amount adsorbed mg/g	
	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)
25	26.80	28.70	7.32	35.64	5.36	28.72
50	47.65	51.48	5.24	24.26	4.76	25.74
75	62.80	67.84	3.72	16.08	4.18	22.61
100	75.50	82.50	2.45	8.75	3.77	20.62
125	85.10	92.48	1.49	3.76	3.40	18.49
150	91.20	97.16	0.88	1.42	3.04	16.19
175	96.30	99.04	0.37	0.48	2.75	14.14
200	100.00	100.00	0.00	0.00	2.50	12.50

3.5 Effect of Particle Size

To study the effect of particle size, adsorbent particles of sizes 0.6 mm, 0.8 mm and 1.7 mm were used. In each study 150 mg of adsorbent in 50 ml of 10 mgL^{-1} of Cr (VI) solution was agitated to equilibrium time of 60 min, the adsorbent was separated and the supernatant solution was analyzed for chromium concentration and the values are noted in Table 3 the amounts adsorbed for 0.6 mm, 0.8 mm and 1.7 mm particle size were 3.01, 2.66 and 2.34 mg/g, respectively. It is evident from (Fig. 7) that increase in particle size decreased the percent removal, this results were also applicable to nickel ions. At a fixed adsorbent dosage, the decrease in particle size increases the metal uptake. The increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. Similar trend had been observed on removal of Cr (VI) by using *Pitchellobium dulce* Benth – A Kinetic Study [30].
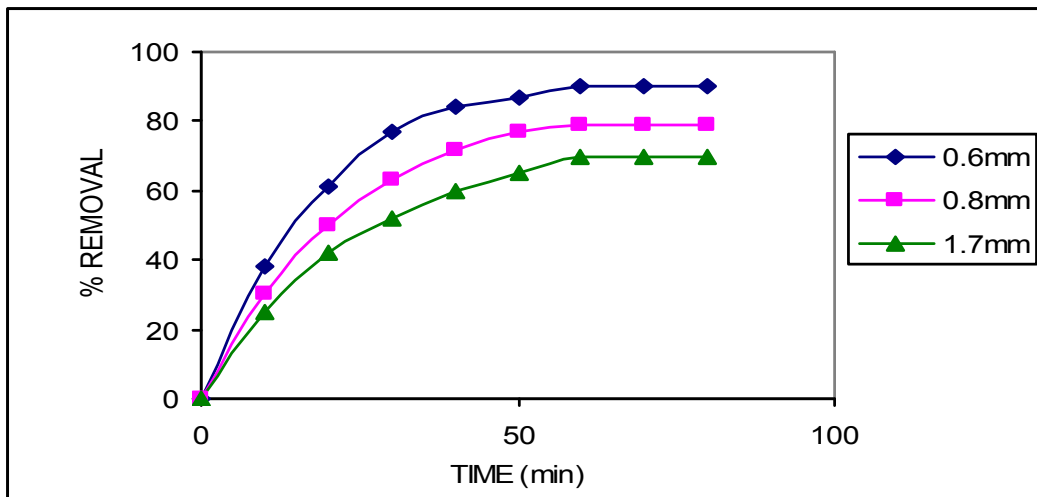

Fig. 7. Relationship between particle size, % removal at different times

Table 3. Adsorption of chromium (VI) on different particle sizes (mm) of the adsorbent

| | Particle size in mm | | | | | | | | |
| | 0.6 mm | | | 0.8 mm | | | 1.7 mm | | |
Agitation time in minutes	Amount of Cr (VI) adsorbed q (mgL^{-1})	qe-q (mgL^{-1})	% Removal	Amount of Cr (VI) adsorbed q (mgL^{-1})	qe-q (mgL^{-1})	% Removal	Amount of Cr (VI) adsorbed q (mgL^{-1})	qe-q (mgL^{-1})	% Removal
10	1.33	1.68	40.18	1.13	1.53	34.20	0.94	1.40	**28.40**
20	2.09	0.92	62.75	1.75	0.91	52.50	1.47	0.87	**44.22**
30	2.48	0.53	74.69	2.12	0.54	63.85	1.82	0.52	**54.74**
40	2.77	0.24	83.11	2.43	0.23	72.95	2.08	0.26	**62.50**
50	2.94	0.07	78.02	2.60	0.06	78.02	2.21	0.13	**66.46**
60	3.01	-	90.58	2.66	-	80.05	2.34	-	**70.13**
70	3.01	-	90.58	2.66	-	80.05	2.34	-	**70.13**
80	3.01	-	90.58	2.66	-	80.05	2.34	-	**70.13**

3.6 Adsorption Isotherms

Isotherms relate metal uptake per unit weight of adsorbent to equilibrium adsorbate concentration in the bulk fluid phase. The Langmuir isotherm was based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption was constant and there was no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm was expressed in the following formula

$$\frac{Ce}{qe} = \frac{1}{Q_o b} + \frac{Ce}{Q_0} \tag{1}$$

Where Ce was the equilibrium Concentration (mgL^{-1}) qe was the amount adsorbed at equilibrium time (mg/g) and Qo and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. Data for Langmuir plot are given in Table 4, which fitted well in regression analysis of the Langmuir data Ce/qe Vs Ce. It resulted in high correlation coefficient which indicated the applicability of Langmuir isotherm (Figs. 8 and 9.) The Langmuir constants Qo and b for adsorption of chromium (VI) at 10 mgL^{-1} concentration at pH 2.0 evaluated from the slope and intercept were 7.51 mg/g and 1.69 L/mg, respectively .Where as the Langmuir constants Q0 and b for adsorption of Nickel (II) evaluated from the slope and intercept are 29.41 mg/g and 0.4789 L/mg, respectively. Q0 value is less than the value of adsorption capacity of bagasse studied [31].
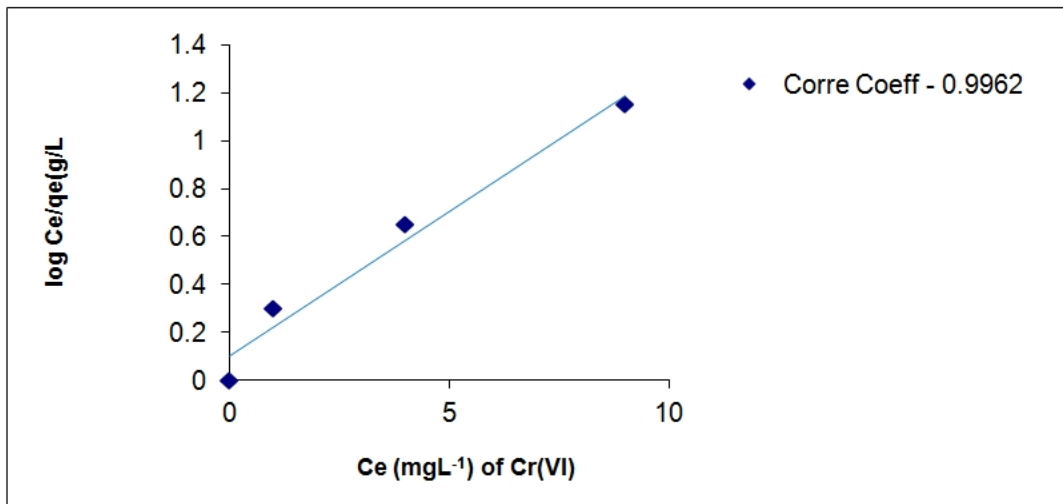

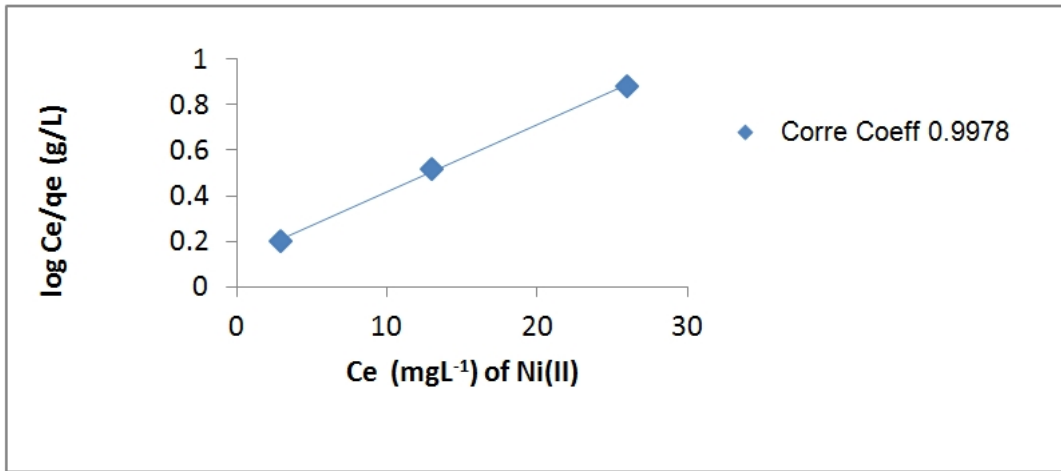**Fig. 8. Langmuir isotherm showing initial concentration vs. equilibrium concentration chromium ions**

Fig. 9. Langmuir isotherm showing initial concentration vs. equilibrium concentration nickel ions

Table 4. Equilibrium concentrations of chromium (VI) at constant adsorbent dose and particle size

Initial concentration (C_i mgL^{-1})		Equilibrium concentration (Ce mgL^{-1})		Qe (mg /g)		Ce /qe (gL^{-1})	
Cr (VI)	Ni (II)	Cr (VI)	Ni(II)	Cr (VI)	Ni(II)	Cr (VI)	Ni (II)
10	50	0.872	3.72	3.04	18.51	0.312	0.256
20	75	4.980	13.00	5.03	24.80	0.701	0.975
30	100	10.130	26.18	6.62	29.52	1.158	1.530

The essential characteristics of Langmuir are expressed in terms of a dimensionless constant separation factor R_L (Equilibrium Parameters) that is given by :

$$R_L = \frac{1}{1 + bc_i} \tag{2}$$

Where Ci was the initial concentration mgL^{-1} and b was the Langmuir constant. The value of (R_L) Table 5 indicates the nature of isotherm.

Table 5. Ranges of R_L values

R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In the present investigation the characteristic equilibrium parameter R_L of Langmuir isotherm was calculated and the values of 0.055, 0.028 and 0.019 for the metal ion concentration of 10, 20 and 30 mg L^{-1}, respectively and all the values were between zero and one indicating

the favorable adsorption of chromium on the adsorbent. Where as in Ni(II)R_L values were 0.040, 0.027 and 0.020 for Ni (II) concentration of 50,75,and100 mgL^{-1},respectively which were less than unity showing that the adsorption of metal ion onto Powder of Mosambi Fruit Peelings was favorable.

The Freundlich isotherm is generally used for mathematical description of adsorption in aqueous system and describes heterogeneous surface energies. The equation is expressed in logarithmic form as

$$\log x/m = \log k_f + \frac{1}{n}\log Ce \qquad (3)$$

Where (x/m was the amount adsorbed in mg/L), Ce was the equilibrium concentration (mgL^{-1}) and K_f and n were Freundlich constants. K_f [mg/g, L/mg] was the capacity of the adsorbent and n indicated the favorability of adsorption. The plot of log (x/m) Vs log Ce indicated in (Fig. 10) was linear, indicated that adsorption data obeyed Freundlich adsorption isotherm. The Freundlich constant Kf was 2.94 which is compared with the value of Bengal gram husk was 2.81. According to [32] the value of n between 2 and 10 indicates good adsorption. The calculated value of n for the adsorption of Cr(VI) is 3.41, showing very good efficiency for chromium adsorption by powder of Mosambi fruit peelings adsorbent .This isotherm was applied for the adsorption of Ni(II) on powder of Mosambi fruit peelings adsorbent and plot of log x/m vs log Ce is shown in (Fig. 11). The linearity of the plot shows that adsorption followed Freundlich isotherm and the constants K_f and n calculated from the intercept and slope are 23.92 and 2.24, respectively. The results indicated that the adsorbent has several different types of adsorption sites. Accordingly to [33] the n values between 2 and 10 represent good adsorption. The calculated n value of 2.24 indicates good adsorption of Ni (II) on PMFP.
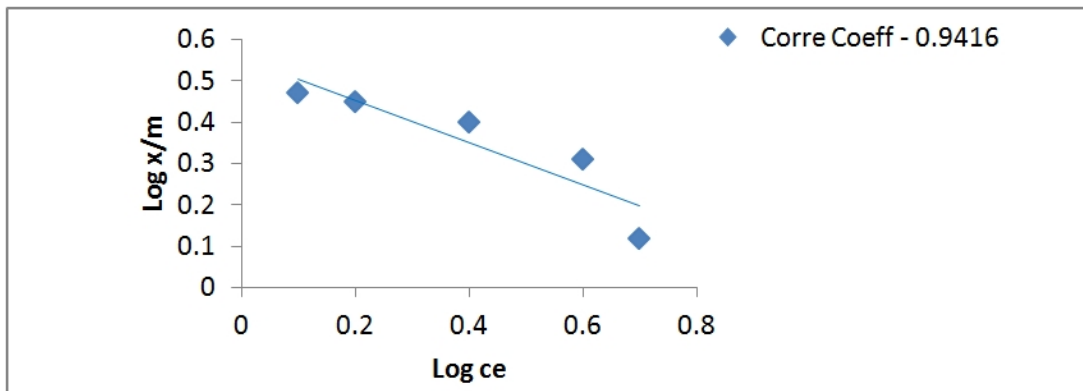

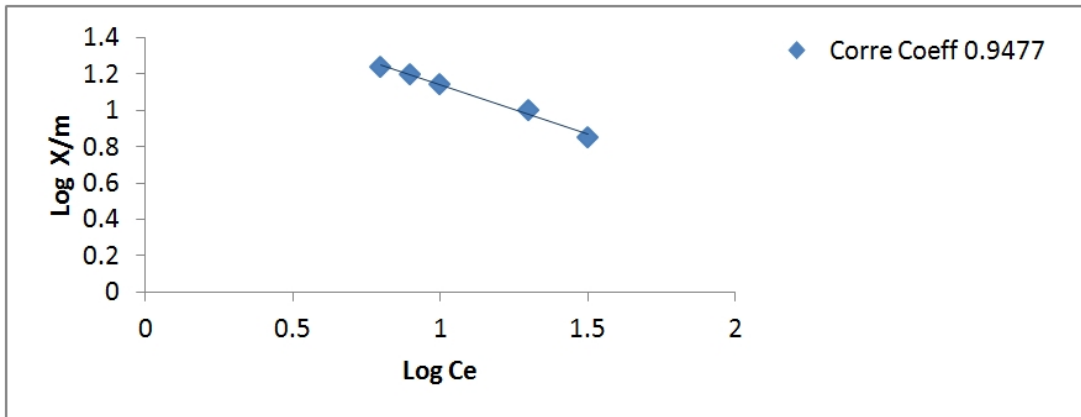**Fig. 10. Freundlich isotherm shown amount of chromium adsorbed and equilibrium concentration of chromium ions**

Fig. 11. Freundlich isotherm shown amount of chromium adsorbed and equilibrium concentration Nickel ions

3.7 Adsorption Kinetics

3.7.1 Effects of metal ions concentration on lagergren rate constant

The kinetics of Ni (iI) adsorption followed the first order rate Equation given by Lagergren was:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t \qquad (4)$$

Where q and qe were the amounts of metal ion adsorbed (mg/g) at time t (min) and at equilibrium time, respectively and K_{ad} was the rate constant of adsorption (min^{-1}). From the (Fig. 11), it was evident that, the linear plots of log (qe-q) Vs time at different concentrations show the applicability of the Lagergren equation The adsorption data were fitted in the Lagergren equation (4). The straight line plots of log (qe-q) Vs time for Chromium (VI) Concentrations of 10, 20 and 30 mgL^{-1}, are shown in (Fig. 12) and Nickel concentrations of 50, 75, and 100 mgL^{-1}, respectively in (Fig. 13). The rate constants of adsorption K_{ad} determined from the slope of the plots are given in Table 5. From this table it is evident that the initial concentration did not have much significant effect on rate constant.
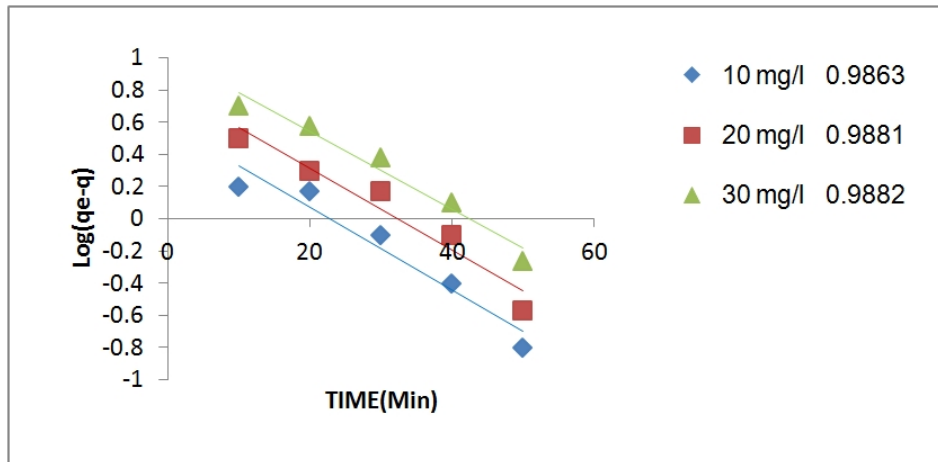
Fig. 12. Relationship between the time in minutes and log concentrations of Cr(VI) for various known concentrations
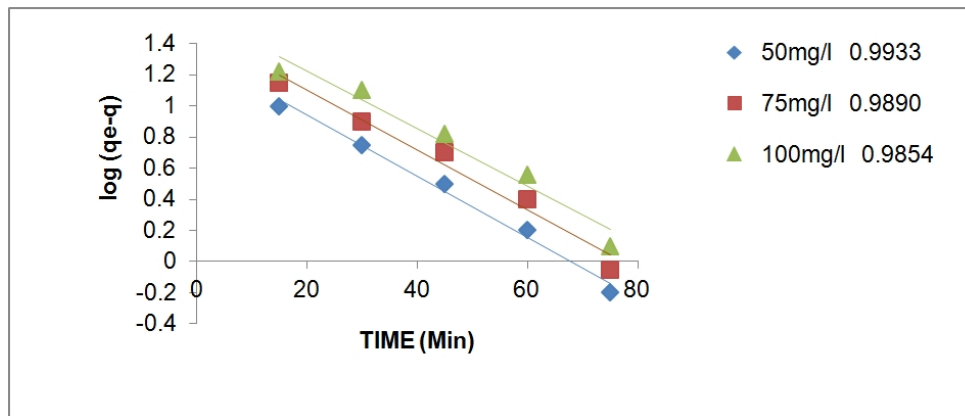

Fig. 13. Relationship between the time in minutes and log concentrations of Ni (II) for various known concentrations

The K_{ad} values calculated from the slopes of the linear plots are presented in Table 6.

Table 6. Calculated values for the rate constants for different concentrations of Cr(VI) &Ni (II)

Cr(VI) mg/L	Ni(II) mg/L	Rate constant K_{ad} (min^{-1})	
		Cr(VI)mgL^{-1}	Ni(II) mgL^{-1}
10	50	5.75 x 10-2	4.37 x 10^{-2}
20	75	6.05 x 10-2	4.37 x 10^{-2}
30	100	5.91 x 10-2	4.23 x 10^{-2}

These results indicated that the metal ion concentration has no significant effect on the rate. The values were comparable with those results obtained by [34].

3.8 Effect of Particles Size on Lagergren Rate Constant

The effect of particle size on the rate of adsorption was shown in (Fig. 14) and the rate constant K_{ad} values calculated are given in Table 7. For the adsorption of Cr(VI) increase in particle size from 0.6 mm to 1.7 mm decreased the rate of adsorption from 6.01×10^{-2} to 4.37×10^{-2} min^{-1}. The higher rate of metal uptake by smaller particles was due to greater accessibility to pores and greater surface area for bulk adsorption per unit weight of the adsorbent [35] have stated that the breaking up of larger particles to form smaller ones opens some tiny sealed channels that will be available for adsorption and therefore the rate of uptake by smaller particles was higher than that larger particle.

Table 7. Lagergren rate constants calculated for different particle sizes (mm)

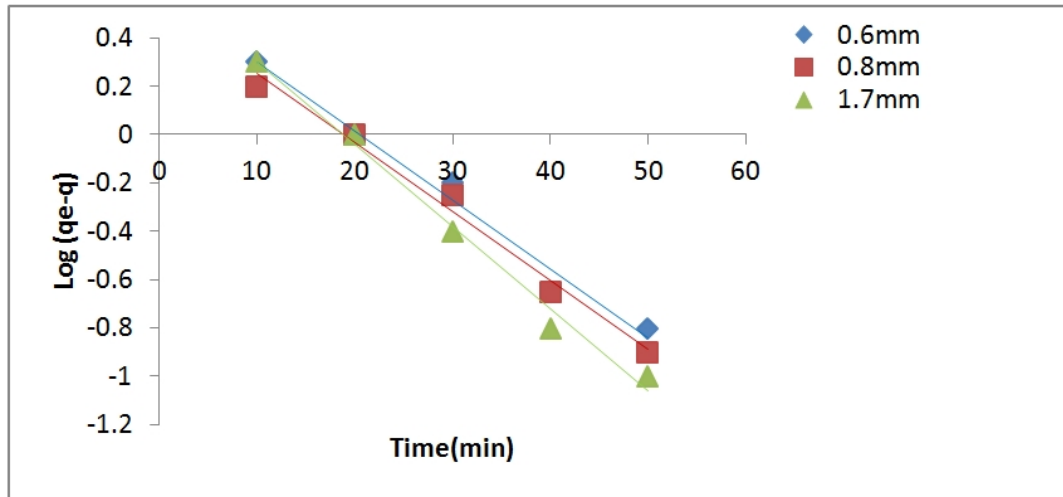| Particle size (mm)	Rate Constant K_{ad} (min^{-1})
0.6	6.01×10^{-2}
0.8	5.21×10^{-2}
1.7	4.37×10^{-2}

Fig. 14. Relationship between different particle size and time of adsorption

4. CONCLUSION

1. In this study the heavy metals, namely, Chromium(VI) and Nickel (II) were selected for removal from aqueous solutions using adsorption technique. Batch experiments were conducted to study the impacts of particle size, pH, agitation time, adsorbent dose and initial metal ion concentrations. A particle size of 0.6 mm was observed to be highly efficient for Chromium(VI) and nickel (II). A decrease in the size of the particle increased the adsorption, as a decrease in size of the particle increased the availability of the number of active sites. The increase of pH showed a negative impact on the adsorption of nickel (II). Maximum adsorption was recorded at pH 2.0 for Cr(VI) and pH 4.0 for Ni (II). An increase in the adsorbent dosage gave increased adsorptions for Chromium and nickel, whereas the adsorption decreased with increase of initial metal ion concentrations.

2. The adsorbent selected for the present study proved to be good adsorbent which was evident with the adsorption data obeying the Langmuir and Freundlich isotherms. The equilibrium parameter RL in Langmuir isotherm, the Langmuir constants and Freundlich adsorption constants for Chromium(VI) and nickel (II) by PMFP indicated that the adsorption of Chromium(VI) and nickel (II) on PMFP was favorable. The kinetics of the adsorption of the metal ions also obeyed Lagergren equation. This results shows that PMFP has a considerable potential as an adsorbent for the removal of Chromium(VI) and nickel (II) from aqueous solutions.

3. If low cost adsorbents perform well in removing heavy metals at low cost, they can be adopted and widely used in industries not only to minimize cost inefficiency, but also to improve profitability. In addition to this, the alternative adsorbents are found highly efficient for heavy metal removal, not only in the industries, but also in the living organisms. The surrounding environment will be also benefited from decrease or elimination of potential toxicity due to the heavy metal. Thus, the use of low cost adsorbents may contribute to the sustainability of the surrounding environment. Undoubtedly, low cost adsorbents offer a lot of promising benefits for commercial purpose in the future. Heavy metal removal with the above adsorbent appears to be technically feasible, ecofriendly and has high efficacy.

4. Extensive research was in progress in Department of Chemistry, University of Toronto, Ontario, Canada regarding the results obtained from Batch adsorption tests like physico-chemical key parameters, initial metal ion concentration, pH, agitation time, particle size, adsorbent dosage, adsorption isotherms and adsorption kinetics etc. in the direction of pilot- scale reactor operation for removal of heavy metals from the aqueous solutions and contaminated fields.

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COMPETING INTERESTS

The author declare that they have no competing interests

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