

ORIGINAL ARTICLE

Non-Equilibrium Multi-Ion Biosorption Isotherms for Removal of Heavy Metals from Drinking Water

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ABSTRACT

Biosorption isotherms define the relationship between biosorption capacity of the biosorbent and the equilibrium concentration of the ions in solution, at a constant temperature. Experiments are routinely performed under near-equilibrium because it is impossible to determine the exact time at which equilibrium was attained. A novel attempt to study multi-ion biosorption in non-equilibrium conditions has been made, based on the Probability Isotherm theory. *Materials and Methods:* Probability Isotherm theory was examined with cucumber and kiwifruit peel beads which are reported to be efficient biosorbents. The peels were incubated in a cocktail of seven ions (As, Cd, Cr, Cu, Hg, Pb and Ni) at the same initial concentration (0.1-15 mgL⁻¹) and four different temperatures (25-55°C). Non-equilibrium biosorption data were modeled by Langmuir isotherm model. Data were analyzed using a one-way ANOVA coupled with a Bonferroni post-hoc test on GraphPad Prism 8 software. Cd and Ni ions showed the most well-defined trends with Langmuir isotherm model. The binding of ions was physico-chemical with simultaneously occurring physisorption and chemisorption reactions. *Conclusions:* Probability Isotherm theory can be applied to multi-ion biosorption in non-equilibrium conditions. The behavior of each ion is unique and no two biosorption systems are alike.

KEYWORDS | kiwifruit peel, non-equilibrium isotherms, heavy metals

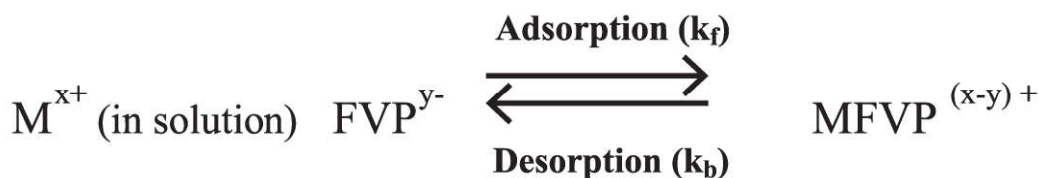
INTRODUCTION

THE LOW COST BIOSORPTION methods for the decontamination of drinking water have been in research for decades. Peels from a range of fruits and vegetables have the ability to remove toxic ions from a cocktail solution. Some examples include peels from apple (AP)¹, cucumber (CP)², banana (BP)³, orange (OP)³, potato (PP)³ and kiwifruit (KP)⁴ immobilised on sodium alginate (SA) that can remove As, Cd, Cr, Cu, Hg, Pb and Ni. Biosorption is a complex physical and/or chemical process.⁵ A simplified theoretical description of the biosorption process is as follows: when a

solid biosorbent with functional groups comes in contact with biosorbate ions in solution, the reaction tends to move towards a dynamic equilibrium where the rate of adsorption is balanced by the rate of desorption (*Equation: 1*).⁶ Hence, biosorption equilibrium is not a steady state but a state of dynamic equilibrium defined by equal forward and backward rate constants ($k_f = k_b$) involving simultaneously occurring adsorption and desorption. Thus, the understanding of biosorption isotherms gives the overall direction of the reaction.



How to cite this article
Risha Jasmine Nathan. Non-Equilibrium Multi-Ion Biosorption Isotherms for Removal of Heavy Metals from Drinking Water. *Indian J Forensic Med Pathol.* 2021;14(2 Special):246-255



M^{x+} = biosorbate ions; FVP^{y-} = active sites on biosorbent surface; $MFVP^{(x-y)+}$ = biosorbate ions bound to the active sites on biosorbent surface k_f = rate constant for forward reaction (adsorption); k_b = rate constant for backward reaction (desorption)

Isotherms define the relationship between the biosorbent and the biosorbate ions when the system is at equilibrium⁷. The equilibrium time is usually determined by biosorption kinetic studies prior to arriving at biosorption isotherms. The concentration of the solution is analyzed at different time points and the point beyond which there is no significant decrease in solution concentration is the equilibrium time. However, such estimation may produce erroneous results since it is difficult to ascertain the exact point at which the reaction reaches equilibrium. Thus, when biosorption isotherm studies are performed, data are generated for biosorption system approaching equilibrium which in theoretical terms, is a non-equilibrium state. Additionally, various contact times ranging from 1 min to 75 days have been used by other researchers depending on the biosorption system and the time required to reach equilibrium.^{8,9} However, in case of a multi-ion solution, the ions may or may not have similar equilibrium times. For example, in the studies on Cd and Cu ions, equilibrium was attained by 24 and 48 h, respectively.¹⁻⁴ Therefore, it is not possible to perform the experiment with the same equilibrium time for all ions as the ions physically bound to the biosorbent may desorb from the surface back into the solution upon continued agitation beyond equilibrium. Therefore, one or more ions may be in a non-equilibrium state in a multi-ion solution.

Chapman *et al.*,¹⁰⁻¹² have applied the Probability Isotherm theory, a probabilistic expression of the second law of thermodynamics, as a method for describing biochemical reactions that are valid both for equilibrium and non-equilibrium conditions. This approach is true for all isothermal conditions and is different from the typical kinetic expression that can be applied to equilibrium

$$K_{ne} = \frac{P_f}{P_b}$$

Equation 2:

$$G = - RT \ln \frac{P_f}{P_b}$$

Equation 3:

conditions only. They suggested that the equilibrium constant can be represented as a ratio of the overall probability of forward to backward reaction (*Equation - 2*), which is dependent on the concentration of the reactants and products but independent of the mechanism of reaction.¹⁰⁻¹² The modified form of the Van't Hoff equation equating the Gibbs free energy change (ΔG) with the equilibrium constant would then be valid for non-equilibrium conditions as well (*Equation - 3*).

We have utilized this concept for multi-ion biosorption isotherms to analyze the uptake of heavy metal ions from water under non-equilibrium conditions. A comparative study of sodium alginate beads immobilised with various fruit and vegetable peels demonstrated that CP and KP beads had the highest biosorption capacities¹⁻⁴ and therefore these were selected for isotherm analysis. The aim of the present work was to use the Probability Isotherm theory to study the biosorption of heavy metals in non-equilibrium conditions. This novel concept will ease the strict requirements of fixed equilibrium time and allow further characterization of the non-equilibrium biosorption by CP and KP. This additional information will inform the potential practical use of these beads for treating drinking water contained with multiple ions.

MATERIALS AND METHODS

CP and KP Bead Preparation

CP and KP beads were prepared as described for other peels by Nathan *et al.*¹⁻⁴ Briefly, 6 cucumbers and 6 kiwi fruits were purchased from a supermarket in Dunedin, New Zealand. These

were pulverized and immobilised on sodium alginate (1%). Beads were formed by dropping them in 0.1 M CaCl₂ and dried to increase their shelf life.

2.2 Batch biosorption experiments and ICP-MS analyses

Cocktail solutions were prepared by spiking deionized water with standard solutions of As (V), Cd (II), Cr (VI), Cu (II), Hg (II), Pb (II) and Ni (II) all at equivalent concentrations ranging between 0.1 and 15 mgL⁻¹. The pH of the solution (25 ml) was adjusted to 7.0 ± 0.1 and the solutions were shaken with 4 beads of each type at 250 rpm for 10 h. The experiments were performed at four temperatures 25, 35, 45 and 55°C and all experiments were performed in triplicate. The results are expressed as the mean ± the standard error of the mean (SE).

All solutions before and after biosorption were analyzed by an Agilent 7900 quadrupole inductively coupled plasma detector coupled with mass spectrometry (ICP-MS) after appropriate dilutions with HNO₃.

2.3 Statistical analysis

All analyses were performed using GraphPad Prism 8 software. Since metals were not compared with each other, all experiments contained only one factor. Thus, data were analyzed using a one-way ANOVA coupled with a Bonferroni post-hoc test. In all cases, p < 0.05 was the minimum requirement for a statistically significant difference.

RESULTS

Non-equilibrium Biosorption

To determine the equilibrium time for each of the ions a 15 mgL⁻¹ cocktail solutions was incubated with four beads at 45°C. The results showed that the equilibrium time for each of the ions on both CP and KP beads was beyond 24 h and the difference between biosorption at 10 and 24 h was statistically significant (Figure 1). Therefore, 10 h was used as the non-equilibrium time in the remaining studies.

Effect of initial ion concentration and temperature

To determine how temperature and ion concentration affected the biosorption performance of CP and KP beads, experiments

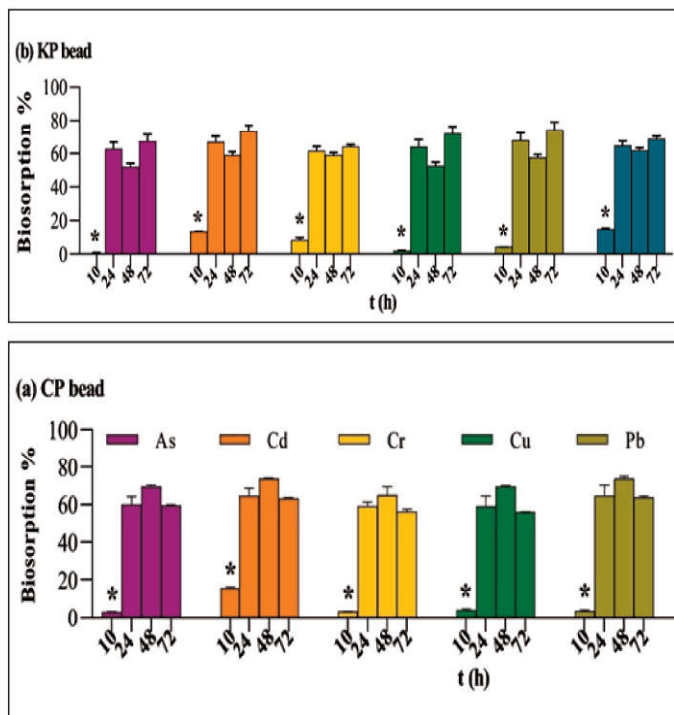


Figure 1: Equilibrium and non-equilibrium biosorption. Four beads of each type were incubated in a cocktail solution containing all seven ions each at 15 mgL⁻¹, pH 7.0, 45°C with continuous shaking at 250 rpm for 10-72 h. The bars represent the mean ± SE for N=3. Data were analysed by a one-way ANOVA coupled with Bonferroni post-hoc test. *Significantly different to all other time points for each ion, p < 0.05. (a) CP bead, (b) KP bead.

were performed at a range of ion concentrations and temperatures. The results indicated that biosorption capacity increased with an increase in ion concentration (Figure 2a, 3a). In contrast, biosorption percentage decreased with an increase in initial ion concentration (Figure 2b, 3b). Interestingly, the biosorption of Cd and Ni by CP beads increased with an increase in temperature at 1 mgL⁻¹ and 6 mgL⁻¹, respectively (Figure 2c,d). For KP bead, there was a significant increase in biosorption of ions (Figure 3c-e).

Biosorption Isotherms

Biosorption isotherms were plotted with data collected at 10 h (non-equilibrium). Only Cd and Ni ions showed defined trends (R² > 0.8) (Figure 4). Non-equilibrium data obtained for CP and KP beads at 10 h of contact time were then modeled using Langmuir isotherm model to describe the mechanism of biosorption.

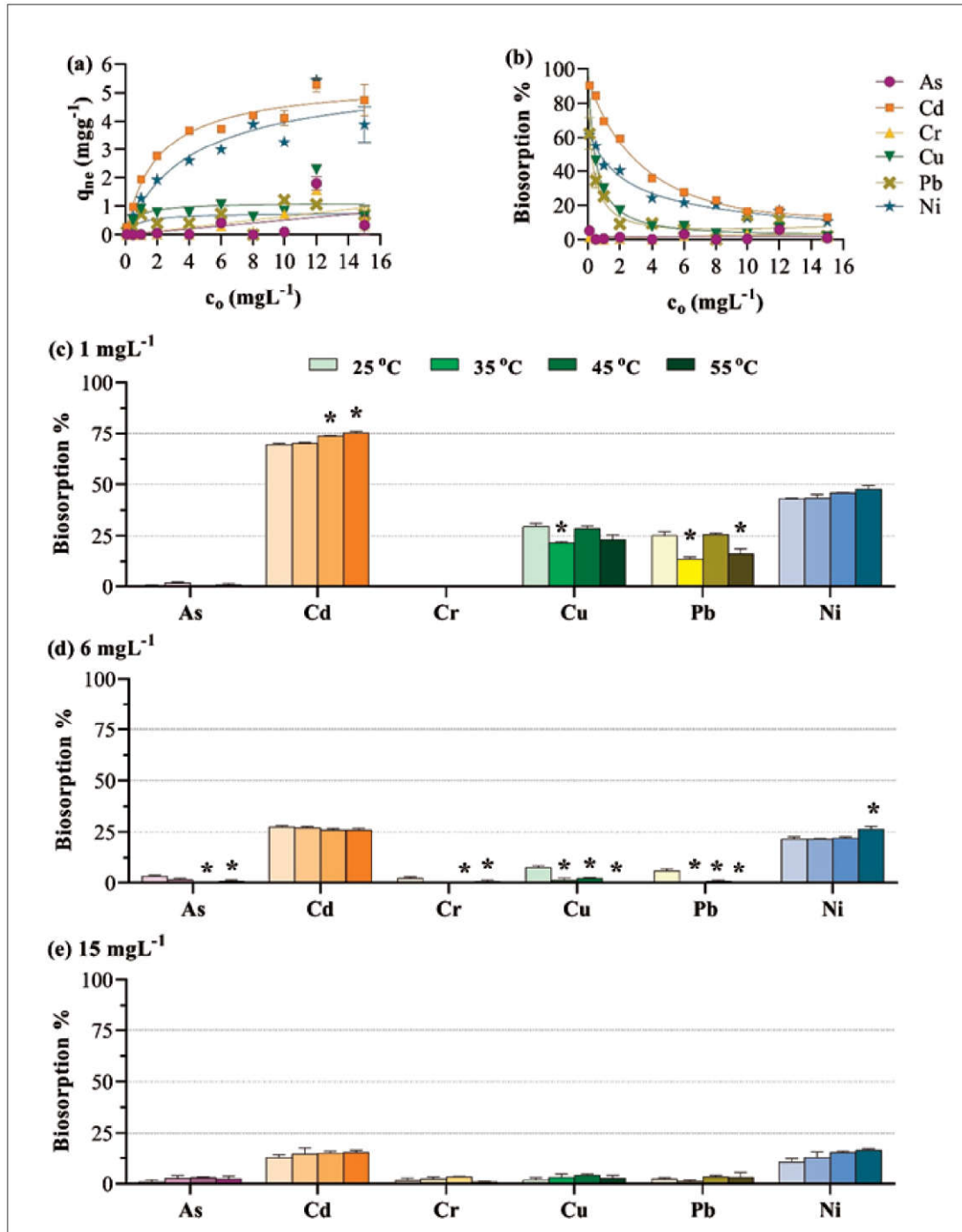


Figure 2: CP bead non-equilibrium biosorption. Four beads of each type were incubated in a cocktail solution containing all seven ions at pH 7.0 with continuous shaking at 250 rpm for 10 h. The points represent the mean \pm SE for N=3. Data were analysed by a one-way ANOVA coupled with Bonferroni post-hoc test. *Significantly different from the corresponding value at 25°C, $p < 0.05$. (a) Biosorption capacity at 25°C, (b) biosorption percentage at 25°C, (c) biosorption percentage for ions at 1 mgL⁻¹, (d) biosorption percentage for ions at 6 mgL⁻¹, biosorption percentage for ions at 15 mgL⁻¹.

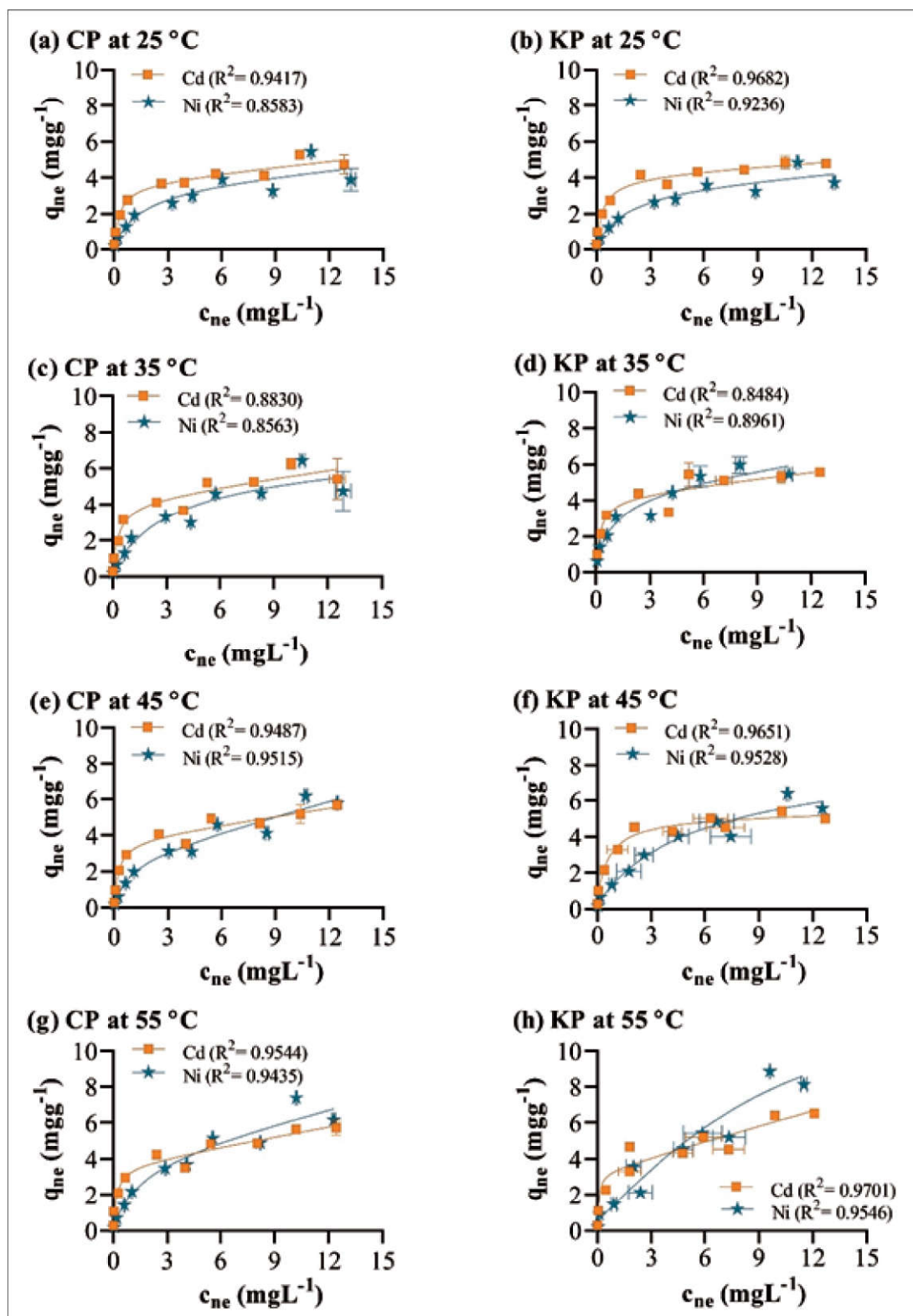


Figure 4: Non-equilibrium biosorption isotherms. Four beads of each type were incubated in a cocktail solution containing all seven ions each at 0.1-15 mgL⁻¹, pH 7.0 with continuous shaking at 250 rpm for 10 h. The points represent the mean \pm SE for N=3. (a) CP bead at 25 °C, (b) KP bead at 25 °C, (c) CP bead at 35 °C, (d) KP bead at 35 °C, (e) CP bead at 45 °C, (f) KP bead at 45 °C, (g) CP bead at 55 °C, (h) KP bead at 55 °C.

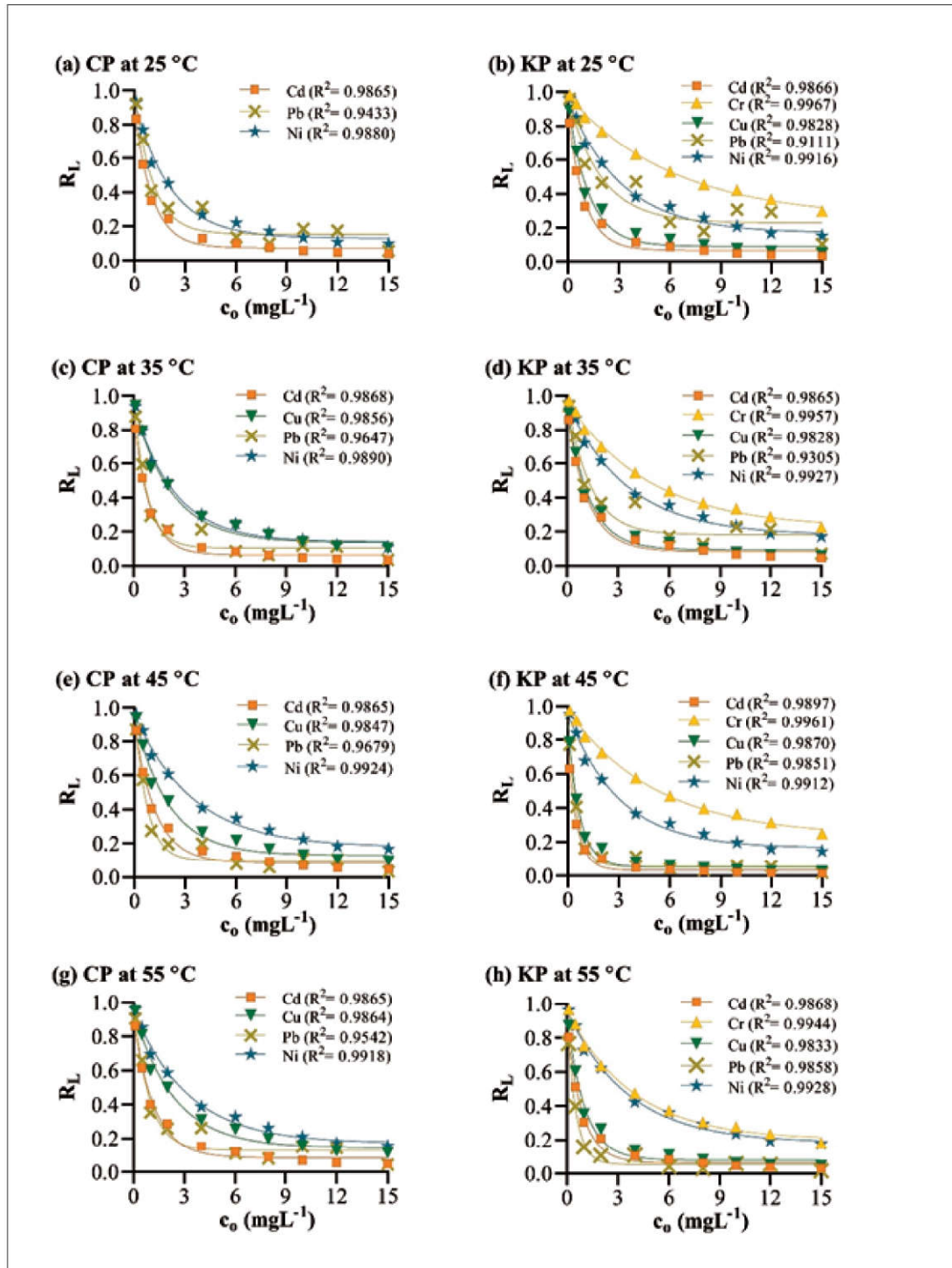


Figure 6: Non-equilibrium Langmuir separation factor. Four beads of each type were incubated in a cocktail solution containing all seven ions each at 0.1-15 mgL^{-1} , pH 7.0 with continuous shaking at 250 rpm for 10 h. The points represent the mean \pm SE for N=3. (a) CP bead at 25 °C, (b) KP bead at 25 °C, (c) CP bead at 35 °C, (d) KP bead at 35 °C, (e) CP bead at 45 °C, (f) KP bead at 45 °C, (g) CP bead at 55 °C, (h) KP bead at 55 °C.

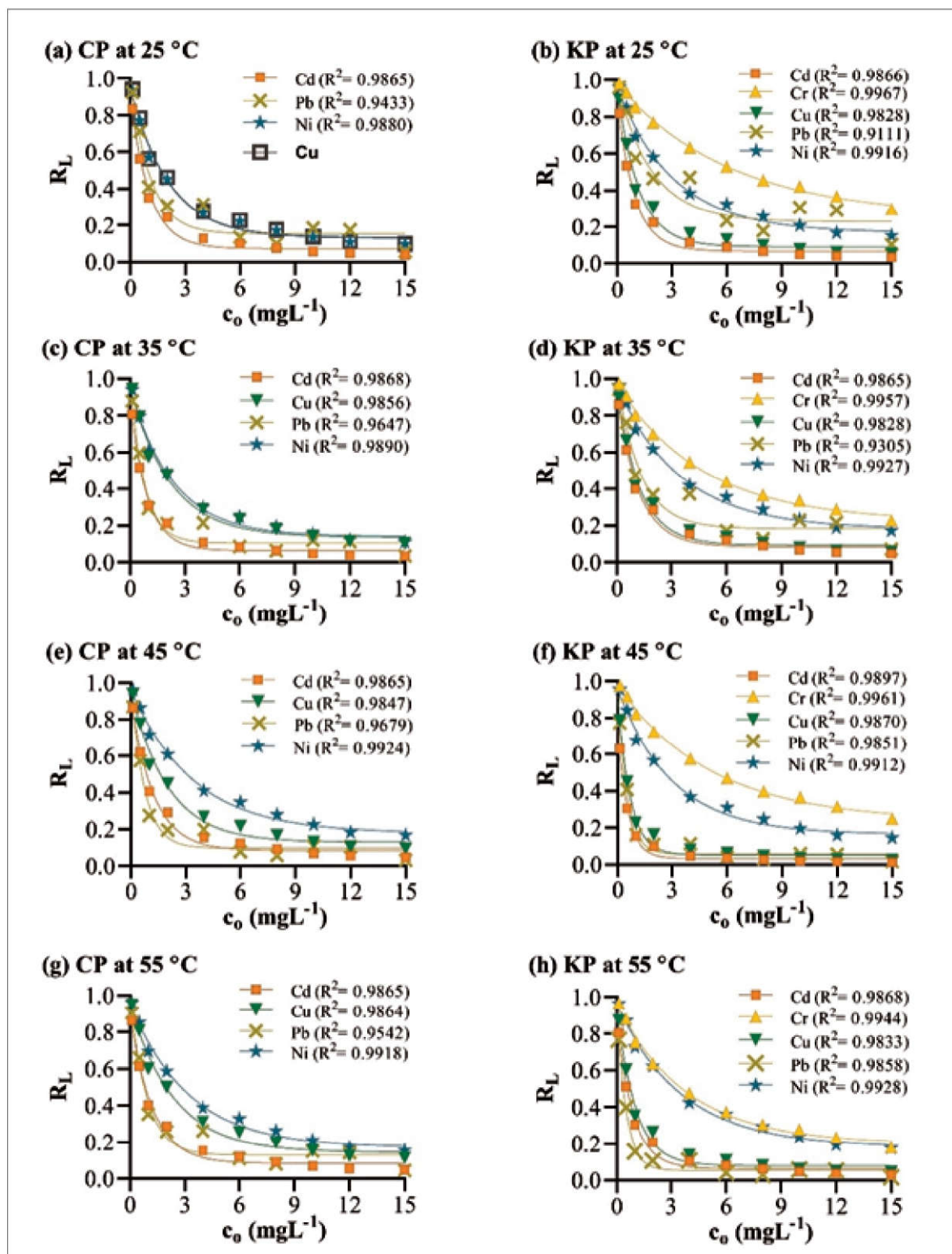


Figure 5: Non-equilibrium Langmuir isotherms. Four beads of each type were incubated in a cocktail solution containing all seven ions each at 0.1-15 mgL⁻¹, pH 7.0 with continuous shaking at 250 rpm for 10 h. The points represent the mean \pm SE for N=3. (a) CP bead at 25 °C, (b) KP bead at 25 °C, (c) CP bead at 35 °C, (d) KP bead at 35 °C, (e) CP bead at 45 °C, (f) KP bead at 45 °C, (g) CP bead at 55 °C, (h) KP bead at 55 °C.

Parameters	Cd	Cr	Cu	Pb	Ni
CP beads at 25°C					
Q _{max}	4.85	--	--	0.95	4.49
K _L	1.66	--	--	1.28	0.63
R _L	0.83-0.04	--	--	0.92-0.06	0.93-0.10
at 35°C					
Q _{max}	5.42	--	1.28	0.78	5.46
K _L	2.00	--	0.60	2.13	0.55
R _L	0.81-0.03	--	0.94-0.10	0.88-0.03	0.94-0.11
at 35°C					
Q _{max}	5.50	--	1.38	1.10	6.74
K _L	1.32	--	0.66	2.34	0.34
R _L at 55°C	0.86-0.05	--	0.94-0.09	0.87-0.03	0.96-0.17
Q _{max}	5.71	--	0.88	0.63	7.58
K _L	1.34	--	0.54	1.63	0.37
R _L	0.86-0.05	--	0.95-0.11	0.90-0.04	0.96-0.16
KP beads at 25°C					
Q _{max}	4.87	2.41	2.14	1.97	5.20
K _L	1.86	0.16	1.22	0.65	0.36
R _L	0.82-0.040	0.98-0.300	0.89-0.05	0.96-0.10	0.96-0.15
at 35°C					
Q _{max}	5.84	2.85	3.58	2.43	6.89
K _L	1.35	0.23	1.16	0.98	0.32
R _L	0.86-0.050	0.98-0.230	0.90-0.06	0.94-0.07	0.96-0.17
at 45°C					
Q _{max}	5.09	3.63	2.16	1.49	6.62
K _L	4.88	0.21	2.79	4.59	0.40
R _L	0.63-0.010	0.98-0.250	0.78-0.02	0.77-0.02	0.96-0.14
at 55°C					
Q _{max}	6.28	5.07	2.33	1.48	9.64
K _L	2.04	0.31	1.50	4.75	0.32
R _L	0.80-0.030	0.97-0.180	0.87-0.04	0.76-0.02	0.96-0.18

Table 1: Four beads of each type were incubated in a cocktail solution containing all seven ions each at 0.1-15 mgL⁻¹, pH 7.0 with continuous shaking at 250 rpm for 10 h. q_{max}= maximum biosorption capacity (mgg⁻¹); K_L=Langmuir constant (Lmg⁻¹); R_L=Langmuir separation factor (dimensionless). -- Parameters could not be derived.

Non-equilibrium Biosorption Isotherms

In the present study, biosorption capacity increased with an increase in ion concentration (Figure 2a, 3a). This is likely due to the increase in the concentration gradient driving the reaction¹³. On the other hand, the decrease in biosorption percentage with an increase in initial ion concentration (Figure 2b, 3b) is because of the limited number of active sites on the surface for binding of ions at a fixed biosorbent concentration¹⁴. An interesting trend of increase with an increase in temperature for biosorption of Cd and Ni by CP beads (Fig-

ure 2c,d) and all ions by KP bead (Figure 3c-e) was observed. This may be due to the increase in the kinetic energy of the ions thus increasing the probability of collision with the biosorbent surface increasing their ability to diffuse into the pores of the bead. Additionally, there could be enlargement of pore sizes and/or an increase in the number of active binding sites due to the rupture of surface functional groups.¹⁵ Similar results have been reported as biosorption increased with an increase in temperature for the uptake of As by date palm fibers and OP¹⁶, Cd by bagasse¹⁷, Cr by citrus peel¹⁸, Cu by OP carbon¹⁹, Hg by water hyacinth carbon²⁰, Pb by modified walnut shell²¹ and Ni by banana leaf.²² For KP bead, there was a significant increase in biosorption with increase in temperature thus indicating the more endothermic nature of the reaction (Figure 3c-e).

To further understand the biosorbent-biosorbate interactions, biosorption isotherms²³ were plotted in non-equilibrium conditions for both bead types and the data modeled using Langmuir isotherm model.

Langmuir Isotherm

The Langmuir isotherm describes the availability of a finite number of identical active sites that permit the formation of a monolayer (i.e. no stacking occurs) on a homogeneous biosorbent surface.^{24,25} Thus, all binding sites have an equal affinity for biosorbate ions.^{26, 27}

An increased rate of biosorption of these ions from solution at elevated temperature is determined by an increase in the q_{max} values with increase in temperature. This was observed in the uptake of Cd and Ni by CP and KP beads, and Cr by KP bead (Figure 5, Table 1). Similar observation was reported for the biosorption of Ni by activated carbon between 20 and 50°C from banana peel²⁸ and Cu by peanut hulls between 25 and 65°C,²⁹ where the values of q_{max} increased with increase in temperature. On the other hand, q_{max} for Cu and Pb biosorption by both CP and KP beads first increased and then decreased with a further increase in temperature which was also reported for the biosorption of Ni by OP in the temperature range 25- 50°C.³⁰ This suggests that beyond a certain temperature, the ions may have started desorbing from the bead. This may have been due to the weakening of the binding forces.³¹

The dimensionless Langmuir separation factor (RL) (eq 5) indicates whether the biosorption is favorable or not; $0 < RL < 1$ suggests a favorable reaction, $RL > 1$ indicates unfavorable biosorption, $RL = 1$ represents linear biosorption and $RL = 0$ shows that biosorption is irreversible.³²⁻³⁴ All the RL values obtained were favorable for reaction, although for dilute solutions (closer to 0.1 mgL⁻¹) the reaction was least favorable with a larger separation factor ($RL \leq 1$) and for concentrated solutions (closer to 15 mgL⁻¹) the reaction was more favorable and irreversible with a smaller separation factor ($RL \geq 0$) (Figure 6, Table 1). The significant decrease in the affinity of the CP bead binding sites (KL) for Cu ions with an increase in temperature can be explained by the increase in the separation factor (RL) for moderately concentrated solutions. Similarly, the significant increase in KP bead KL values with respect to the uptake of Pb ions is confirmed by the corresponding decrease in RL values with increase

Nature of biosorption - physisorption and chemisorption

From the values of biosorption isotherm constants, the forces holding the biosorbate on the biosorbent surface can be determined. In physisorption, multilayer biosorption takes place.³⁵ While all multilayer adsorptions are physical in nature, monolayer adsorptions may occur via physisorption or chemisorption.³⁶⁻³⁷ The results from Langmuir isotherm modeling suggest that the ion binding on CP and KP peel immobilised beads was physico-chemical in nature.

Acknowledgement:

The authors would like to thank the Department of Forensic Science, Galgotias University, Greater Noida, Uttar Pradesh, for their constant support and encouragement.

Conflict of Interest:

The author declares there is no conflict of interest in this project.

Source of Funding:

This work was supported by funding from a School of Biomedical Sciences Deans Bequest Grant and Doctoral Scholarship from the University of Otago, Dunedin, New Zealand. The authors would like to thank Dr. Candace Martin from Geology Department, Mr Dave Barr from Centre for Trace Element Analysis, Chemistry Department, and Liz Girvan from Otago Centre for Electron Microscopy, University of Otago for their assistance.

CONCLUSIONS

We have shown that the Probability Isotherm theory given by Chapman *et al.*, for biochemical reactions can also be used to study multi-ion biosorption of heavy metal ions in non-equilibrium conditions. The uptake of Cd and Ni ions on CP and KP beads was most useful for calculating parameters in the Langmuir isotherm model as these ions gave the best fit among the seven ions in the cocktail solution. Langmuir was a suitable isotherm model with up to five ions showing intermediate to good fits ($R^2 > 0.8$), and binding of the ions was physico-chemical in nature. This novel concept has opened new avenues for the study of biosorption in non-equilibrium conditions. **IJFMP**

LIST OF ABBREVIATIONS

AT	: Equilibrium binding constant corresponding to the maximum binding energy
cads	: Adsorbed biosorbate concentration
CO	: Initial ion concentration
CP	: Cucumber peel
ICP-MS	: Inductively coupled plasma coupled with mass spectrometry
kb	: Rate constant for backward reaction
kf	: Rate constant for forward reaction
KL	: Langmuir constant
KP	: Kiwifruit peel
N	: Number of experiments/ Sample size
PFO	: Pseudo-first order
PSO	: Pseudo-second order
qe	: Biosorption capacity at equilibrium
qmax	: Maximum biosorption capacity
qne	: Biosorption capacity at non-equilibrium
R ²	: Coefficient of determination
RL	: Langmuir separation factor
RSD	: Relative standard deviation
SE	: Standard error of the mean
Tb	: Terbium
V	: Volume of solution

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