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GREEN AND ECONOMICAL ADSORBENT FOR ZINC (II) IONS REMOVAL BY ADSORPTION FROM WATER ENVIRONMENT USING BATCH MODE AND FIXED BED COLUMN EXPERIMENTS

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ABSTRACT

Detoxification of zinc (II) ions from *Punica granatum* shell carbon (PSGC) and commercial activated carbon (CAC) were carried out at 30±1 °C under various experimental conditions. Effect of various process parameters has been investigated by following the batch mode and fixed bed column experiment at 30 ±1°C. The percentage removal increased with decrease in initial concentration and particle size and increase in contact time and dose of adsorbent. As initial pH of the slurry increased, the percentage removal increased, reached a maximum. The adsorption is highly pH sensitive. Adsorption data were modelled with various isotherms and first order kinetic equations proposed by Natarajan-Khalaf, Lagergren and Bhattacharya-Venkobachar and intra-particle diffusion models found to be applicable. Kinetics of adsorption is observed to be first order with intra-particle diffusion as one of the rate determining steps. The monolayer adsorption capacities of PSGC also studied by Langmuir isotherms. PSGC could be used as low-cost adsorbents in effluent treatment, especially for the removal of metal ions, particular in Zn^{2+} ions. It is confirmed by SEM (Scanning Electron Microscope) analysis before and after adsorption.

KEYWORDS

Zinc (II) ions, *Punica granatum* shell carbon, commercial activated carbon, adsorption isotherms, first order kinetic equations, SEM analysis.

INTRODUCTION

The presence of metal ions in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies, is one of the most important environmental issues. Effluents containing heavy metals are discharged from various industrial processes. According to World Health Organization (WHO) the metals of the most immediate concern are copper, cadmium, nickel, mercury, lead, chromium, manganese, zinc and aluminium. Zinc (II) ions may be found in wastewater discharges from the plating industry, the manufacture of fertilizers, pesticides, pigments dyes and textile operations[1]. The major ill-effects caused by zinc (II) ions are inhibition of enzyme activity, head ache, Wilkinson disease, dizziness, nausea and vomiting, chest pain, tightness of chest, dry cough, shortness of breath, rapid respiration, nephritis, cyanosis and extreme weakness. The use of activated carbon for the removal of the zinc (II) ions present in lower concentration in aqueous solution is of considerable importance. Activated Carbon (AC) adsorption is being widely used in effluent treatment. Because of high cost of commercial AC (CAC) and difficulty in its procurement low-cost adsorbents alternative to CAC are to be developed from abundant agricultural wastes[2]. This has necessitated the titled investigation to find out the suitability of *Punica granatum* shell carbon for the removal of zinc (II) ions (Zn^{2+}). The objectives of this study is to indigenously prepare AC (IPAC) from *Punica granatum* shell to study the effect of various process parameters on the extent of removal of zinc (II) ions and to model the adsorption data with various isotherms, first order kinetic equations and intra-particle diffusion model.

MATERIALS AND METHODS

Punica granatum shell was carbonized with sodium bicarbonate at 300-400°C and kept at 600°C in a muffle furnace (Neolab, India) to get carbon. The carbon was sieved (90, 125, 150, 180, 210, 250 micron), activated by acid digestion (4 N HNO_3; 2hr at 80°C) and dried in an air – oven (at 120°C for 2hr). CAC was procured commercially from BDH, India. Batch type adsorption studies[6] were carried out under various experimental conditions. Zinc sulphate was suitably diluted individually with deionised water and estimated by sodium salt of ethylenediaminetetraacetic acid (EDTA) using xylenol orange. Adsorption experiments were carried out at room temperature (30±1 °C) under batch mode[7]. Zinc (II) ions concentration was estimated complexometric titration as per the literature methods[5]. Effect of various process parameters on the extent of removal of zinc (II) ions was studied. The data were analysed statistically and interpreted.

ADSORPTION EXPERIMENTS

Adsorption experiments were carried out at room temperature (30±1 °C) under batch mode and fixed bed column experiments[4]. Stock solution of Zinc (II) ions (AR) was prepared suitably diluted with DD water and estimated by EDTA method using[5] xylenol orange indicators. Exactly 50mL of metal ion solution of known initial concentration was shaken with a required dose of adsorbent (PSGC =2-20 g/L and CAC = 3-5 g/L) of a fixed particle size (PSGC=90-250 micron and CAC=90 micron) in a thermostatic orbit incubator shaker ions (Neolab, India) at 300 rpm after noting down the initial pH of the solution (pH = 5.9 for Zn^{2+} ions). The initial pH was adjusted to the required pH value (range: 2-10) by adding either 1 M HCl or 1 M NaOH solution. After equilibration, the final concentrations (C_e) were also estimated complexometrically[5]. The value of percentage removal and amount adsorbed were calculated using the following relationships:

Percentage removal $= 100 (C_i – C_e) / C_i$ ……………………………………………………(1)
Amount adsorbed $(q) = (C_i – C_e) / m$…………………………………….(2)

Where, C_i and C_e are initial and equilibrium (final) concentration of zinc (II) ions (ppm), respectively and m is the mass of adsorbent, in g/L.

FIXED BED COLUMN EXPERIMENTS

The column tests were carried out in a glass column with an inner diameter of 1.5cm and height of 15cm. The adsorbents with known weight were placed into the column in form of slurry and packed uniformly. The column was safe-guarded with glass wool. The influent/feed solution of metal ions of known initial concentration, at specified pH was fed from the glass bottle container (5L capacity). The initial pH of the solutions was adjusted by adding 1N HCl solution. Auto flow meter (McClins, India) was used to adjust the required flow rate. The effluent from the column was collected at desired intervals of time (30–45 min.) and the metal ions were estimated[4]. The effect of process parameters like initial concentration, bed height, flow rate and initial pH was determined and the experimental conditions are presented in Table 5.

RESULTS AND DISCUSSION

SCANNING ELECTRON MICROSCOPE

SEM (JEOL JSM Model – 6360) photos (Figues. 1-4) before and after adsorption of Zn (II) ions reveal the surface texture and porosity of the samples. The particle can be roughly approximated as spheres or globules, if the roughness factor is taken into account for approximation of the irregularities in shape.

The individual particles are distinctly visible and are almost uniform. It also depicts the porosity nature of PSGC and the presence of grains in the Zn-loaded PSGC. The adsorbed Zn (II) ions are either engulfed or present in the surface of the PSGC particles, as revealed by the bright spots in the SEM photos of Zn-loaded PSGC. The pore size of cavity in the PSGC samples is clearly detectable and is roughly of the order of 10-50 μm, which is approximately 1000 times greater than the ionic radii of divalent metal ions (r=0.09-0.11 nm).

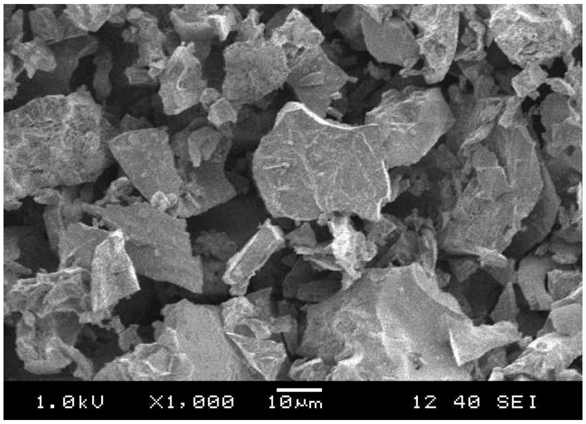

Figure 1 SEM photograph for before adsorption of CAC.

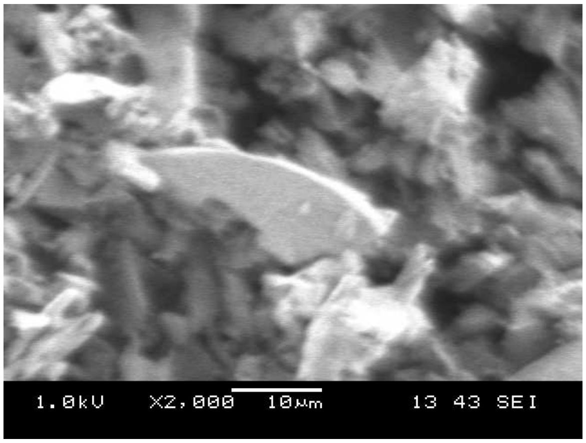

Figure 2 SEM photograph for after adsorption of CAC.

The colours of PSGC seem to be black or blackish gray, when viewed under powerful microscope. The presence of particles with almost spherical and elliptical shapes was observed. The presence of metal ions on the surface of PSGC as noted by the bright spots indicates that the removal of metal ions by adsorption on PSGC is a surface phenomenon.

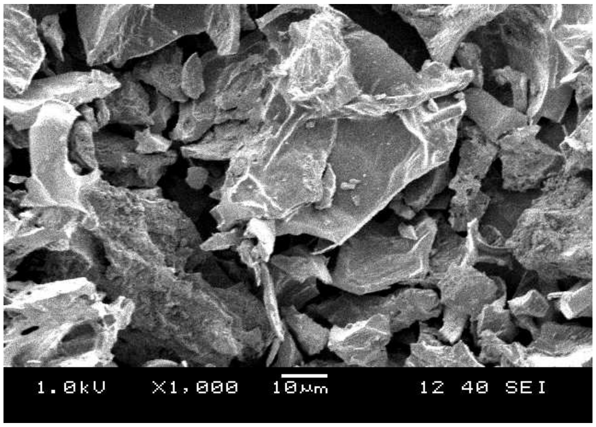

Figure 3 SEM photograph for before adsorption of PSGC.

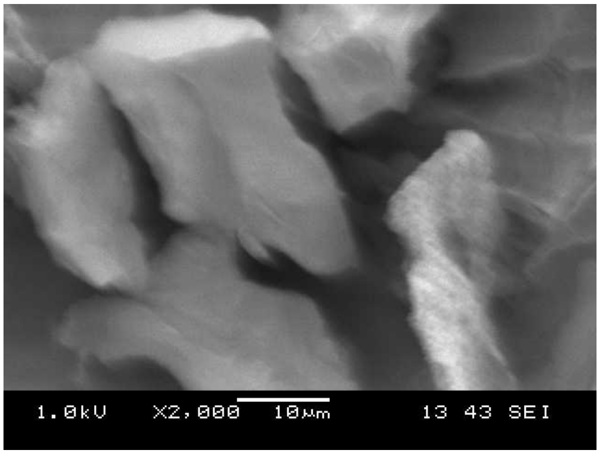

Figure 4 SEM photograph for after adsorption of PSGC.

EFFECT OF PROCESS PARAMETERS

The adsorption experiments were carried out at different experimental conditions (Table 1) and the results obtained are discussed below:

EFFECT OF INITIAL CONCENTRATION

The results on the extent of removal of zinc (II) ions under various experimental conditions are given in Table 1. The percentage removal (% R) decreased with increase in initial concentration, due to the limited number of available active sites on the surface of PSGC to accommodate higher concentration of zinc (II) ions (Zn^{2+}). The effect of initial concentration is shown in Figure 5.

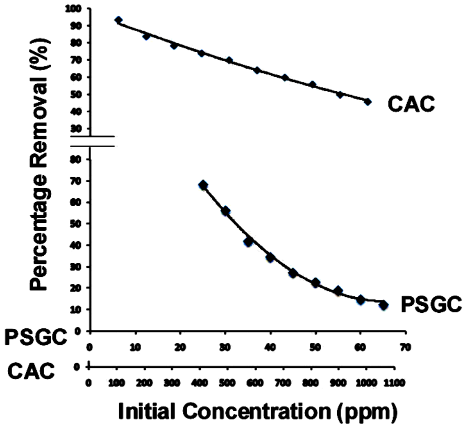

Figure 5 Effect of initial concentration for the removal of Zn^{2+} ions onto PSGC.

Table 1 - Effect of process parameters on the extent of removal of zinc (II) ions by CAC and PSGC at 30 ± ºC

Process parameter	**Range**	**Percentage Removal (%)**		**Amount adsorbed (in mg/L)**	
		CAC	**PSGC**	**CAC**	**PSGC**
Initial conc. (ppm)	100-1000 (CAC) 25-70 (PSGC)	93.46-45.73	68.61-10.32	7.79-38.11	0.60-1.43
Contact time (min.)	5-55	23.71-72.75	16.30-37.23	11.86-36.38	0.68-1.55
Dose of adsorbent (g/L)	3-5 (CAC) 2-20 (PSGC)	46.60-89.10	20.22-54.23	23.30-44.55	0.84-2.26
Initial pH	2.0-10.0	35.70-84.74	21.53-47.69	17.85-42.37	0.90-1.99
Particle size (μ)	90-250	-	37.23-18.92	-	1.55-0.79

Adsorption isotherms

Adsorption data were fitted with Freundlich and Langmuir isotherms by carrying out the correlation analysis. The results are given in Table 2. The observed r-values close to unity indicate the applicability of these two isotherms. PSGC, as evidenced from Q_o (monolayer adsorption capacity, in mg g^{-1}) values.

Freundlich isotherm: $\log q = \log K + (1/n) \log C_e$……………………………………(3)
Langmuir isotherm : $(C_e/q) = (1/Q_o b) + (C_e/Q_o)$…………………………(4)

Where, K and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively ; q is the amount adsorbed per unit mass of adsorbent (in mg/g); Q_o and b are Langmuir constants, which are the measures of monolayer adsorption capacity (in mg/g) and surface energy (mg/L), respectively.

Table 2 – Adsorption isotherm data for removal of zinc (II) ions by CAC and PSGC at 30 ± ºC

S.No.	**Parameter**	**CAC**	**PSGC**
1.	**Freundlich isotherm**		
	Slope (1/n)	0.412	0.289
	Intercept (log K)	1.024	0.447
	Correlation coefficient (r)	0.998	0.955
	Δq (%)	0.051	0.120
2.	**Langmuir isotherm**		
	Slope ($1/Q_o$)	0.008	1.230
	Intercept ($1/Q_o b$)	0.453	6.894
	Correlation coefficient (r)	0.989	0.992
	b (g/L)	0.018	0.178
	Q_o (mg/g)	121.12	0.813
	R_L	0.157	0.179
	Δq (%)	1.435	6.245

In order to compare the validity of each model (isotherm) more efficiently a normalised standard deviation, Δq(%) is calculated using the following equation:

$\Delta q\ (\%) = 100 \times \{ (\sum [(q_t^{exp.} - q_t^{cal.}) / q_t^{exp.}]^2) / (n - 1) \}^{1/2}$……...............(5)

where, the superscripts, exp. and cal. are the experimental and calculated values of q_t viz., the amount adsorbed at different time t and n is the number of observations. The $\Delta q(\%)$ values are also given in Table 2. Based on the low values of $\Delta q(\%)$, it is concluded that the adsorption of zinc (II) ions can be best described by the Langmuir adsorption isotherm. The monolayer adsorption capacities (Q_o) of the adsorbents are found to be of the order given below:

CAC >PSGC

Further, the essential characteristics of the Langmuir isotherm can be described by a **Separation factor, R_L**, which is defined by the following equation:

$R_L = [\ 1 / (\ 1 + bC_i\ )\ ]$……………………………………………………(6)

where, C_i = optimum initial concentration of Zn^{2+} ions (in mg L^{-1})
b = Langmuir constant (in L mg^{-1})

The values of **separation factor**, R_L indicate the nature of the adsorption process as given below:

R_L values	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the present study, the computed values of R_L (Table 2) are found to be fraction in the range of 0-1(0.157 for CAC and 0.179 for PSGC), indicating that the adsorption process is favorable for this adsorbent (PSGC) for the removal of zinc (II) ions.

EFFECT OF CONTACT TIME

The % R increases with increase in contact time (45 min., for CAC and 35 min., for PSGC) due to more amounts of Zn^{2+} ions removed due to effective contact and due to the availability of active sites. The effect of contact time is shown in Figure 6. At the initial stage, the rate of removal of zinc (II) ions was higher, due to the availability of more than the required number of active sites on the surface of carbons and became slower at the later stages of contact time, due to the decreased or lesser number of active sites. Similar results have been reported in literature for the removal of dyes[8], organic acids and metal ions[9] by various adsorbents.

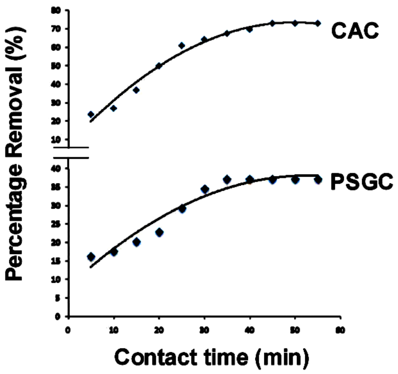

Figure 6 Effect of contact time for the removal of Zn^{2+} ions onto CAC and PSGC.

KINETICS OF ADSORPTION

The first order kinetic equations like Natarajan-Khalaf[14, 12] and Bhattacharya-Venkobachar[3] equations were applied to the adsorption data (Table 3).

Natarajan and Khalaf equation:

$$\text{Log}\ (C_i / C_t) = (k / 2.303)\ t \qquad \ldots(7)$$

Lagergren equation:

$$\text{Log}\ (q_e - q_t) = \log q_e - (k / 2.303)\ t \qquad \ldots(8)$$

Bhattacharya and Venkobachar equation:

$$\text{Log}\ [1 - U(T)] = - (k / 2.303)\ t \qquad \ldots(9)$$

where,

C_i and C_t = concentration of Zn^{2+} ions at time zero and time t, respectively (in mgL^{-1})
q_e and q_t = amount of Zn^{2+} ions adsorbed at equilibrium time and time t, respectively (in $mg\ g^{-1}$)
U (T) = $[(C_i - C_t) / (C_i - C_e)]$
C_e = equilibrium Zn^{2+} ions concentration (in $mg\ L^{-1}$)
k = first order adsorption rate constant (in $min.^{-1}$)

The r-values (correlation coefficient close to unity) indicate the applicability of these kinetic equations and the first order nature of adsorption of Zn^{2+} ions on PSGC. The rate of adsorption of Zn^{2+} ions is calculated. The presence of intra-particle diffusion as the rate limiting step was tested by applying the intra-particle diffusion model.

$$q_t = k_p\, t^{1/2} + c \qquad \ldots(10)$$

The higher value of k_p (k_p values: CAC=6.739; PSGC=0.253) indicate that PSGC are highly porous in nature. The value of intercept (c) give an idea about the boundary layer thickness, i.e., larger the intercept (CAC>PSGC) greater is the boundary layer effect[15].

Table 3 – Kinetics of adsorption for removal of zinc (II) ions by CAC and PSGC at 30 ± ºC

S.No.	Parameter	CAC	PSGC
1.	**Natarajan – Khalaf eqn.**		
	Correlation coefficient (r)	0.985	0.975
	k (/min.) x 10^{-2}	3.169	1.034
	Δq (%)	2.506	13.17
2.	**Lagergren equation**		
	Correlation coefficient (r)	0.944	0.983
	k (/min.) x 10^{-2}	5.610	2.535
	Δq (%)	1.677	18.44
3.	**Bhattacharya & Venkobachar eqn**.		
	Correlation coefficient (r)	0.944	0.983
	k (/min.) x 10^{-2}	5.610	2.535
	Δq (%)	19.81	36.81
4.	**Intra-particle diffusion model**		
	Correlation coefficient (r)	0.978	0.950
	k_p (mg/g/min.$^{1/2}$)	6.739	0.253
	Intercept	5.481	0.027
	Δq (%)	1.357	1.463
	Log (% removal) vs log (time)		
5.	Correlation coefficient (*r*)	0.970	0.932
	Slope (*m*)	0.605	0.446
	Δq (%)	16.93	37.07

The values of log (% R) are found to be linearly correlated (r values CAC=0.970; PSGC=0.932) with log (time), with slope values are greater than 0.5 (slope: CAC=0.605; PSGC=0.446). This indicates that besides the intra-particle diffusion, there may be other processes controlling the rate of adsorption, all of which may be operating simultaneously. The results of the present study conclude that PSGC could be used as low-cost adsorbent in effluent treatment, especially for the removal of zinc (II) ions.

EFFECT OF DOSE OF ADSORBENT

The % R increased with increase in dose of adsorbent owing to the increase in surface area and number of active sites for the adsorption of Zn^{2+} ions or due to the conglomeration of carbons at higher doses[13, 8]. The effect of dose is shown in Figure 7.

The relative increase in the percentage removal of zinc (II) ions is found to be insignificant after a dose of 20 g/L of PSGC, which is fixed as the optimum dose. This suggests that the adsorbed zinc (II) ions (Zn^{2+} ions) may either block the access to the internal pores of carbons or may cause particles to aggregate and thereby minimizing the availability of active sites for adsorption[13, 9].

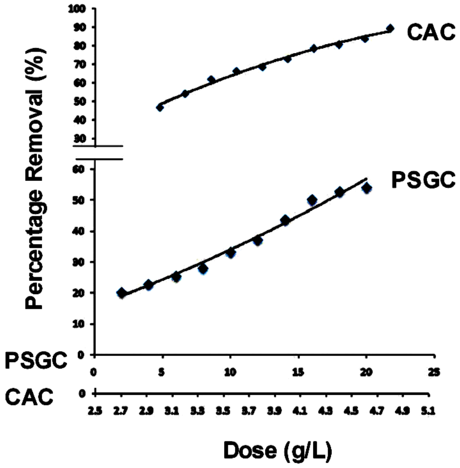

Figure 7 Effect of dose for the removal of Zn^{2+} ions onto PSGC

EFFECT OF INITIAL PH

As initial pH increases, the extent of removal (% R), increases reaches a maximum value[9]. The effect of initial pH is given in Table 4. The optimum pH for removal of Zn^{2+} ions is fixed as 5.9. The near neutral pH is found to be favourable. The pH value slightly decreases and change in pH (ΔpH = initial pH - final pH) values after adsorption are found to decrease in the order of 0.3-0.5 units[10]. This suggests that during the adsorption of zinc species, protons are released from the surface functional groups like phenolic, carboxylic and enolic groups present on the carbons.

Table 4 Effect of initial pH for removal of zinc (II) ions by CAC and PSGC at 30 ± ºC.

S.No.	Initial pH	Percentage Removal (%)		Amount adsorbed (mg/L)	
		CAC	PSGC	CAC	PSGC
1.	2.0	35.70	21.53	53.55	0.90
2.	3.0	47.69	22.84	71.53	0.95
3.	4.0	58.59	29.38	87.87	1.22
4.	5.2	69.48	34.61	104.2	1.44
5.	6.1[*]	78.20	41.15	117.3	1.71
6.	7.0[#]	84.74	47.69	127.1	1.99
7.	8	83.65	45.07	125.5	1.88
8.	9	81.47	43.76	122.2	1.82
9.	10	80.38	37.22	120.6	1.55

[*] Solution pH = 6.1; [#]optimum pH = 7.0

EFFECT OF PARTICLE SIZE

The amount of zinc (II) ions adsorbed increases with decrease in particle size of the adsorbent. The effect of particle size is shown in Figure 8. This is due to the availability of surface area with the decrease in particle size[11].

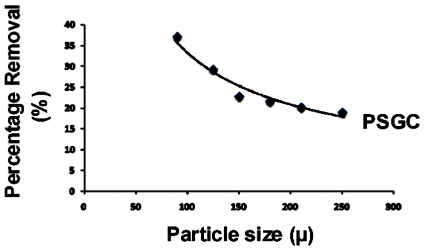

Figure 8 Effect of particle size for the removal of Zn^{2+} ions onto PSGC.

The optimum conditions fixed for the effective removal of zinc (II) ions are: Initial concentration= 600ppm for CAC and 50 ppm for PSGC; contact time= 45 min., for CAC and 35 min., for PSGC; Dose = 4 g L^{-1} for CAC and 12 g L^{-1} for PSGC; particle size = 90 micron and pH = 7.0 for Zn^{2+} ions at 300 rpm speed and 30±1 °C.

FIXED BED COLUMN EXPERIMENT

The effect of process parameters like initial concentration, bed height, flow rate and initial pH was determined and the experimental conditions are presented in Table 5. The concentration of zinc (II) ions in the column effluents was determined by complexometric titration as per the literature methods[5].

Table 5 Experimental conditions of fixed bed column studies for the removal of Zinc (II) ions at 30 ± ºC

Variable	Initial concentration (ppm)	Bed height (cm)	Flow rate (mL $min.^{-1}$)	Initial pH
Initial concentration	CAC : 500, 600 and 700 PSGC : 40, 50 and 60	2.5	1.0	Zn: 7.0
Bed height	CAC : 600 PSGC : 50	1.5 2.5 3.5	1.0	-do-
Flow rate	-do-	2.5	0.5, 1.0 and 1.5	-do-
Initial pH	-do-	2.5	1.0*	4, 5, 6 and 7

* Optimum condition

RELATIVE ADSORPTION CAPACITY

The values of relative adsorption capacity of CAC and PSGC are calculated from the Q_o values, obtained from Langmuir isotherm, which are given in Table 2. The increasing order of relative adsorption capacity of CAC and PSGC are: CAC>PSGC.

CONCLUSION

Zinc ion (adsorbate) species are found to adsorb strongly on the surface of PSGC. The faster adsorption kinetic data may be useful for environmental technologists in designing Zn^{2+} ions containing waste water. The adsorption process is found to be first order with intra-particle diffusion as one of the rate determining steps. PSGC possess the maximum adsorption capacity and hence, it is an effective adsorbent for the removal of zinc (II) ions, PSGC could be considered as cost-effective adsorbent and useful for the economic treatment of waste water containing Zn^{2+} ions to use an agricultural material *Punica granatum* shell as an adsorbents. The fixed bed column experiment may highly effective removal for effluent containing metal ions, zinc ions in particular.

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