

Biosorption of Co(II) Metal by Original and KMnO_4 Pretreated *Trapa natan* Biopolymer

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Abstract

Bioadsorption of Co(II) metal ions from the aqueous medium using *Trapa natan* peels biomass was examined for preliminary pH, initial metal absorption and contact time. Pretreatment of biomass were carried out with oxidizing agents. The maximum uptake q (mgg^{-1}) for Co(II) obtained by KMnO_4 -TNP was about (53.92) as compared to Native-TNP (24.28) at pH 5. The equilibrium and kinetics models were applied over data. The Langmuir and Freundlich equilibrium adsorption models were investigated and observed to the fit the data. The Freundlich model gave better fit than the Langmuir model with R^2 value of 0.9951. Kinetic study revealed that adsorption was fast in first 60 minutes and equilibrium was achieved after 120 minutes for Co(II) metal. The suitability of a pseudo second order chemical reaction for the sorption of Co(II) onto this biosorbent was apparent. The results revealed that *Trapa natans* peels biomass is effective, potential and best beneficial biosorbent for removal of heavy metals.

Keywords: Biosorption; *Trapa natan* peels; KMnO_4 ; Co(II)

Introduction

Heavy metals pollution arises from different sources in the result of industrial actions and scientific improvement but most commonly is due to purification of metals. Discharge of the Heavy metals in the water bodies because of Anthropogenic actions is most important water pollution source. Co, Zn, Cu, Ni, Pb, Hg, are frequently detected in engineering wastewaters, which instigate as of metal plating, mining activities, smelting, battery construct, tanneries, oil refining, smear manufacture, pesticides, dye manufacture, printing and picturesque industries, etc. [1]. Heavy metals must be removed before discharge because unlike organic wastes, heavy metals are non-biodegradable and build up in gulp of air tissues, and responsible for various diseases and disorders [2]. Cobalt is an odorless, steely-gray, shimmering, rigid metal. Everyone is unwrapping to the fundamentals to small levels of Cobalt in atmosphere, stream and foodstuff. 2 gdm^3 of Cobalt in consumption water has been estimated. Cobalt has both advantageous and destructive special effects on physical condition. Important natural sources of Cobalt in the atmosphere are loam, grime and marine irrigate. The sensitive Co (II) poisoning cause dangerous health hazards in humans like asthma, failure of heart, harm to liver and thyroid [3].

Many physicochemical techniques have been urbanized in favor of the eradication of metals from wastewater, for example mining, ion exchange, chemical rainfall and crust intake partition process. Development of professional and inexpensive partition processes is therefore of tremendous significance. Adsorption is another established technique for the exclusion of heavy metals from wastewater [4]. Biosorption is the potential of dynamic sites on the shell of biomaterials to connect and deliberate heavy metals from even the most adulterate aqueous solutions. [5]. The effectiveness of biomass be determined by on factors such as no. of sites on the biosorbent matter, their ease of access and chemical state such that the availability and the resemblance between sites and metal [6]. The largest advantage of biosorption are the low working rate, chemical's capacity to be minimized and disposal of organic slush and many competence in detoxifying very thin effluents [6].

Physical pretreatment method such as heat, autoclaving, glacial, ventilation and baking and substance pretreatment by means of alkali and organic chemicals showed improvement and diminution

in metal bioadsorption, [7] *Trapa natans* fruit belonging to the family *Trapaceae*, its root is fine long and many in number, leaves are triangular, fan shaped. *Trapa natans* are nut like and one to two inches in diameter. The species are floating annual aquatic plant, growing in slow moving water up to 5 meters deep. The dried peels of *Trapa natans* are used in bleeding disorders, threatened abortion, dysuria, polyuria and oedema. The purpose of this stuff will be conclude the effect of element pretreatment for heavy metals elimination from biomass and to charge the changes in the uptake capacity of metals weather decrease or increase after the pretreatments.

Materials and Methods

Sample collection

The research work reported in this text was performed in the Research laboratory of Department of Chemistry, University of Agriculture Faisalabad, Pakistan. The research was carried out during 2013 to observe the biosorption of heavy metals from the aqueous solutions by waterchest nuts (*Trapa natans*. L) peels as biosorbent. All the samples of *Trapa natans* L. used were collected from Jhung bazaar of Faisalabad. This sampling area does not have any aforementioned history of contamination by heavy metals.

Preparation of biosorbents

Peels of *Trapa natans* L. were boiled in hot boiling water to made lenience to remove its peels, that are the biosorbent material then peels were washed with water to remove dust, cut into small pieces and first sun dried and then oven dried at 65°C for 48 hours. Dried biomass was

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ground and screened using Octagon Siever (OCT- DIGITAL 4527-01); uniform particle size fraction of 0.25 mm was obtained and stored in air tight container.

Pretreatment of biosorbents

Prior to use sample was pretreated with the Oxidizing Agents (KMnO₄, H₂O₂ and K₂Cr₂O₇) in the following way:

- 10 g of biosorbent having particle size 0.25 mm was taken in conical flask and in it added 100 mL of 0.1M solution of KMnO₄.
- 10 g of biosorbent having particle size 0.25 mm was taken in conical flask and in it added 100 mL of 0.1M solution of K₂Cr₂O₇.
- 10 g of biosorbent having particle size 0.25 mm was taken in conical flask and in it added 100 mL of 0.1M solution of H₂O₂ and kept these three flasks in the shaker for constant shaking for 24 hours.

Samples were filtered, filtrate was useless and discarded. Extensive washing of biosorbent with distilled water was carried out to remove any unreacted chemical [7].

Preparations of metals solutions

The Co (II) stock solution having concentration 1000 mg/L was prepared by dissolving 4.15 g of cobalt chloride powder in 1000 mL of distilled water. Co (II) stock solution then prepared was immediately stored in airtight plastic bottles. From these stock solutions, solutions of different concentrations were prepared to be used in biosorption studies.

Metal uptake

The amount of Co (II) taken up by biomass in each flask was calculated using following mass balance equation (Eq. 1) [8]. The percentage removal was determined by equation 2.

$$qe = (C_i - C_e)V / 1000 W \quad (1)$$

$$\% \text{ sorption} = [(C_i - C_e)100] / C_i \quad (2)$$

Where “C_i (mg L⁻¹)” and “C_e (mg L⁻¹)” are the initial and equilibrium metal concentrations (mg L⁻¹), respectively, qe (mgg⁻¹) is the equilibrium sorption.

Batch biosorption studies

All glassware used for experimental purpose was washed with 60% (v/v) nitric acid and subsequently rinsed with DW to remove any possible interference by other metals. Biomass concentrations (0.1 g per 100 mL), biosorbent particle size (0.250 mm), contact time (24 h), temperature (30°C), shaking speed (150-200 rpm) to check the possible maximum removal of metal ions. Control assay was accompanied with each experiment. At the end of each experiment, flasks were removed from the shaker and solutions were separated from the biomass by filtration through filter paper.

Analytical procedure

Samples were filtered to remove solid particles and then were analyzed to determine the ion concentration by an atomic absorption spectrophotometer (Model: AAAnalyst 300, Perkin-Elmer). Co(II) uptake was calculated by simple concentration difference method. Uptake of Co(II) was calculated from the mass balance equation.

$$qe = V(C_i - C_e) / m$$

where V is the volume of the solution (L),

C_i is the initial concentration (mg/L),

C_e is the final concentration in solution (mg/L) and m is mass of the sorbent (g).

% sorption is given as

$$\% \text{ sorption} = (C_i - C_e) / C_i \times 100$$

Statistical analysis

Mean and standard error values were calculated from triplicate sets of experiments. All statistical analysis was performed using Microsoft Excel 2007, Version office XP.

Results and Discussion

In this research work, dried biomass of *Trapa natans* peels was used by the side of with pretreated biomass. The principle of inventive biomass of *Trapa natans* peels were to know its biosorption capability and then evaluate with the adsorption capacity of chemically pretreated biomass.

Effect of pretreatment

Comparing the results of pretreatments on *Trapa natans* peels 100 mgL⁻¹ of Co (II) solutions were shaken at 200 rpm with 0.1 gm of pretreated *Trapa natans* peels. The particle size of the biomass was 0.25 mm at the pH of 5 for Co (II). One can notice that the pretreatment of biomass by KMnO₄, K₂Cr₂O₇ and H₂O₂ increased the sorption capacity (mgg⁻¹) of biomass in order:

For Co(II) Nat-TNP (24.28) < H₂O₂-TNP (33.32) < K₂Cr₂O₇-TNP (39.022) < KMnO₄-TNP (53.92)

Generally, oxidizing agents treatment has been used for metal removal causing increase in sorption capacity. KMnO₄ treatment showed remarkable increase in sorption capacity of biomass. KMnO₄ pretreated biomass showed more sorption capacity and it was due to solubility of more mineral matter of biomass which resulted more porosity in biomass. According to this property it is also used in sterilizing wells of drinking water.

Chemical mechanism of KMnO₄ pretreated TNP for adsorption

Adsorption mechanisms: Result from KMnO₄ pretreated biomass suggesting that the precipitation was not an important mechanism for Co(II) removal. Compared with Native biomass, the amount of oxygen containing groups such as hydroxyl groups, phenolic hydroxyl and carboxyl functional groups increased significantly on the surface of the biomass after the KMnO₄ pretreatment of the TNP. In addition, the pretreated biomass surface was also covered with ultrafine manganese oxide (MnO₂ /Mn₃O₄) particles. In this work, both the functional groups and the MnO particles could serve as the main adsorption sites for heavy metal ions in aqueous solutions. As a result, the KMnO₄ treated biomass showed much stronger binding affinity to the three heavy metal ions than native biomass particles.

Effect of pH

The outcome of pH on the elimination of Co (II) from aqueous solution by *Trapa natans* peels was studied by varying the pH (1-7) values while the other operational parameters were kept constant. Results of present investigation showed that sorption capacities (mgg⁻¹)

enlarged with growing pH from 1 to 7 for both metals. The absorption capacity (mgg⁻¹) of Co (II) increased from 19.2 to 29.02, 27.7 to 39.1, 29.33 to 49.93 and 39.02 to 59.67 for Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP, and KMnO₄-TNP when pH values of the solutions changed from 1 to 7. The results revealed that KMnO₄-TNP possessed maximum biosorption capacity of 53.92 for Co (II) at pH value 5. Lower or high pH has resulted either in low biosorption or precipitation of the corresponding metal ions [9]. The segregation of metal ions from distilled water solution by adsorption depended on the pH of solution, as the latter affected the surface charge of biosorbent, solution chemistry of metals, activity of functional group in the biomass, the degree of ionization and the species of adsorbate [10]. Due to high proton focus at small pH, there is a decrease in metal ion biosorption. It is due to the positive charge accumulation on metal binding sites, hence protons struggle efficiently with metal ions for their binding. The cell surface of the biosorbent become more negative with rising pH due to deprotonation. Due to this more metal ions were attached with active sites. The positively charged ions of the metals then race more affectively for existing binding sites, which increased the sorption [11]. The selection of the optimum pH must take into account for proper sorption of the metal ions. At optimum pH value (pH 5 for Co (II) metal) the surface of the *Trapa natans* peels is negatively charged due to the dissociation of the COOH groups [12]. Related results have been accounted in literature by [13] in his study of Utilization of *Blighia sapida* (Akee apple) pod in the removal of Pb (II), Cd (II) and Co (II) ions from aqueous solution.

Effect of initial metal concentration

The above-mentioned effect on the deletion of Co (II) from the aqueous solutions by *Trapa natans* L. peels in its native as well as pretreated form were studied at pH 5.0 by changing the amount of the system from 25 to 400 mgL⁻¹. Results showed that biosorption power increased with increased in initial metal ion concentration of Co (II) on the biomass and %age removal decreased with increased in initial metal concentration. The Figures 1-3 shows that sorption capacities (mgg⁻¹) in case of Co (II) increased from 9.33 to 80, 16.21 to 122.1, 19.33 to 149.50 and 21.07 to 204.4 while % removal decreased from 37.32 to 20, 64.84 to 31.52, 77.32 to 37.37 and 84.28 to 51.1 for Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP as concentration increased from 25 to 400 mgL⁻¹. The maximum uptake q (mgg⁻¹) obtained by biomass TNP was (204.4) for Co (II) with KMnO₄-TNP in contrast with native-TNP at 400 mgL⁻¹. The concentration of metal ions present initially

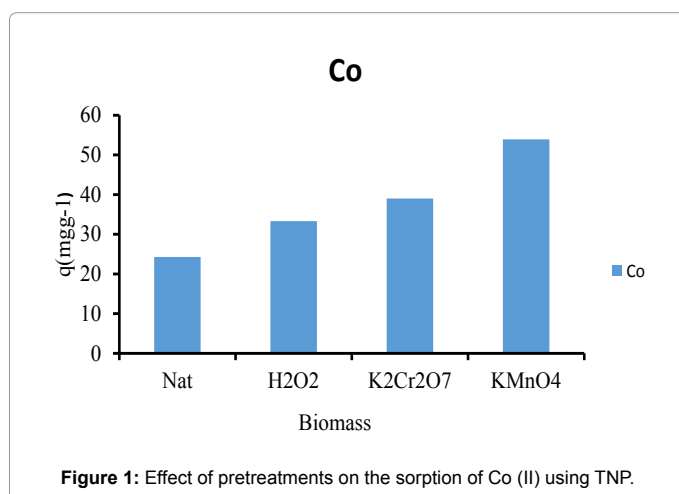


Figure 1: Effect of pretreatments on the sorption of Co (II) using TNP.

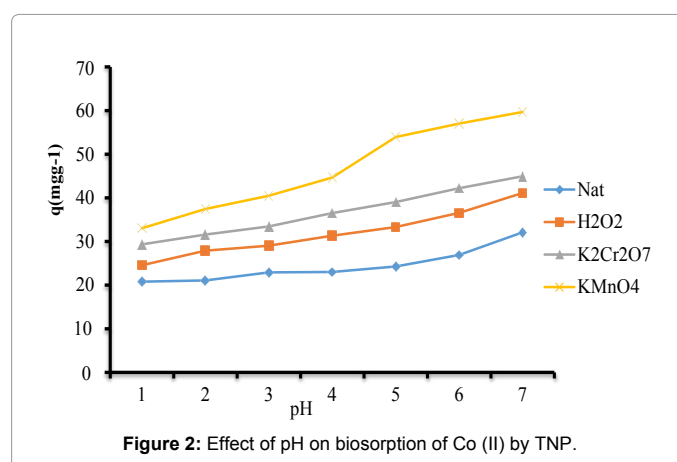


Figure 2: Effect of pH on biosorption of Co (II) by TNP.

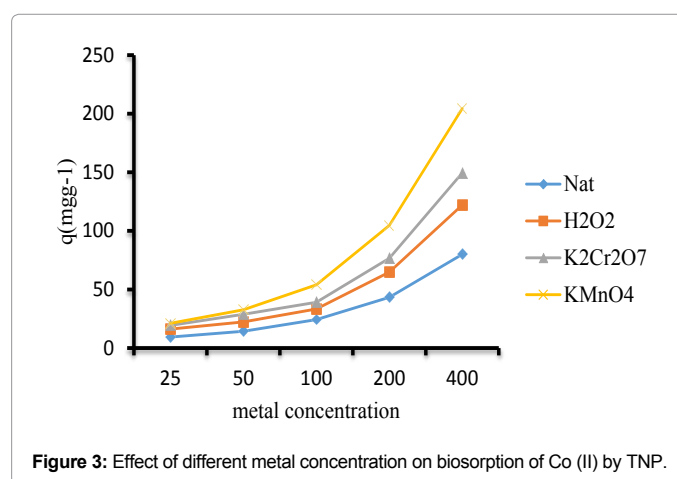


Figure 3: Effect of different metal concentration on biosorption of Co (II) by TNP.

is an important factor here. It offers a vital energetic force to prevail over all mass shift confrontation of metal ions between the its solution form and pure solid form, for this reason, the elevated the early focus of metal ions, the more the adsorption capacity and decrease the percentage adsorption of dried biomass. Biosorbents show a controlled number of dynamic sites and at a certain concentration these become occupied [14]. Adsorption isotherms of Co (II) concentration from 25 to 400 mgL⁻¹ at pH 5.0 were studied keeping a permanent adsorbent dose (0.1 g/100 mL).

Equilibrium modeling

Adsorption isotherms of Co (II) concentration from 25 to 400 mgL⁻¹ with a fixed adsorbent dose (0.1 g/100 mL) at pH 5 was studied. Freundlich and Langmuir adsorption isotherms were applied to describe the equilibrium relationships between sorbent and sorbate in solution. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is dynamic balance with that of the interface [15]. To get the equilibrium data, initial concentration of Co (II) were varied while the weight of biomass was kept constant. Twenty-four hours of equilibrium period for sorption experiments were used to ensure equilibrium conditions.

Langmuir isotherm

The general form of Langmuir isotherm equation is written as:

$$1/q_e = 1/q_{max} + 1/(b q_{max}) C_e \quad (3)$$

According to this model, all adsorbed species interact only with a site and not with each other and the adsorption is limited to monolayer. It is then assumed that once a metal ion occupies a site, no further sorption can take place. A monolayer was formed when the equilibrium was attained. The linearized form of Langmuir isotherm equation is written as:

$$C_e/q_e = 1/X_m K_L + C_e/X_m \quad (4)$$

By using the Linearized Langmuir equation Langmuir parameters were calculated.

Langmuir isotherms are presented in Figure 2 for Co (II) which is plots of C_e/Q_e gL⁻¹ versus C_e mgL⁻¹ under different concentrations of metals. Straight lines with R² values as shown in Table 1, 0.943, 0.976, 0.993 and 0.999 for Co (II) sorption by Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP were obtained. Linearization of graph and theoretical monolayer capacity (q_{max}) calculated for Co (II) on the Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP found to be agreeing with the experimentally determined sorption.

Freundlich isotherm

The general form of Freundlich isotherm equation is written as:

$$q_e = KC_e^{1/n} \quad (5)$$

The Freundlich isotherm equation assumes that a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. The linearized form of Freundlich isotherm equation is written as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

The linear plot of the Freundlich isotherm model for sorption of Co (II) is presented in Figure 3 for Co (II). From Table 1, R² values with respect to the sorption of Co(II) for Freundlich isotherm model was noted to be 0.913, 0.687, 0.693 and 0.761 Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP respectively, these values are greater than R² values obtained in case of Langmuir model.

Effect of contact time

For the sorption mechanism of Co (II) metal cation onto Nat-TNP, KMnO₄-TNP, K₂Cr₂O₇-TNP and H₂O₂-TNP, a kinetic investigation with different time intervals ranging from 0 to 1440 minutes (0, 15, 30, 60, 120, 180, 240, 360, 480, 720, 960 and 1440) was conducted having metals concentration 100 mgL⁻¹. In order to determine the contact time taken to reach the equilibrium and to study the effect of the sorbent particle size. It can be seen that the cobalt (II) removal increase rapidly with the contact time up to 15 min and reached maximum at 1440 minutes. For Co (II), uptake capacity (mgg⁻¹) increased from 12.21 to 24.28, 13.67 to 33.32, 17.17 to 39.03 and 21.89 to 53.92 for Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP as time increases from 0 to 1440 minutes. The maximum uptakes (mgg⁻¹) obtained by TNP was (53.92) for Co (II) with KMnO₄-TNP in contrast with native at 1440 minutes. The initial sorption rate was quick and can be explained on the fact that the metal ions interact easily with the adsorption sites which are open and extra cellular binding takes place causing adsorption rate to become high. During the first few minutes, adsorption rate was extremely sharp then the rate began to drop toward a steady state and reached maximum at 1440 minutes with insignificant levels of adsorption [15]. There are two basic reasons to account for the slow sorption stage. According to the first reason sluggish sorption was resulted by intracellular binding and per the second it was due to slower distribution of solute particles into the core of the adsorbent (biomass) [16].

Kinetics modeling

In order to examine the mechanism of kinetics of Co(II) adsorption and rate controlling step, two kinetic models, Lagergren's pseudo 1st order and pseudo 2nd order were fitted to data [17]. The Pseudo 1st order Lagergren model for solid/liquid systems of adsorption is express as:

$$\log(q_e - q) = \log q_e - k_1 t / 2.303 \quad (7)$$

It is clear from Figure 4 that the pseudo 1st order kinetic equation fails to predict the experimental adsorption capacity (q_{exp}) because R² values of pseudo 1st order kinetics are relatively lower than pseudo 2nd order kinetics. From Table 2, the results cleared that q_e mgg⁻¹ (0.587, 0.809, 0.220 and -0.069) for Co(II) sorption values with Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP respectively estimated from the pseudo 1st order kinetic model was found not to be agreeing with the q_{exp} (experimental capacity).

Pseudo 2nd order equation

Adsorption kinetic data was more analyzed by using pseudo 2nd order kinetics model. It is express as:

$$t/q = 1/k_2 q_e^2 + t/q_e \quad (8)$$

k_2 is known as the equilibrium rate constant of pseudo 2nd order biosorption (gmg⁻¹min⁻¹). To calculate the pseudo 2nd order rate constants k_2 and q_e intercept and slope of the plot t/q versus t were used.

While pseudo 2nd order kinetic model q_e mgg⁻¹ (12.65, 20.20, 35.21 and 59.52) was found to be agreeing with the q_{exp} (experimental capacity) (24.28, 33.32, 39.03 and 53.92) for Co(II) sorption values. This confirmed that pseudo 1st order kinetic model is not accurate for sorption kinetics of Co(II) sorption by Nat-TNP, H₂O₂-TNP, K₂Cr₂O₇-TNP and KMnO₄-TNP. Both facts suggested that the adsorption of Co(II) ions follow the 2nd order kinetics model, as shown in Figures 5-8 which depends on the hypothesis that adsorption may be a rate limiting step. During the study of contact time, initial concentration, equilibrium concentration and contact time were used as an experiment variables [18,19].

Conclusion

Even though the technology also suffers inherent disadvantages like early saturation of biomass, little biological control over the characteristics of biosorbents. It offers several advantages, including

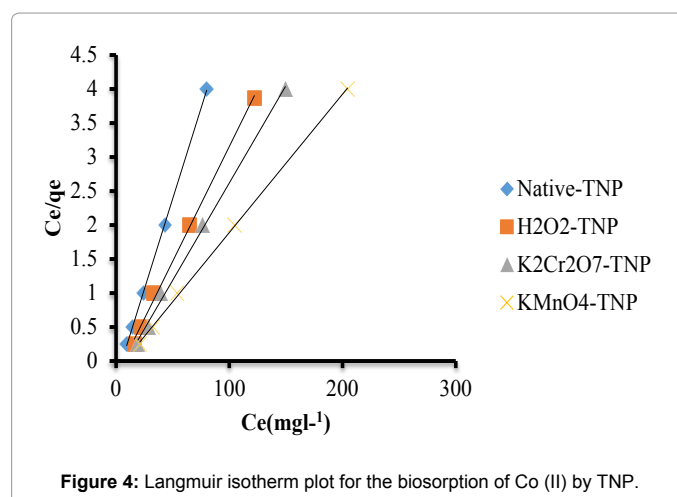


Figure 4: Langmuir isotherm plot for the biosorption of Co (II) by TNP.

Metal	Biosorbent	Langmuir model			Experimental value q_{max} (mgg ⁻¹)	Freundlich model			q_e (mgg ⁻¹)
		X_m (mgg ⁻¹)	K_L (Lmg ⁻¹)	R^2		1/n	K_F (mgg ⁻¹)	R^2	
Co(II)	Nat-TNP	18.83	0.196	0.943	20	0.277	63.21	0.913	8994.9
	H ₂ O ₂ -TNP	29.58	0.150	0.976	31.51	0.312	125.0	0.687	4.9071
	K ₂ Cr ₂ O ₇ -TNP	34.96	0.117	0.993	37.37	0.330	171.7	0.693	84664
	KMnO ₄ -TNP	49.01	0.138	0.999	51.1	0.203	138.6	0.762	26230

Table 1: Comparison of Langmuir and Freundlich isotherm parameters of Co (II) biosorption by *Trapa natans* peels.

Metal Ions	Biosorbent	Pseudo first order			Experimental q_{max} (mgg ⁻¹)	Pseudo second order		
		q_e (mgg ⁻¹)	K_{1ads} min ⁻¹	R^2		q_e (mgg ⁻¹)	K_{2ads} (gmg ⁻¹ min ⁻¹)	R^2
Co(II)	Nat-TNP	0.587	0.017	0.895	24.28	12.65	0.001	0.991
	H ₂ O ₂ -TNP	0.809	0.012	0.973	33.32	20.20	0.0004	0.996
	K ₂ Cr ₂ O ₇ -TNP	0.220	0.010	0.939	39.03	35.21	0.0005	0.997
	KMnO ₄ -TNP	-0.069	0.008	0.984	53.92	59.52	0.0003	0.999

Table 2: Comparison between Lagergren pseudo-first-order and second-order kinetic models for the biosorption of Co (II) using *Trapa natans* L peel.

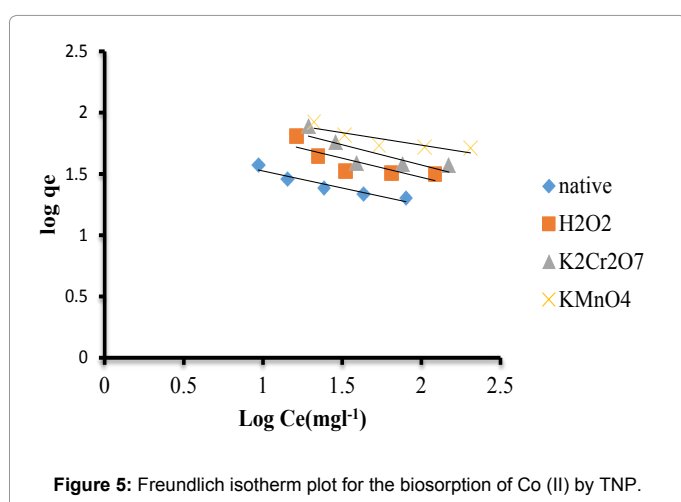


Figure 5: Freundlich isotherm plot for the biosorption of Co (II) by TNP.

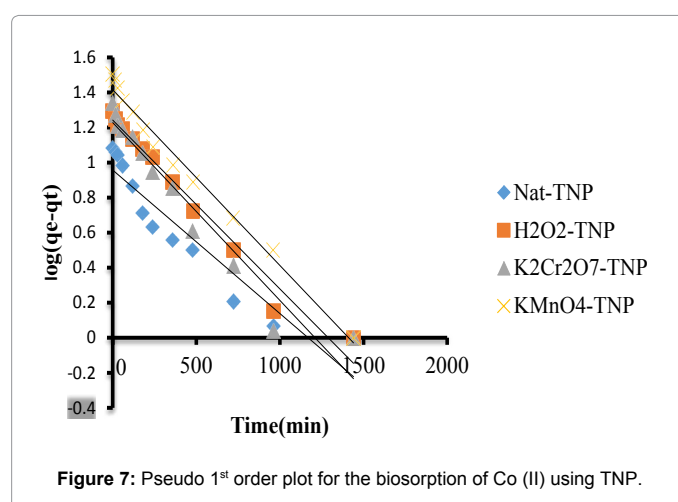


Figure 7: Pseudo 1st order plot for the biosorption of Co (II) using TNP.

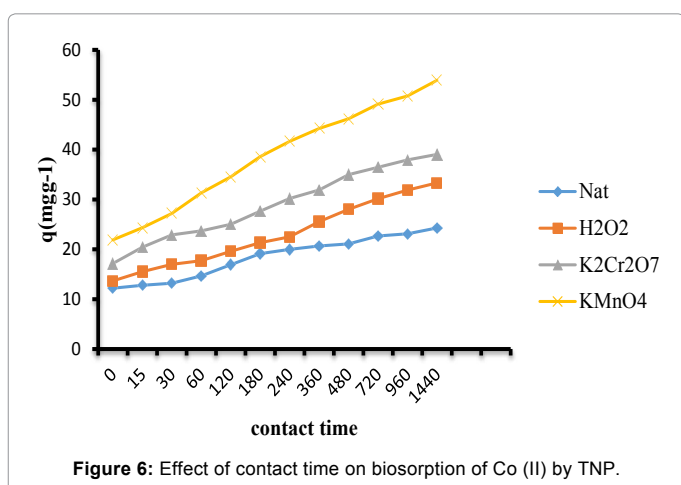


Figure 6: Effect of contact time on biosorption of Co (II) by TNP.

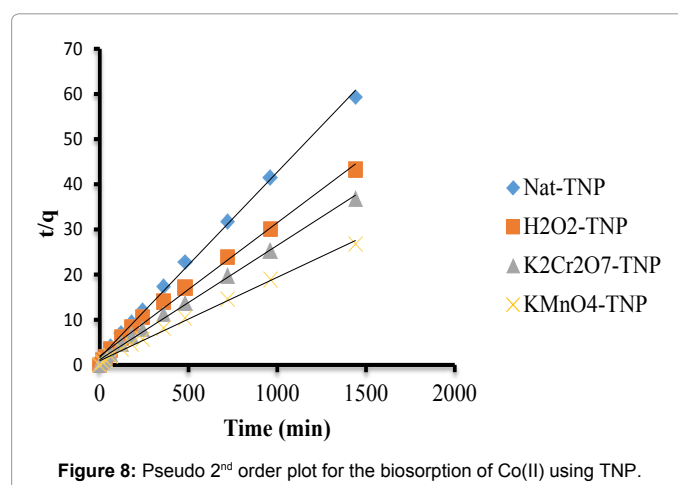


Figure 8: Pseudo 2nd order plot for the biosorption of Co(II) using TNP.

cost effectiveness, high efficiency, minimization of chemical/ biological sludge, and regeneration of biosorbent with possibility of metal recovery. In countries, with the rush for rapid industrial development coupled with lack of awareness about metal toxicity, there is an urgent need for developing an economical and eco-friendly technology which satisfies these demands where other conventional methods fail. These findings demonstrated that *Trapa natans* L. is cost effective, potential

and a novel biosorbent for the removal of heavy metals such as Co (II) from the aqueous solution. The pretreatment method thus can be used to prepare high-efficiency biomass for heavy metal remediation.

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