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ARTICLE

Synthesis of Ionically Crosslinked *N*-Succinyl Chitosan Hydrogel Beads for Recovery of Palladium from Acidic Aqueous Solution

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ABSTRACT

Palladium is used in several biomedical and technological applications and has very low natural abundance in the earth crust. Ionically cross-linked *N*-succinyl chitosan beads (NSCBs) have been synthesized and tested for extraction of palladium from aqueous waste. Batch extraction studies have been carried out to understand the influence of various experimental parameters on the sorption behaviour of palladium. Sorption kinetics is found to be fast and the kinetics data fitted well in to pseudo second-order model for the sorption of palladium ions onto the composite beads. Different sorption isotherm models have also been applied to the experimental data. Equilibrium data are found to be represented well by Langmuir isotherm equation, with monolayer sorption capacity of around 6 mg/g for the swollen beads and 60 mg/g for the dried beads. Reusability of the beads has also been established by multiple sorption-desorption experiments.

KEYWORDS

Chitosan, *N*-Succinyl chitosan, Sorption, Palladium, Polymeric beads.

INTRODUCTION

Palladium is extensively used in biomedical and technological applications, such as dentistry, medicine, organic synthesis, electronics, fuel cells, hydrogen storage materials, various fields of catalysis and many more [1]. The natural abundance of palladium in the earth crust is very low and the present residue will not be enough to accommodate its rising demand in near future [2]. This has resulted in exploring different techniques for separation and recovery of palladium from suitable secondary resources, such as high level waste (HLW) solutions generated from reprocessing of spent nuclear fuel, spent catalyst originating from automobile and chemical processing industries [3]. Sorbents based on both synthetic and natural polymers are generally employed for extraction of metals but the later ones are preferred due to their environment friendly and biodegradable properties. Naturally occurring polysaccharides, such as chitosan can be efficiently utilized for removing metal ions, especially precious metals [4]. Its sorption properties can be upgraded by chemical alteration of the polymer.

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The increasing demand for the newly developed environmental friendly commercial methods for the regeneration of precious metal ions from industrial waste water have attracted too many researchers to investigate the probability to utilize bio-materials for metal uptake [5]. There are various materials, such as chelating resins, solvent-impregnated resins, *etc.*, available for the metal extraction [6-8]. Recently extensive work has been done for the treatment of waste solution containing low concentration of metal ions due to both increasing demand and stringent environment pollution control rules [9]. Biosorption has been an effective substitute to regain metal ions from dilute solutions [10] and studies have been focused on the sorption of important metal ions using different biopolymers [11-13]. Chitosan is a well known biopolymer used in sorption of metals, due to its high nitrogen content, which helps in its binding with metal ions present in wastewater [14]. Chitosan chelates metal ions generally *via* the free amino groups. Sorption capacity of chitosan differs due to crystallinity, percent deacetylation and content of amino group [15,16]. Among the biopolymers, chitosan is an amphiphilic macromolecule, in which the ratio between acetylated and deacetylated residues is accountable to maintain equilibrium between hydrophilic and hydrophobic interactions [17,18]. Chitosan is not soluble in water due to strong intramolecular hydrogen bonding, but if some alterations are carried out on -OH and -NH₂ groups of chitosan its water solubility changes.

So here we have attempted to introduce succinyl moiety at the NH₂ position of chitosan to improve its water solubility as well as metal extraction capacity. The easily accessible-COOH groups, to which the metal ion can form a complex through ionic interaction, are mainly responsible for the improved properties. Also the synthesized *N*-succinyl chitosan can form ionically cross linked beads and the crosslinking density can be altered by varying the degree of succinylation [19]. Further, porous nature of the beads helps in enhancing palladium sorption capacity, due to increased surface area.

In the present study, we have synthesized and characterized the ionically crosslinked *N*-succinyl chitosan beads for the recovery of palladium from various aqueous wastes and also studied the effect of different physical parameters on the extraction process.

EXPERIMENTAL

Chitosan with molecular weight about 1,25,000 and 85 % deacetylation was purchased from Sigma, Aldrich. Succinic anhydride was supplied by Fluka, all other reagents (calcium chloride, sodium hydroxide, HCl, acetic acid, *etc.*) used were of analytical grade. Aqueous solutions were prepared using water purified by Millipore-Q water purification system, having conductivity of 0.6 $\mu\text{S cm}^{-1}$ or lower.

Palladium feed solution: Stock solution containing 10^{-2} M Pd(II) in water was prepared by dissolving appropriate amount of PdCl₂ in water. Aliquots were taken from this stock solution and properly diluted to the required Pd(II) concentrations, for different sorption experiments.

***N*-Succinyl chitosan synthesis:** A known amount of chitosan (3 g) was dissolved in 1 % acetic acid solution in a round bottom flask. Succinic anhydride (6 g) was then dissolved in acetone

and added drop wise into the round bottom flask, at room temperature. This reaction mixture was refluxed for 8 h at 60 °C. The reaction mixture was allowed to cool to room temperature and the synthesized *N*-succinyl chitosan (NSC) was precipitated out using acetone. The *N*-succinyl chitosan precipitate was then filtered and washed thoroughly with acetone water mixture, dried at 45 °C under vacuum to obtain a white powder (yield 89.9 %). The synthesized *N*-succinyl chitosan was characterized using ¹H NMR and FTIR, techniques.

***N*-Succinyl chitosan bead (NSCBs) preparation:** Aqueous solution of *N*-succinyl chitosan (4 w/v %) was added drop-wise into an aqueous bath containing (4 w/v %) calcium chloride, using a syringe with needle of appropriate diameter, to form the beads. The aqueous bath solution was stirred slowly to prevent agglomeration of the beads. Soft beads obtained initially were then incubated in calcium chloride solution for a few hours, for complete crosslinking.

Atomic absorption spectroscopy (AAS): Quantitative determination of palladium metal ions present in aqueous waste solution was carried out using atomic absorption spectrometry technique (AAS). The GBC Avanta Pm instrument was used in this study. The error on the measured concentrations was within ± 5.0 %.

FT-IR analysis: The FT-IR spectra of the synthesized vacuum dried bead samples were recorded using diamond ATR holder, employing IR Affinity-1 FT-IR spectrophotometer, in the range 500-4000 cm^{-1} .

Thermogravimetric analysis: Composition and thermal stability of the beads were investigated using thermogravimetric analysis (TGA) on STAR[®] System METLER TOLEDO instrument. Thermogravimetric curves of a few mg of the sample in an alumina sample holder, were recorded from 25 to 900 °C, in N₂ atmosphere at a heating rate of 10 °C min⁻¹.

Optical microscopy and SEM: Morphology of the beads was determined by microscopy techniques. A simple microscopy, using QX5 DIGITAL BLUE computer microscope and scanning electron microscopy, using TESCAN VEGA MV 2300 T/A microscope were used to characterize the beads morphology. The beads were dried at room temperature and then vacuum sputtered with a thin layer of Au prior to the SEM analysis.

Sorption procedures: The batch experiment method was used for the metal extraction study at room temperature. About 0.018 g of the ionically cross linked polymeric bead samples were shaken with 2 mL aqueous solution of palladium ions (pH 4), using a controlled rotospin rotor (at a rpm of 21) for different time periods, depending on the objective of the experiment: variable time for kinetics study and 180 min in order to attain equilibrium, for sorption isotherm determination. The leftover, metal ion concentration in the aqueous phase was measured by AAS. The amounts of palladium sorbed per gram (q_e) and % sorption (% A) were determined using the following equation.

$$q_e = (v/w) \times (C_o - C_e) \quad (1)$$

$$\% A = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where, V is the volume (mL) of the Pd(II) ion solution, ' m ' is the weight (g) of the swollen ionically crosslinked *N*-succinyl chitosan beads, C_0 and C_e are the initial and the equilibrium concentrations of Pd(II) ion, in ppm, respectively.

Back extraction experiments: The back extraction of the sorbed Pd²⁺ was carried out by batch method. For this purpose, 2 mL of stripping reagent (0.01 M thiourea in 0.1 M HNO₃) was added to the 0.018 g of metal loaded ionically crosslinked *N*-succinyl chitosan beads and the mixture were shaken for 180 min [7]. The concentrations of metal ions in the aqueous phase, after the back extraction step, were also determined by AAS.

RESULTS AND DISCUSSION

Characterization of the synthesized beads

Surface morphology of beads: Morphology of the beads was determined by optical and scanning electron microscopy. The optical images of the beads, before and after loading palladium, are given in Figs. 1A and 1B, also the SEM images of surface of bead at higher and lower magnification are shown in Figs. 1C and 1D. Both these pictures clearly show that the bead surface is quite rough and has enough porosity, which enhances the surface area for metal ion sorption.

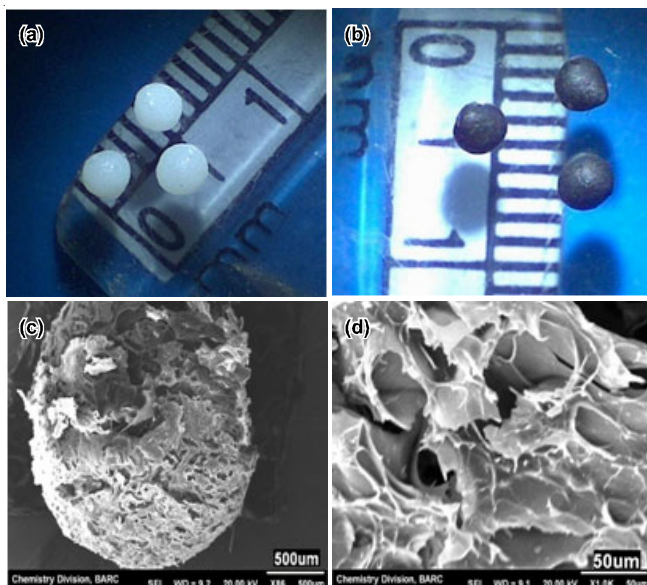


Fig. 1. Optical photographs of *N*-succinyl chitosan beads (A) without Pd, (B) with Pd after four cycles, (at 10 X magnification). The SEM images of surface of *N*-succinyl chitosan beads at (C) lower magnification, (D) higher magnification.

Thermogravimetric analysis: Fig. 2 shows the TGA profiles of (A) chitosan, (B) *N*-succinyl chitosan and (C) *N*-succinyl chitosan beads, respectively. Results of the thermogravimetric analysis indicate that the water content in the swollen beads is very high. The thermogram of chitosan shows 90 % weight loss at 600 °C while that of *N*-succinyl chitosan shows 70 % weight loss at the same temperature, indicating greater thermal stability of *N*-succinyl chitosan. If we compare the thermo gram of the *N*-succinyl chitosan and *N*-succinyl chitosan swollen beads, *N*-succinyl chitosan beads shows 90 % weight loss at 100 °C, which shows very high water content in

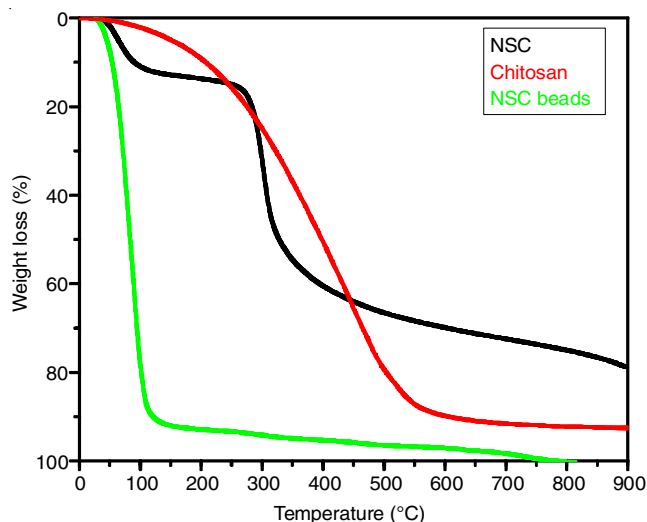


Fig. 2. Thermograms of (A) chitosan, (B) *N*-succinyl chitosan and (C) the synthesized swollen *N*-succinyl chitosan beads

the swollen beads and hence high porosity. These swollen beads were used for extraction of palladium. Here we are assuming that the volume of the water present in the swollen beads corresponds to the volume of the pores, which was helpful for efficient metal extraction.

FTIR studies: The FTIR spectra of the chitosan and *N*-succinyl chitosan are shown in Fig. 3. The chitosan spectrum clearly indicates that distinctive absorption bands appear at 1646 cm⁻¹ (amide I) and 1593 cm⁻¹ (amide II). Peaks at 1149 cm⁻¹ (asymmetric stretching of C-O-C bridge), 1068 and 1027 cm⁻¹ (skeletal vibration involving the C-O stretching) are also the characteristic peaks of the saccharine structure. While in case of *N*-succinyl chitosan, a new peak comes in to view at 1421 cm⁻¹ matching with the symmetric stretching of -COO⁻ group. The peak at 3085 cm⁻¹ corresponding to (stretching of -CH₂) is observed in the spectrum of *N*-succinyl chitosan. Compared with that of chitosan, the peak at 1593 cm⁻¹ (-NH₂ bending, amino group characteristics) decrease greatly and the peak at 1545 cm⁻¹ (assigned to secondary amines) appears. These results indicate that the succinyl derivatization reaction took place at the *N*-position and -NH-CO- groups have been formed.

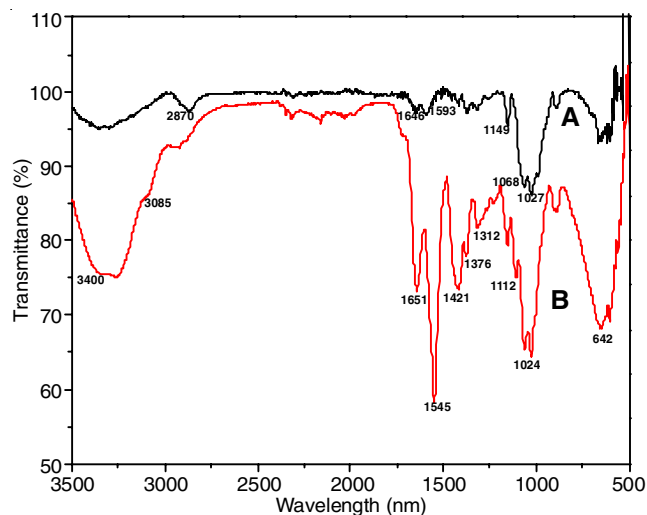


Fig. 3. FT-IR spectra of (A) chitosan and (B) *N*-succinyl chitosan

¹H NMR spectra: The proton nuclear magnetic resonance (¹H NMR) spectra of chitosan and *N*-succinyl chitosan are shown in Figs. 4A and 4B respectively. The ¹H NMR positions of *N*-succinyl chitosan were as follows: ¹H NMR (deuterium [D₂O]) δ = 1.90 ppm (NH[CO]CH₃); δ = 2.33–2.70 ppm (CH₂CH₂ of succinyl); δ = 2.77 ppm (H-2 of D-glucosamine unit); δ = 3.39–3.79 ppm (H-3, H-4, H-5, H-6, H-6₂ of D-glucosamine unit), δ = 4.69 ppm (H-1 of D-glucosamine unit). Based on the ratio of the integral peak of H in succinyl to H-2 in the D-glucosamine unit, the succinylation degree of *N*-succinyl chitosan was determined to be 88.25 % [20].

Effect of sorption time: Kinetics of sorption is one of the significant parameters in the sorption process, since it helps in finding the contact time required for optimum sorption, which depends on the type of the system used. The outcome of the effect of contact time on the sorption of palladium ions onto the ionically crosslinked *N*-succinyl chitosan beads, at a fixed Pd concentration and at constant temperature (T = 298 K) is illustrated in Fig. 5A. The sorption mixtures were sampled at different time intervals, ranging from 1 to 180 min, to identify the effect of contact time on the sorption of palladium ions. It is observed that the amount of palladium sorbed onto the beads increases with time up to a certain time and after that there is no increase in the sorption. It clearly indicates that initially sorption is quite fast, becomes slow with lapse of time and equilibrium is reached at approximately 180 min. From experimental results it was decided that the maximum amount of sorption was achieved in about 180 min, at the studied temperature, which can be considered neither too slow nor too fast for practical efficiency of the synthesized beads. Therefore, the time period of 180 min has been used in further sorption experiments, as the most suitable contact time for the highest sorption.

Sorption kinetics models: In order to study the controlling mechanism of the sorption, such as mass transfer, chemical reaction, *etc.*, a number of kinetic models were used to test the experimental data. A straight forward kinetic analysis of the sorption is usually carried out by the pseudo first-order and pseudo second-order models.

Pseudo first-order model: The pseudo-first order model of Lagergren is given as [21].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e and q_t are the amount of metal ions sorbed onto the ionically crosslinked *N*-succinyl chitosan beads in (mg/g), at equilibrium and at time t , respectively and k_1 is the first-order rate constant (min^{-1}).

The integrated form of eqn. 3 can be written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

Pseudo second-order model: The pseudo second-order kinetics model has been used, can be given by the equation [21].

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where, k_2 , ($\text{g mg}^{-1}\text{min}^{-1}$) is the rate constant of second-order sorption. The integrated form of the eqn. 5 can be written as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

It can be rearranged to obtain the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The data was fitted into both pseudo first order and pseudo second order models. The linear pseudo second order plot of t/q_t vs. t gives a straight line, as shown in Fig. 5B and that of pseudo first order plot of $\log(q_e - q_t)$ versus t , (not shown here). It has correlation coefficient value 0.9322 which is less than that of the pseudo second-order kinetic model, at the studied concentrations of palladium (Table-1). The values of intercept and slope obtained from the plot are 3.4767 and -0.01014, respectively. The value of R^2 for pseudo second order model is 0.9976, which indicates that the sorption of palladium ions onto the ionically crosslinked *N*-succinyl chitosan beads can be explained by the pseudo second-order kinetic model. The pseudo second-order model assumes that chemisorption is

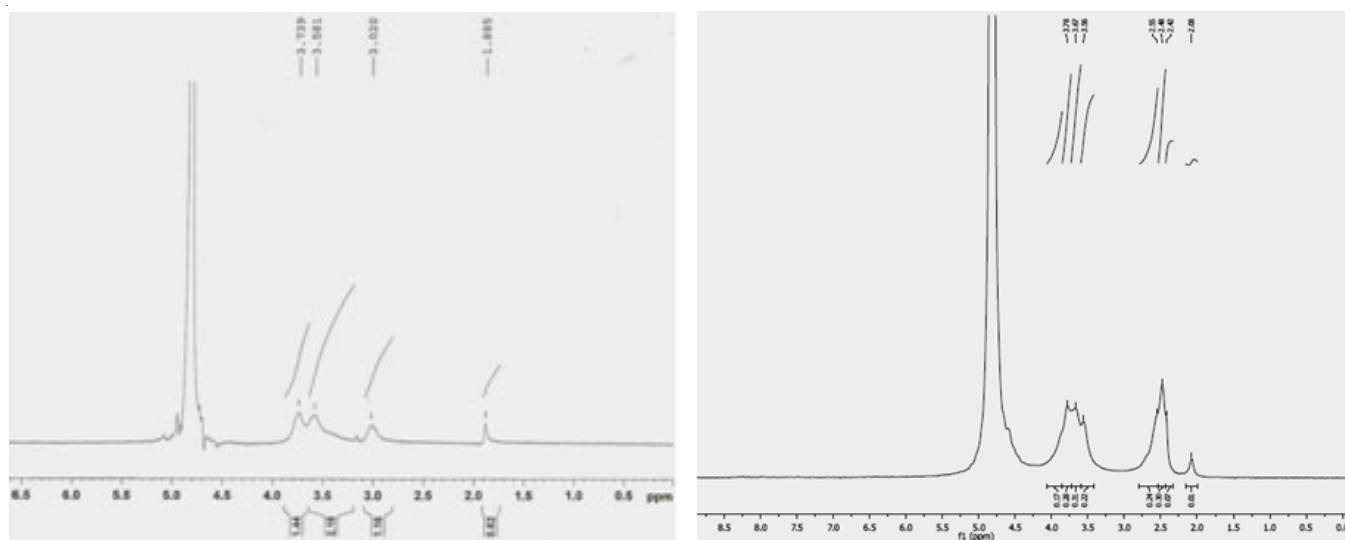


Fig. 4. ¹H NMR spectra of (A) Chitosan, (B) *N*-succinyl chitosan

TABLE-1
PSEUDO-FIRST AND PSEUDO-SECOND-ORDER EQUATION CONSTANTS AND VALUES OF R^2 FOR THE SORPTION OF PALLADIUM ONTO IONICALLY CROSSLINKED *N*-SUCCINYL CHITOSAN BEADS

Palladium conc. (mg/L)	Pseudo first-order model			Pseudo second-order model			q_e experimental
	k_1 (min^{-1})	R_1^2	q_e (mg g^{-1})	k_2 (min^{-1})	R_2^2	q_e (mg g^{-1})	q_e (mg g^{-1})
100	2.34×10^{-2}	0.9331	3.0	1.815×10^{-5}	0.9976	6.06	6.00

the rate controlling step. The value of slope and intercept obtained from the plot are 1.6485×10^{-4} and 0.00138 respectively. The calculated values of q_e and rate constant obtained from the observed intercept and the slope is given in the Table-1. In comparison to the first-order kinetic model, the values of q_e obtained from the second-order model are in excellent harmony with the experimental q_{exp} values of 6.06 mg/g, at the studied initial concentration of 100 ppm. As a result, this model seems to be more suitable for the sorption process at the studied concentration and it is concluded that the pseudo second order model explains the kinetics of the Pd sorption on to the *N*-succinyl chitosan beads.

The intraparticle diffusion model was also used to test the kinetics results and explain the mechanism of sorption kinetics. It involves the equilibrium changes as a function of $(Dt/r^2)^{1/2}$, where D is the diffusivity within the particle and r is

the radius of particle [22]. The linearized form of intraparticle diffusion were obtained from the equation represented as:

$$q_t = k_{id} t^{1/2} + I \quad (8)$$

where k_{id} is the intraparticle diffusion rate constant and intercept I is the thickness of boundary layer. The intraparticle diffusion plot shown in Fig. 5C, have three linear portions which elucidate the three sorption stages: external mass transfer at initial period followed by intraparticle diffusion of palladium onto the ionically crosslinked *N*-succinyl chitosan beads. The larger is the intercept I the greater is the boundary layer effect. Previous works showed that such plots show multi-linearity, which means that two or more steps are involved [23]. The first, sharp portion is the external surface adsorption. The second portion which indicates the gradual adsorption stage, where the rate controlling step is the intraparticle diffusion

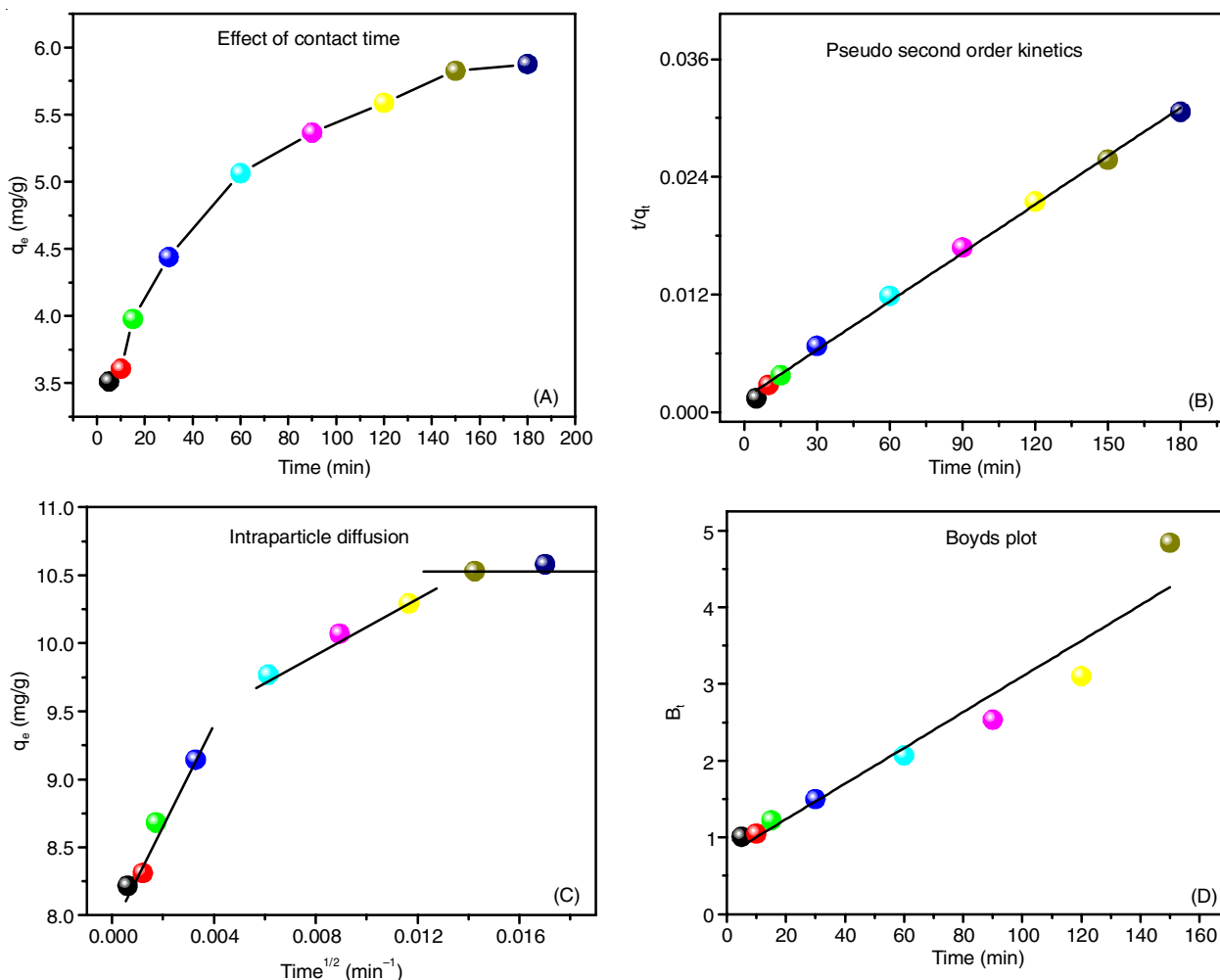


Fig. 5. (A) Effect of sorption time on the extraction of Pd(II) ions by the *N*-succinyl chitosan beads at 298 ± 1 K. (B) Pseudo second-order plots (C) Intra-particle diffusion plots and (D) Boyd's plots for the Pd ion sorption onto the ionically cross linked *N*-succinyl chitosan beads, at a fixed concentrations of palladium ions at 298 ± 1 K

phenomenon. The third portion is final equilibrium stage. A good correlation of rate data with this model justifies the sorption mechanisms.

The equilibrium concentration q_e increases accordingly with the increase in initial palladium concentration. The kinetic data was also analyzed using the kinetic expression given by Boyd *et al.* [24] in order to further confirm whether the sorption proceeds *via* film diffusion or intra-particle diffusion mechanism.

$$F = 1 - \frac{6}{\pi^2} \exp(-B_t) \quad (9)$$

where F is the fraction of solute sorbed at a given time t and B_t is a mathematical function of F .

$$F = \frac{q_t}{q_e} \quad (10)$$

where, q_t and q_e represents the amount sorbed (mg/g) at any time t and at infinite time (in the present study 180 min, respectively). Solutions to the equation (9), depending on the value of F , are given by eqns. 11 and 12.

$$B_t = 2\pi - \frac{\pi^2 F}{3} - 2\pi \left(1 - \frac{\pi F}{3}\right)^{1/2} \quad (11)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (12)$$

Thus, the value of B_t can be calculated for each value of F , using eqn. 11 for values of F up to 0.85 and, eqn. 12 for higher F values.

Film diffusion and the intraparticle diffusion mechanism of sorption can be distinguished from the linearity of B_t vs. t plot. The evidence for intraparticle-diffusion mechanism of the sorption is a straight line passing through the origin; if not, the film diffusion mechanism is the governing factor. Further these data were fitted into the Boyd's plot. The plot of B_t against time (t) is shown in Fig. 5D. The fitted line, for the concentration studied, do not pass through the origin, indicating that the sorption process is by the external mass transport and intra-particle diffusion may not be the only rate controlling step in the removal of the sorbate by these beads.

Effect of pH on sorption of palladium: Stability of the synthesized *N*-succinyl chitosan beads was examined at different pHs before studying the effect of pH on the sorption of palladium. It was observed that the beads were stable in the pH range of 2-4, but they slowly disintegrated into small pieces on keeping in aqueous solution having pH 5 or more. The $-\text{COOH}$ groups present in the polymeric chains of the beads deprotonate to form $-\text{COO}^-$ groups as pH increases, which results in swelling of the beads due to the electrostatic repulsion. This is the probable reason for the disintegration of the beads at higher pH. Further, mechanism of the sorption is basically by exchange of Ca^{2+} with Pd^{2+} ions. Because of the larger ionic radius of Pd^{2+} compared to Ca^{2+} the beads swell upon sorption of Pd^{2+} , which also reduces the stability of the beads.

Thus, the sorption studies were carried out in the pH range of 2-4, using 100 ppm Pd^{2+} solution in order to study the effect of pH. The % sorption (% A) of Pd^{2+} is found to increase with pH from 2 to 4. The sorption results are shown in Fig. 6. These

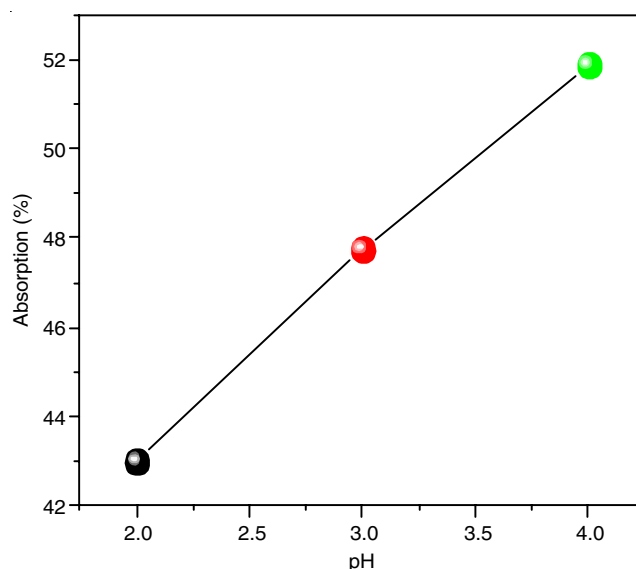


Fig. 6. Effect of feed pH on the % sorption of Pd^{2+} onto the ionically crosslinked *N*-succinyl chitosan beads

results indicate that the *N*-succinyl chitosan beads are not suitable for the extraction in basic pH and can only be employed for efficiently extracting Pd from acidic aqueous waste.

Sorption isotherms: Sorption isotherms explain how the sorbate interacts with the sorbents and are significant in optimizing the utility of sorbents. The sorption studies were carried out from 2 to 400 ppm of Pd^{2+} at pH 4. It was observed that the beads dissolved at lower concentration of Pd^{2+} (2-40 ppm) and the sorption increased from 50-400 ppm of Pd^{2+} retaining the spherical nature of beads. The disintegration of beads at lower concentration of Pd^{2+} , confirms that the sorption is due to exchange of Ca^{2+} with Pd^{2+} . At low concentration of Pd^{2+} , there aren't sufficient Pd^{2+} to replace the Ca^{2+} which affect the sorption capacity of the beads. Hence the sorption studies were carried out from 50-400 ppm. The HLW generated from reprocessing plant contains 105 ppm of palladium and the solutions are acidic. Both these conditions of concentrations of palladium and pH are suitable for extraction of palladium by the synthesized beads. The experimental sorption data of palladium on the ionically crosslinked *N*-succinyl chitosan beads are shown in Fig. 7A. The results obtained from the sorption experiment, confirm that with an increase of initial palladium ion concentration, the sorption capacity of palladium beads increases appreciably. At lower initial metal ions concentration, the sorption capacity increases linearly with the initial metal ion concentration, indicating that the adsorption sites on the ionically crosslinked *N*-succinyl chitosan beads are sufficient and in this case, the amount of sorption depends on the number of metal ions transported from bulk of solution to the surfaces of the ionically crosslinked *N*-succinyl chitosan beads. However at higher initial metal ions concentration, the sorption capacity can't increase proportionally with the concentration, representing that the number of sorption sites on the surface of *N*-succinyl chitosan beads in fact limit the sorption capacities. The sorption data have been subjected to various sorption isotherms, namely the Freundlich, Temkin and Langmuir models. These models indicate the presence of

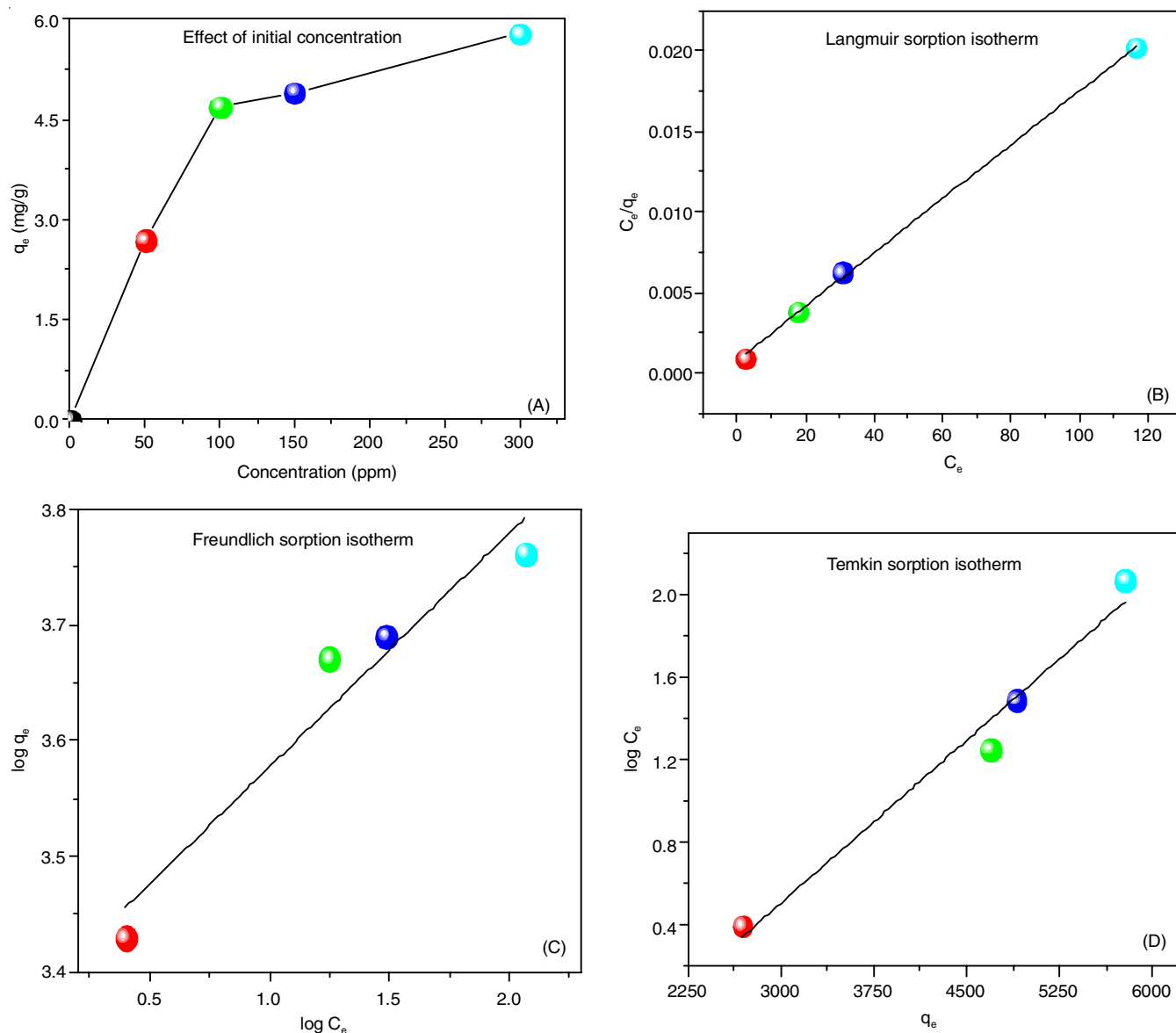


Fig. 7. (A) Effect of initial concentration on the uptake of metal ion, (B) Langmuir isotherm plot, (C) Freundlich isotherm plot, (D) Temkin isotherm plot, for sorption of Pd on to the ionic crosslinked *N*-succinyl chitosan beads

various sorption modes with different interactions between the adsorbed molecules or ions. In case of the Langmuir model, the energetic distribution of sites is homogeneous and sorption follows monolayer pattern. However in Freundlich model, the energetic distribution of sites is heterogeneous, due to the variety of sorption sites. Temkin isotherm model deals with the heat of sorption of all the molecules or ions in the layer decreases linearly with the thickness due to the sorbate interactions. In order to optimize the applicability of a sorption system, it is essential to find out the most proper correlation for the equilibrium curve, using the isotherm models.

Langmuir isotherm: Langmuir isotherm [25] has the correlation coefficients are listed in Table-2. The theoretical Langmuir isotherm is plotted in Fig. 7B. The monolayer saturation capacity for palladium (q_m), is found to be 5.99 mg/g. Based on the b values (Langmuir constant related to the affinity of binding sites), ionic crosslinked *N*-succinyl chitosan beads showed a higher affinity for Pd^{2+} ions. This correlates very well with the higher sorption capability obtained for the ionic crosslinked *N*-succinyl chitosan beads. The value of the correlation coefficient is higher than the obtained values of other two isotherms. In this case, the Langmuir equation

TABLE-2
DIFFERENT ISOTHERM CONSTANTS AND CORRESPONDING R^2 VALUES FOR THE ADSORPTION OF PALLADIUM ONTO THE IONICALLY CROSSLINKED *N*-SUCCINYL CHITOSAN BEADS

Langmuir parameters			Freundlich parameters			Temkin parameters		
b (L mg^{-1})	q_{max} (mg g^{-1})	R^2	k_f (mg g^{-1})	n	R^2	B	A (L g^{-1})	R^2
0.21035	5.99	0.99862	2.37	4.9372	0.91501	1908.57	11.5909	0.98442

represents the most excellent fit of experimental data than the other isotherm equations. Moreover an important parameter, R_L , called the equilibrium parameter was intended to detect the applicability of adsorption system.

$$R_L = \frac{1}{1 + bc_0}$$

The calculated value of R_L , for the entire studied concentration range lies between 0 and 1, indicating favourable sorption, as reported by McKay *et al.* [26].

Langmuir isotherm [25] has found wide range of applications in many actual adsorption processes and it is expressed as:

$$q_e = q_{\max} \left(\frac{bc_e}{1 + bc_e} \right) \quad (13)$$

here, b (l/mg) is the Langmuir equilibrium constant, which is interconnected to the affinity of the binding sites and q_{\max} (mg/g) is the maximum sorption capacity (theoretical monolayer saturation capacity). The main uniqueness of the Langmuir equation is that the constants b and q_{\max} , can be determined from the linear form of the Langmuir equation, as follows:

$$\frac{C_e}{q_e} = \frac{1}{(q_{\max} b)} + \frac{C_e}{q_{\max}} \quad (14)$$

The binding sites have similar affinity for adsorption of a single molecular layer. The binding to the adsorption sites can be moreover chemical or physical but essentially strong enough to stop displacement of the adsorbed molecules [25]. The values of the Langmuir constants q_m and b with the correlation coefficients are listed in Table-2. The theoretical Langmuir isotherm is plotted in Fig. 7B The monolayer saturation capacity for palladium (q_m), is found to be 5.99 mg/g. Based on the b values (Langmuir constant related to the affinity of binding sites), ionically crosslinked *N*-succinyl chitosan beads showed a higher affinity for Pd^{2+} ions. This correlates very well with the higher sorption capability obtained for the ionically crosslinked *N*-succinyl chitosan beads. The value of the correlation coefficient is higher than the obtained values of other two isotherms. In this case, the Langmuir equation represents the most excellent fit of experimental data than the other isotherm equations. Moreover an important parameter, R_L , called the equilibrium parameter was intended to detect the applicability of adsorption system.

$$R_L = \frac{1}{1 + bc_0} \quad (15)$$

The calculated value of R_L , for the entire studied concentration range lies between 0 and 1, indicating favourable sorption, as reported by McKay *et al.* [26].

Freundlich isotherm: The well-known Freundlich isotherm [27] is frequently used for heterogeneous surface energy systems. The form of the Freundlich equation is given as:

$$q_e = k_f c_e^{1/n} \quad (16)$$

The above equation can be represented in the following linear form, to verify the applicability of the model to the present data.

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (17)$$

where, k_f and n are Freundlich constants representing adsorption capacity and intensity, respectively. Freundlich model considers a multi-layer adsorption pattern assuming that the adsorbent is a heterogeneous surface with dissimilar affinity for adsorption [27]. The values of the Freundlich constants together with the correlation coefficient are presented in Table-2. The theoretical Freundlich isotherm is shown in Fig. 7C. Based on the correlation coefficient (R^2) value of 0.9150, it can be accomplished that the experimental results cannot be represented by the Freundlich isotherm model.

Temkin isotherm: Temkin isotherm [28] has been used in many sorption processes. A linear form of the Temkin isotherm can be expressed as:

$$q_e = \left(2.303 \frac{RT}{b} \right) \log A + \left(2.303 \frac{RT}{b} \right) \log C_e \quad (18)$$

It can be simplified to eqn. 19, by substituting B for $2.303RT/b$.

$$q_e = B \log A + B \log C_e \quad (19)$$

The adsorption data can be analyzed according to eqn. 18. Therefore a plot of q_e versus $\log C_e$ enables one to find out the values of constants A and B . The values of the Temkin constants A and B and the correlation coefficient are listed in Table-2. Temkin isotherm is plotted in Fig. 7D.

From the slope the value of B was evaluated as 1908.57 and the value of A was calculated as 11.5909 from the intercept. It is clear from the plot with R^2 , values of 0.98442 that the Temkin isotherm may also be used to explain the adsorption results. On comparing the R^2 values, given in Table-2, for different isotherms, it can be concluded that among the three models the Langmuir isotherm is a better fit for the given sorption process.

Back extraction and reusability study of ionically crosslinked *N*-succinyl chitosan beads: In our previous work we have tested various strippants, like EDTA, deionized water (pH 7) and 0.01 M thiourea in 0.1 M nitric acid solution and found that thiourea is the best strippant for back extraction of palladium ions from the loaded beads [29]. Therefore, we have used this strippant in the present study. In order to find out practical applicability of the ionically crosslinked *N*-succinyl chitosan beads for separation and recovery of Pd(II), repeated sorption and back extraction (with 0.01 M thiourea in 0.1 M HNO_3) experiments were performed with the same set of beads. After loading Pd onto the beads by equilibrating for 180 min, these beads were washed with water and kept in contact with the stripping solution, to ensure quantitative recovery of the loaded Pd(II). This process was repeated up to four cycles. It was observed that the beads illustrate very small reduction in capacity up to the four studied cycles. Hence, proficiently we can use these beads in several sorptions-desorption cycles, for recovery of palladium. The small decrease in percent sorption of palladium ions is probably due to incomplete leaching of the palladium ions with 0.01 M thiourea in 0.1 M HNO_3 . These results prove suitability of the synthesized beads, for extraction of Pd, under the specified experimental conditions.

Conclusion

In the present study, a novel sorbent, in the form of ionically crosslinked polymeric *N*-succinyl chitosan beads, was synthe-

sized by ionic crosslinking method and characterized by various techniques *viz.* FT-IR, optical microscope, SEM and TGA. Its efficiency in the separation and recovery of Pd(II) was tested by batch sorption technique. The kinetics of extraction is quite fast, since quantitative recovery of Pd(II) can be achieved in ~180 min at pH 4. The sorption kinetic data have been analyzed by the Lagergren first-order model, the pseudo-second order model and the intraparticle diffusion model. The results indicate that the sorption of palladium onto *N*-succinyl chitosan beads could be best described by the pseudo second-order model. The results of the sorption study show that the maximum loading capacity of the beads is about 6 mg/g of the swollen beads which corresponds to about 60 mg/g with respect to the dried beads. The Langmuir sorption model shows better fit for the present study at the studied experimental conditions. The results indicate that the synthesized beads can be used for effective removal of palladium from acidic aqueous wastes, like HLW from reprocessing plants.

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REFERENCES

- M.S. Saurat and J. Bringezu, *J. Ind. Ecol.*, **12**, 754 (2008); <https://doi.org/10.1111/j.1530-9290.2008.00087.x>.
- L. Erdmann and T.E. Graedel, *Environ. Sci. Technol.*, **45**, 7620 (2011); <https://doi.org/10.1021/es200563g>.
- C. Hagelüken, *Chimica Oggi/Chemistry Today*, **2**, 14 (2006).
- K. Inoue, T. Yamaguchi, M. Iwasaki, K. Ohto and K. Yoshizuka, *Sep. Sci. Technol.*, **30**, 2477 (1995); <https://doi.org/10.1080/01496399508021396>.
- E. Guibal, *Sep. Purif. Technol.*, **38**, 43 (2004); <https://doi.org/10.1016/j.seppur.2003.10.004>.
- A.B. Kanagare, K.K. Singh, K.K. Bairwa, R. Ruhela, V.S. Shinde, M. Kumar and A.K. Singh, *J. Environ. Chem. Eng.*, **4**, 3357 (2016); <https://doi.org/10.1016/j.jece.2016.06.031>.
- A.B. Kanagare, K.K. Singh, G.K. Kumar, V.S. Shinde and M. Kumar, *Int. J. Innov. Res. Sci., Eng. Technol.*, **5**, 265 (2016); <https://doi.org/10.15680/IJRSET.2015.0501033>.
- A.B. Kanagare, K.K. Singh, M. Kumar, M. Yadav, R. Ruhela, A.K. Singh, A. Kumar and V.S. Shinde, *Ind. Eng. Chem. Res.*, **55**, 12644 (2016); <https://doi.org/10.1021/acs.iecr.6b03350>.
- K.K. Singh, R. Ruhela, A. Das, M. Kumar, A.K. Singh, R.C. Hubli and P.N. Bajaj, *J. Environ. Chem. Eng.*, **3**, 95 (2015); <https://doi.org/10.1016/j.jece.2014.11.002>.
- S.-I. Park, I.S. Kwak, S.W. Won and Y.-S. Yun, *J. Hazard. Mater.*, **248-249**, 211 (2013); <https://doi.org/10.1016/j.jhazmat.2013.01.013>.
- J.J. Byerley, J.M. Schärer and S. Rioux, eds.: J. Salley, R.G.L. McCready and P.L. Wichlacz, *Reactions of Precious Metal Complexes with Biopolymers*, In: *Biohydrometallurgy*, CANMET: Montreal, Canada, pp. 301-316 (1989).
- E. Guibal, A. Larkin, T. Vincent and J.M. Tobin, *Ind. Eng. Chem. Res.*, **38**, 4011 (1999); <https://doi.org/10.1021/ie990165k>.
- W.S. Wan Ngah and K.H. Liang, *Ind. Eng. Chem. Res.*, **38**, 1411 (1999); <https://doi.org/10.1021/ie9803164>.
- A.H. Chen, C.Y. Yang, C.Y. Chen, C.Y. Chen and C.W. Chen, *J. Hazard. Mater.*, **163**, 1068 (2009); <https://doi.org/10.1016/j.jhazmat.2008.07.073>.
- G.G. Maghami and G.A.F. Roberts, *Makromol. Chem.*, **189**, 2239 (1988); <https://doi.org/10.1002/macp.1988.021891003>.
- D.J. Knorr, *Food Sci.*, **48**, 36 (1983); <https://doi.org/10.1111/j.1365-2621.1983.tb14783.x>.
- G. Gibbs, J.M. Tobin and E. Guibal, *J. Appl. Polym. Sci.*, **90**, 1073 (2003); <https://doi.org/10.1002/app.12761>.
- H. Yoshida, A. Okamoto and T. Kataoka, *Chem. Eng. Sci.*, **48**, 2267 (1993); [https://doi.org/10.1016/0009-2509\(93\)80242-1](https://doi.org/10.1016/0009-2509(93)80242-1).
- Z. Aiping, C. Tian, Y. Lanhua, W. Hao and L. Ping, *Carbohydr. Polym.*, **66**, 274 (2006); <https://doi.org/10.1016/j.carbpol.2006.03.014>.
- X.-N. Zhang, C. Zhang, Q. Zhu, Y. Zhou, Y. Liu, W. Chen, S. Yang, X. Zhou, A. Zhu, Y. Jin and Z.-Q. Yuan, *Int. J. Nanomedicine*, **9**, 2919 (2014); <https://doi.org/10.2147/IJN.S59799>.
- Y.S. Ho and G. McKay, *Process Saf. Environ. Prot.*, **76**, 183 (1998); <https://doi.org/10.1205/095758298529326>.
- X. Yang and B. Al-Duri, *J. Colloid Interface Sci.*, **287**, 25 (2005); <https://doi.org/10.1016/j.jcis.2005.01.093>.
- R. Ruhela, K.K. Singh, B.S. Tomar, J.N. Sharma, M. Kumar, R.C. Hubli and A.K. Suri, *Sep. Purif. Technol.*, **99**, 36 (2012); <https://doi.org/10.1016/j.seppur.2012.08.018>.
- G.E. Boyd, A.W. Adamson and L.S. Myers Jr., *J. Am. Chem. Soc.*, **69**, 2836 (1947); <https://doi.org/10.1021/ja01203a066>.
- I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918); <https://doi.org/10.1021/ja02242a004>.
- G. McKay, H.S. Blair and J.R. Gardner, *J. Appl. Polym. Sci.*, **27**, 3043 (1982); <https://doi.org/10.1002/app.1982.070270827>.
- H.M.F. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1907); <https://doi.org/10.1515/zpch-1907-5723>.
- S.J. Allen, Q. Gan, R. Matthews and P.A. Johnson, *Bioresour. Technol.*, **88**, 143 (2003); [https://doi.org/10.1016/S0960-8524\(02\)00281-X](https://doi.org/10.1016/S0960-8524(02)00281-X).
- R. Ruhela, S. Panja, B.S. Tomar, A.K. Singh, S.C. Tripathi, P.M. Gandhi and R.C. Hubli, *Sep. Purif. Technol.*, **124**, 49 (2014); <https://doi.org/10.1016/j.seppur.2013.12.040>.