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Fixed bed column studies for the elimination of Cd^{2+} ions by native and protonated Watermelon rind

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Abstract

Watermelon rind (WR) an agro-waste was protonated aiming to eliminate the alkali and alkaline metal ions and investigated towards adsorption of Cd^{2+} ions in a continuous process. The protonation step resulted in elimination of K^{+} and Mg^{2+} ions from the watermelon rind surface and the protonation was confirmed with FTIR and EDX techniques. Comparative investigations were carried out between native and protonated WR in a continuous process and parameters such as rate of flow, feed concentration and bed heights were optimised. At higher bed depths and lower rates of flow and initial feed concentrations, the columns provided maximum adsorption of Cd^{2+} ions. Optimal conditions in this study were found to be 1 ml, 3 cm and 50 mg L^{-1} respectively for flow rate, bed depths and initial concentrations. The adsorption capacity of native and protonated WR were experimentally calculated to be 97.9 and 107.3 mg g^{-1} respectively. The PWR exhibited higher adsorption capacity compared to WR and this is due to the protonation step which eliminated the alkali and alkaline metal ions bound onto the WR surface that blocked the active sites. The data obtained in the continuous columns were fitted to mathematical models such as Adams-Bohart, Thomas and

Yoon-Nelson models, and the later models were able to explain the adsorption process well. Lastly, regeneration of the WR and PWR were investigated and 0.1 M HCl exhibited higher desorption and regeneration efficiency compared to 0.1 M Acetic acid. These results suggest that the protonation of watermelon rind results in enhanced adsorption of Cd ions and both native and protonated are effective adsorbents.

Keywords: Adsorption; Watermelon rind: Protonation: Fixed-Bed:

Introduction

Heavy metal ions find wide applications in industrial products due to their properties and characteristics and use of these heavy metal ions have resulted in water and soil pollution [Georgios et al. 2021, Alice et al. 2021]. Water pollution is one among the leading causes of mortality all over the world and significant in under developed and developing countries [Jingyuan et al. 2022]. Contaminants such as organic and inorganic contaminate the water resources to a greater extent and cause irreversible damage to the ecosystem [Chaka and Munyaradzi 2022]. Inorganic contaminants such as heavy metal ions require special focus since they have multiple effects on human health like drop in energy levels, damage to vital organs and blood composition [Lu et al. 2022]. Cadmium (Cd) a heavy metal is widely used in industries such as batteries, pigments and coatings and these industries discharge enormous quantity of effluents containing cadmium ions and causes water pollution [Julekha et al. 2022]. Cadmium is a cancer causing agent and intake from water and food lead to fragile bones and damage to kidneys [Daniel and William 2021]. Hence it is desirable to eliminate the Cd^{2+} ions from industrial effluents before it enters the water streams and resources.

Water technology is advancing day by day and various techniques are in practice for the elimination and minimization of Cd ions in water. Techniques such as reverse osmosis [Shafaghat et al. 2023], ion-exchange [Prateek et al. 2021], filtration and coagulation [El Samrani et al. 2008] and adsorption [Lakshmipathy et al 2021] are commonly used in industrial waste water treatment process. The adsorption technique is an established and popular technique for waste water due to its simplicity and economic viability. Activated carbon [Samiyammal et al. 2022], zeolites [Prince et al. 2019], nanomaterial's [Aquib et al. 2020], agro-wastes [Devanathan et al. 2021], industrial by-products, etc., are used in the adsorption techniques. Agro-wastes are a class of materials that are rich in organic composition and can facilitate binding of cations and anions from aqueous media. Thus agro-wastes are a superior choice of adsorbents for the adsorption technique.

Fruit peels and vegetable based wastes are explored for its ability to adsorb heavy metal ions [Yoong and Chang 2022]. Orange peels and Banana peels were initially explored as adsorbents for the elimination of Cd ions from wastewater in batch process [Gupta and Nayak 2012, Jamil et al 2010]. Later other peels such as lemon, pomegranate, passion fruit, and dragon fruit were also explored. Similarly, watermelon rind, custard apple shells and seeds were utilised for the adsorption experiments. A useful review on the removal of cadmium ions by potential agricultural wastes was reported by Mihajir et al., [2021]. It is noticed that the majority of the experiments reported for the cadmium ion removal from wastewater are in batch process and a very few reports are available for continuous studies. The continuous column investigations provide a suitable bench scale for the industrial process. Industries always look out for novel and low cost techniques for their implementation. Moreover, the existing literature suggest that the raw and processed materials were individually employed in the column studies but comparative investigations of base material with modifications is not reported. Hence, in this study, a systematic approach was established to prepare watermelon rind as adsorbent and further, the adsorbent was processed to eliminate the alkali and alkaline earth metal ions from the surface of the adsorbent. The native and protonated watermelon rind adsorbents were compared for their efficiency towards the adsorption of Cd ions in continuous column mode.

Materials and Methods

Adsorbents preparation

Watermelon rinds (WR) were sourced from fruit stalls during the summer season and dried under the direct sunlight in order to eliminate the moisture content. Later the dried rinds were cut into smaller pieces and cleaned with tap water to purge dirt and dust. The water washed rinds were dried in an oven overnight at 105 ^{o}C and subjected to a motor grinder to powder it. The powdered rinds were sieved with 100 and 500 BSS mesh to obtain an even particle size. The rinds particles obtained between 100 and 500 mesh were used for the adsorption experiments. For protonation of watermelon rind, the particles obtained between 100 and 500 mesh were dipped in 0.01 M HCl solution for 120 min to remove the alkali and alkaline earth metal ions such as Na^{+} K^{+} and Mg^{2+} ions. The acid dipped particles were water washed to remove any desorbed ions and neutralize the pH. The water washed WR particles were dried in an oven overnight and named as protonated watermelon rind (PWR).

Continuous column studies

Continuous studies were performed in a column made of glass having dimensions 15 cm length with a diameter of 2.5 cm. A peristaltic pump was employed to control the flow rate of the adsorbate solutions fed into the column. The glass column was packed with WR and PWR adsorbents (density 0.367 g/cc) and the Cd^{2+} ions were fed from the top of the glass column with the help of peristaltic pump and the effluents were handled at the exit of the glass column at pre-set time interval. The amount of adsorbent used for 1 cm of the glass column is 0.36 g and multiples of 0.36 g were used in higher bed depths. Preliminary batch studies revealed that the cadmium ions removals were high at pH 6 for both WR and PWR and hence the column experiments were also conducted at pH 6. For column investigations, parameters such as flow rate, bed depth and initial concentrations were optimised. The flow rates were investigated between 1 and 3 ml at a fixed bed depth and feed concentration. Similarly, bed height was varied between 1 and 3 cm and initial concentration was varied from 50 to 150 mg L^{-1} of Cd^{2+} ions. A total of 120 to 600 ml of Cd^{2+} ions solution was consumed for various parameters optimization. Each parameter was optimized by maintaining the other two parameters as constant. The effluents collected at the bottom were subjected to atomic absorption spectrophotometer to estimate the residual quantity of Cd^{2+} ions. The volume of effluent (V_{eff}), amount of Cd^{2+} ions adsorbed (M_{ad}), absolute quantity of Cd^{2+} ions (M_{total}) and removal % of Cd^{2+} ions were arrived with the following equations

$$V_{eff} = Qt_{total} \qquad -1$$

Where the volumetric flow rate is denoted with V_{eff} and the total flow time with t_{total}

$$M_{ad} = \frac{Q}{1000}\int_{t=0}^{t=total} M_{ad}\,dt \qquad -2$$

Where M_{ad} is the amount of Cadmium ions

$$M_{total} = \frac{C_0 Q t_{total}}{1000} \qquad -3$$

$$R\,(\%) = \frac{M_{ad}}{M_{total}} x100 \qquad -4$$

Where R (%) is the removal percentage

WR and PWR Characterization

The WR and PWR were characterized with instrumental techniques such as FTIR and EDX to understand the surface and modifications. The FTIR analysis was carried out in the range of 4000 and 400 cm^{-1} with Thermo Nicolet Avatar 360 equipment. The elemental composition of the WR and PWR was obtained from EDX equipped with SEM instrument (Quanta 200F FEI).

Results and discussion

The comparative investigation of watermelon rind and protonated version in fixed bed columns are first of its kind explored and discussed here for the removal of Cd ions from aqueous solution.

FTIR Characterization

The WR and PWR was analysed with FTIR technique to understand the surface functional groups present on the surface and the type of functional groups can provide valuable information on the mechanism of binding of Cd^{2+} ions onto the surface. The FTIR spectra of WR and PWR are presented in Fig. 1 a&b. It is observed from Fig.1 that the WR and PWR surface contains various functional groups that can facilitate effective binding of the cations onto their surface. The functional groups and respective wavenumbers are summarized in Table-1. It is noticed the FTIR spectra look similar for WR and PWR However, there is a slight change in wavenumbers of the respective functional groups of WR and PWR and these changes are attributed to the elimination of alkali and alkaline earth metals from the surface of the PWR during protonation process.

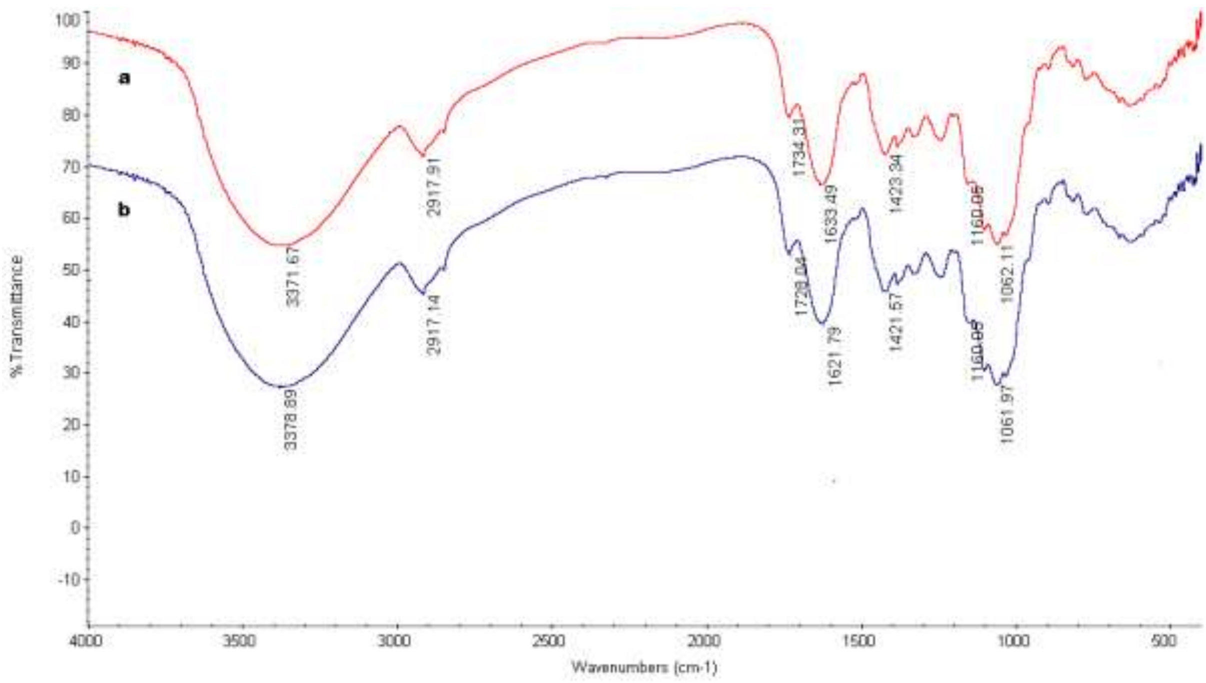


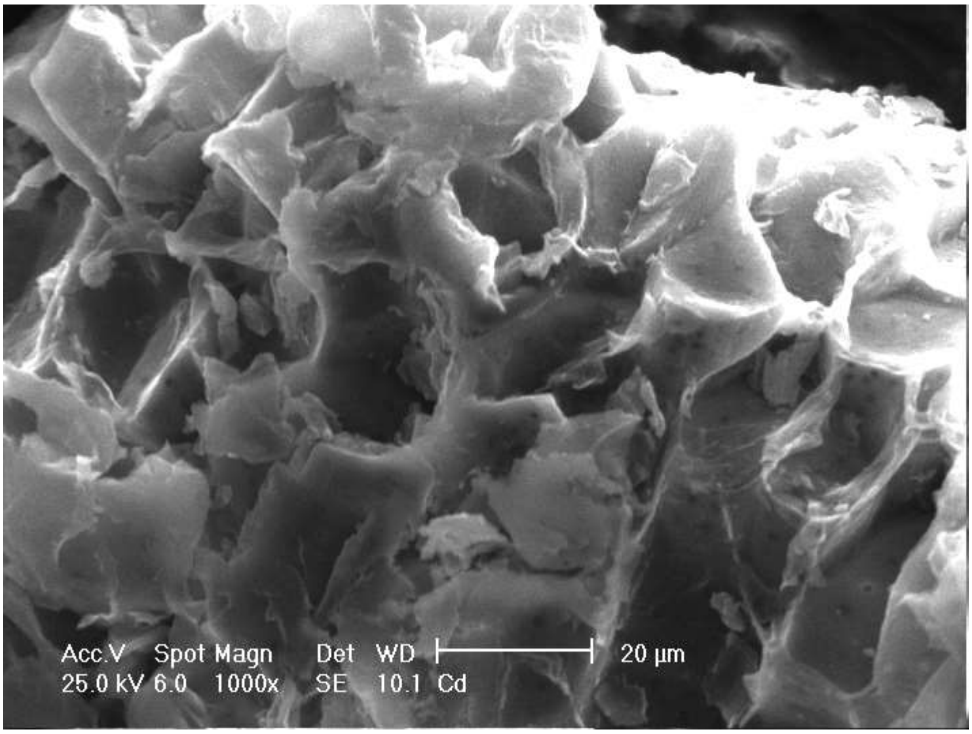
Fig. 1 FTIR spectra of a) native and b) protonated WR

Table-1 Functional groups and wavenumbers of WR and PWR samples

Functional groups	Wavenumbers	
	WR	PWR
O-H (Stretching)	3371	3378
C=O (Stretching)	1734	1728
N-H (bending)	1633	1621
O-H (bending)	1423	1421
C-O (Stretching)	1160, 1062	1160, 1061

SEM analysis

The surface morphology of the WR and PWR was investigated with SEM technique to understand the surface morphology of the native watermelon rind and after protonation. The images captured are represented in fig. 2 a & b and it is observed that the surface is not smooth and seems to be porous in nature for native WR. Similarly, the PWR surface also looks similar to WR with porous structure and this type of surfaces can facilitate effective adsorption of contaminants.



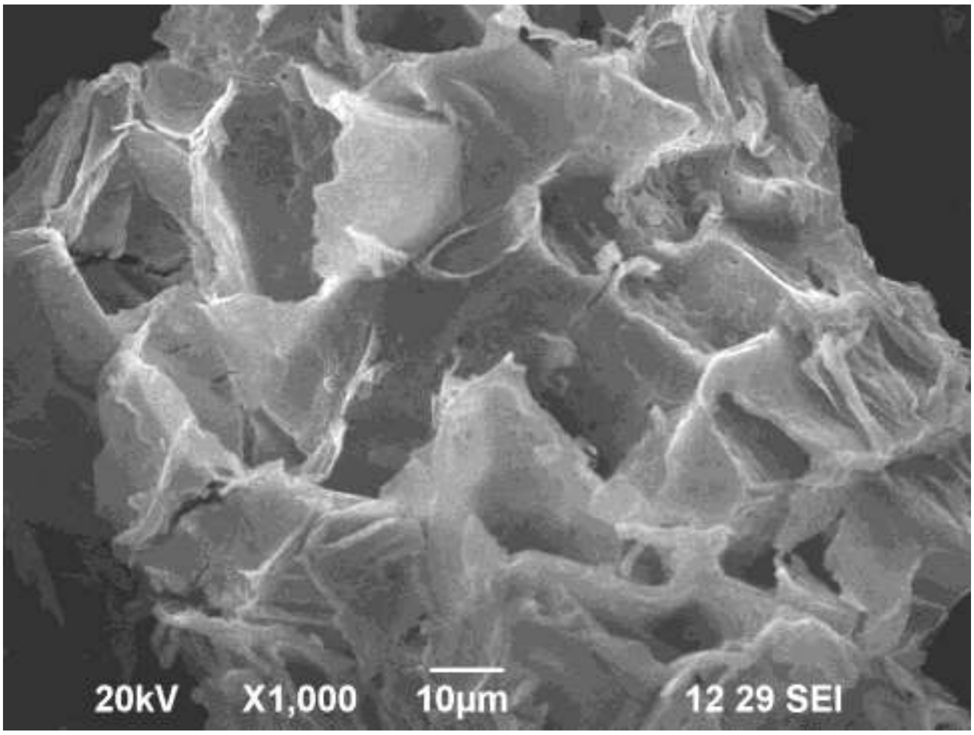


Fig. 2 SEM images of a) WR and b) PWR

EDX analysis

The energy dispersive analysis was carried out for the native and protonated WR samples and the patterns obtained are represented in Fig. 3 a&b. The EDX pattern of WR displayed peaks of Mg and K ions in addition to C, O and Cl suggesting the presence of alkali and alkaline metal ions on the surface of WR. The EDX pattern of PWR displayed peaks of C, O and Cl and interestingly the peaks of Mg and K which were observed in WR are not seen. These observations suggest that during the protonation step, the Mg^{2+} and K^{+} ions were removed from the surface and H^{+} ions occupied the vacant sites. This evidence suggests that the protonation of watermelon rind was achieved successfully.

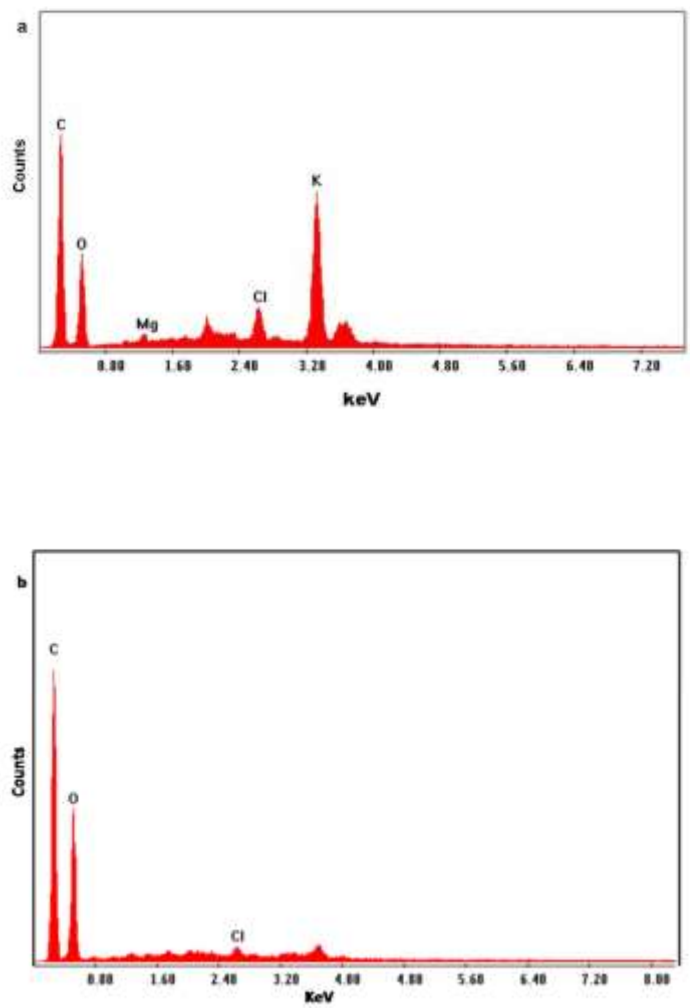


Fig.3 EDX patterns of a) WR and b) PWR

Point zero charge

The point zero charge (PZC) analysis of WR and PWR with respect to pH was investigated to understand the surface charge of the adsorbents at varying pH. The experiments were carried out by adding pre fixed quantity of WR in Torsons tubes containing 30 ml of 0.1 M KCl solution with different initial pH (2-10). The suspension was agitated for 48 h and after filtration the final pH of the solution was noted and difference in the pH was noted. The plots of pH_{pzc} obtained for the WR and PWR are represented in fig. 4. It is observed that the surface charge of WR and PWR were found to be zero at pH 5.4 and 5.6 which suggest that at pH above the point zero charge the surface will be positive and below it will be negative. The negative surface charge will attract the positive charged species such as Cd^{2+} ions used in this study.

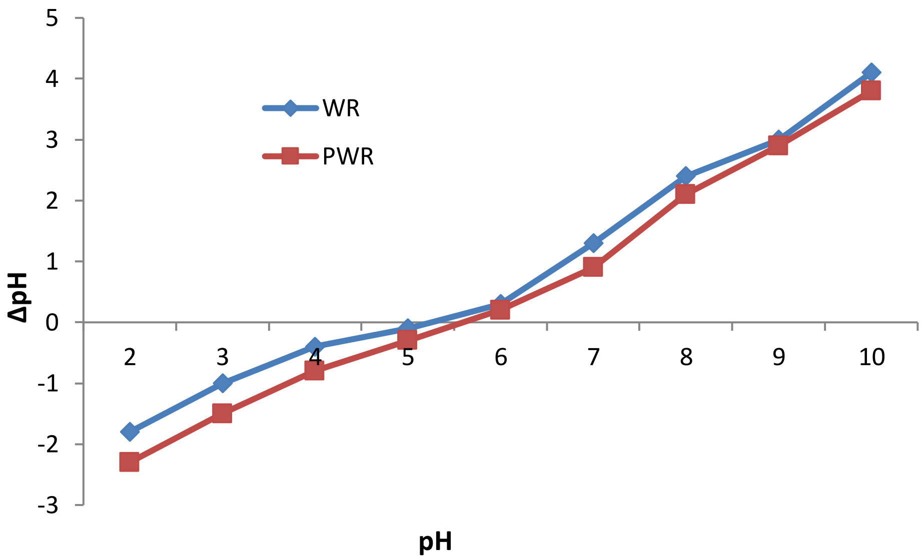


Fig. 4 Point Zero Charge plots for the WR and PWR

Column analysis

The crucial characteristics and dynamic behaviour of fixed bed columns are understood by the breakthrough curve shapes. The S-shaped breakthrough curves indicate the time of breakthrough and saturation points of the fixed-bed columns [Shwetha and Jain 2021]. The data obtained by changing the process parameters for the adsorption of Cd^{2+} ions by WR and PWR are summarized in Tables 2&3. It is observed that the protonated material exhibited higher adsorption ability and removal tendency compared to native towards Cd^{2+} ions. The higher capacity and efficiency observed for PWR compared to WR is due to the absence of alkali and alkaline metal ions on the surface of PWR. In the case of WR, the alkali and alkaline metal ions such as Mg^{2+} and K^{+} were blocking the surface active sites and hence the availability of active sites was less. In PWR, the protonation step has enhanced the surface active sites by eliminating the Mg^{2+} and K^{+} ions which were blocking the surface active sites.

Table-2 Values of column parameters for the removal of Cd^{2+} ions by WR

C_o (mg L^{-1})	Q (ml min^{-1})	H (cm)	M_{ad} (mg)	M_{total} (mg)	R (%)	EBCT (min)
50	1	1	27.1	76.1	35.6	1.7
50	2	1	24.3	69.8	34.8	1.1
50	3	1	19.6	63.7	30.7	0.6
50	1	2	55.9	111.6	50.0	2.9
50	1	3	97.9	176.8	55.6	3.8
100	1	3	79.7	214.2	37.2	-
150	1	3	62.2	215.3	28.8	-

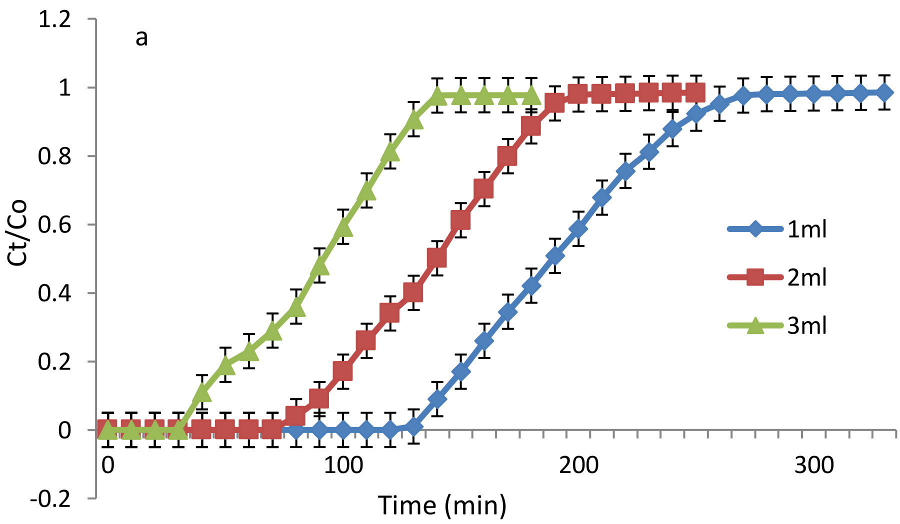
Table-3 Values of column parameters for the removal of Cd^{2+} ions by PWR

C_o (mg L^{-1})	Q (ml min^{-1})	H (cm)	M_{ad} (mg)	M_{total} (mg)	R (%)	EBCT (min)
50	1	1	30.3	78.2	38.7	1.7
50	2	1	27.7	73.3	37.7	1.1
50	3	1	23.9	64.8	36.8	0.6
50	1	2	63.2	115.1	54.9	2.9
50	1	3	107.3	181.9	58.9	3.8
100	1	3	86.5	210.3	41.1	-

150	1	3	76.9	204.2	37.6	-

Column flow rate

Column flow rate determines the performance of the continuous process and it has to be optimised in order to scale up to the industrial stage. In this study, flow rate of Cd^{2+} ions solution fed into the column packed with WR and PWR was varied between 1 ml and 3 ml. The data obtained for the variation in flow rate is summarized and represented in Table-2&3 and the respective breakthrough curves are illustrated in Fig. 5 a&b. It is observed that, the removal efficiency and adsorption capacity declined with increasing flow rates for WR and PWR. The adsorption capacities were decreased from 27.1 to 19.6 mg g^{-1} for WR and 30.3 to 23.9 mg g^{-1} for PWR respectively. The decrease in capacity and efficiency was due to decrease in the residence time of the Cd^{2+} ions in the bed at higher flow rates. The breakthrough curves appeared early with respect to time for higher flow rates compared to lower flow rates. The breakthrough curves appeared at Low flow rates tend to provide greater residence time for the ions in the bend which leads to greater interaction time with the surface active sites of WR and PWR. The saturation time for the curves were found to decrease with increasing flow rates and higher time of saturation point 280 min was observed for 1 ml flow rate. Thus lower flow rates were fixed as optimal flow rate and similar trends were reported by citrus peels [Chatterje and Schiewer 2011].



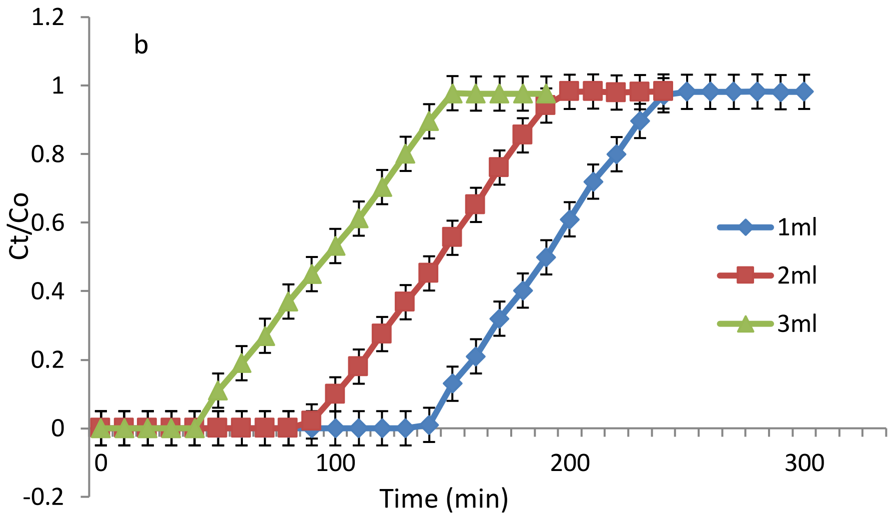


Fig. 5 Breakthrough curves obtained for flow rate variation a) PWR b) WR (Initial concentration 50 mg L^{-1}, pH 6, adsorbent dose 0.36 g)

Column Bed depth

Bed depths are considered to be an imperative parameter since it determines the cost and economic value of the continuous process. Considering the economic importance, bed depths in this study were varied from 1 cm to 3 cm and the resulting data and breakthrough curves are represented in Table-2&3 and Fig. 6 a&b. It is observed that with augmented bed heights, the removal efficiency and adsorption capacity increased for both WR and PWR. The adsorption capacities were calculated to be 97.9 mg g^{-1} and 107.3 mg g^{-1} respectively for WR and PWR at higher bed capacities. It is also observed that the breakthrough points and saturation points of PWR were high compared to WR. The increasing trend is as a result of availability of ample active sites with the augmented bed heights and increased residence time of Cd^{2+} ions in the column. . The time of breakthrough point appearance and saturation point was high for higher bed depths compared to lower bed depths as seen in the Fig. 6 a&b. Similar results were reported for the removal of Cu^{2+} ions by jute fibre [Zhaolin et al 2018].

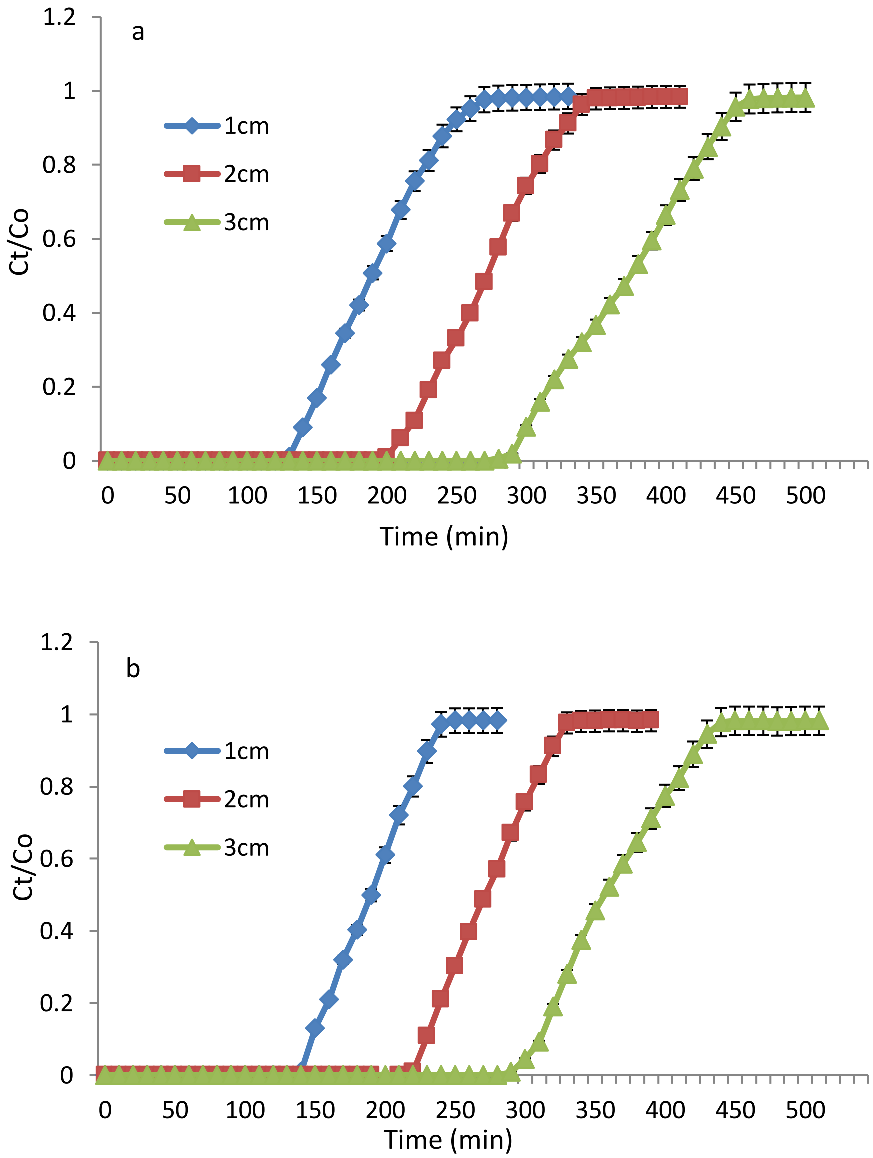


Fig. 6 Breakthrough curves obtained for bed depth variation a) PWR b) WR (Initial concentration 50 mg L^{-1}, pH 6, flow rate 1 ml)

Column initial concentration

The effectiveness of the column can be established based on the initial concentration of analytes sent into the column. Thus the initial concentration of Cd^{2+} ions were varied from 50 to 150 mg L^{-1} and the resulting data and breakthrough curves obtained for WR and PWR are represented in Table-2&3 and Fig. 5 a&b. It is understood that with increasing initial concentration the adsorption capacity and efficiency plunged to lower values. The breakthrough points started to appear early for increasing concentration and similarly the saturation of the column also attained earlier. The time of breakthrough point appearance and saturation point was high for lower initial concentrations compared to higher concentrations as seen in the Fig. 7 a&b. These observations are due to lack of availability of surface sites for high concentration of Cd^{2+} ions coming in and competitive adsorption among the ions. Similar trend was reported for the removal of Cd^{2+} by green adsorbents [Soma et al. 2019].

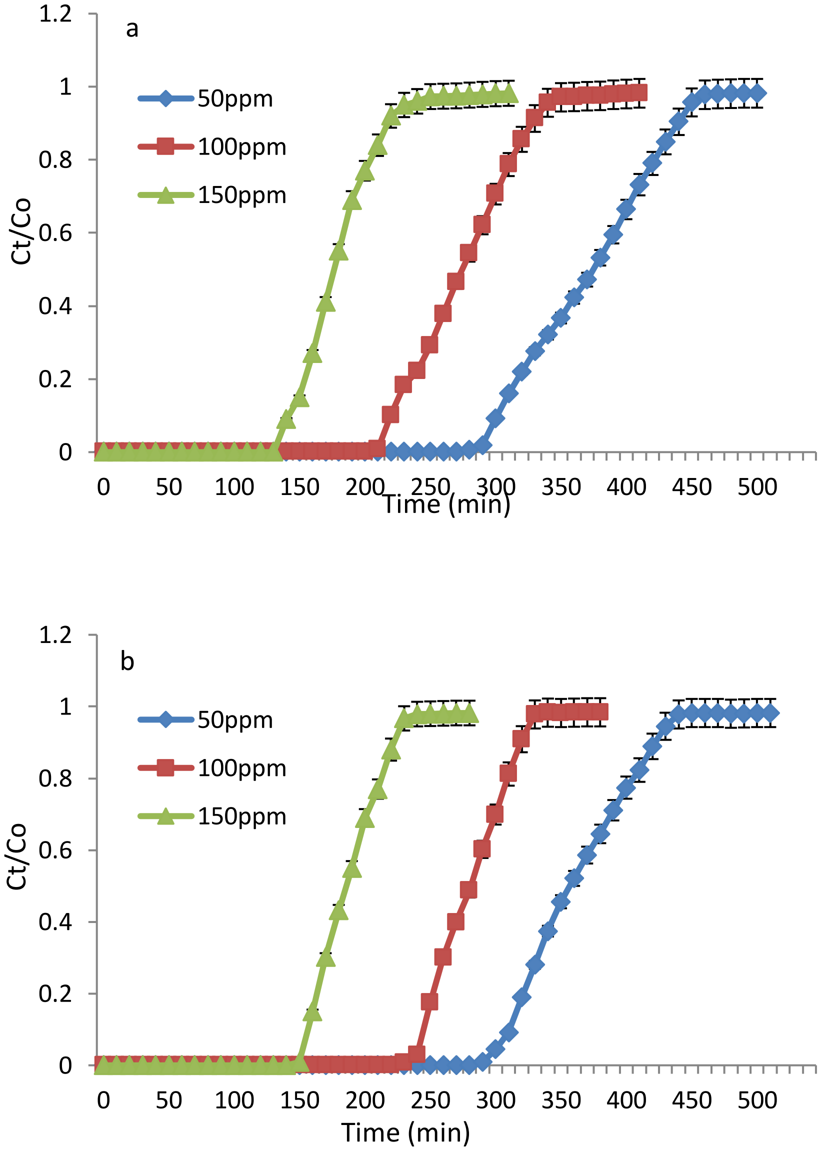


Fig. 7 Breakthrough curves obtained for initial concentration variation a) PWR b) WR (Flow rate 1 ml, pH 6, adsorbent dose 1.1 g)

Models

Mathematical models are very much handy in understanding the data and predicting the behaviour of the continuous process and further help in scaling up the lab-scale process to large scale industrial process. Adams-Bohart, Thomas and Yoon-Nelson are most significantly mathematical models that are employed in prediction of breakthrough curves and column data. In this study, the above three models were adopted to understand the dynamic behaviour of continuous process for the removal of Cd^{2+} ions by WR and PWR.

Adams-Bohart model

Adams-Bohart model is one commonly and easily used model for the continuous systems and predicting the breakthrough curves. In this investigation, the model parameters obtained for the removal of Cd^{2+} ions by WR and PWR are summarised and presented in Table-4. The kinetic constant K_{AB} for WR and PWR reduced with augmented flow rate and initial feed concentration and surged for bed height. An opposite trend was observed in the case of adsorption saturation concentration N_0 compared to kinetic constant K_{AB}. The N_0 values increased for rise in flow rates and initial concentration and plunged for rise in bed heights. The trends suggest the mass transfer is dominating the initial stage of the process in both WR and PWR. The moderate correlation coefficients indicate that this model can be utilised to moderately investigate and understand the initial stages of breakthroughs curves.

Table-4 Constants of Adams-Bohart model for the removal of Cd^{2+} by WR and PWR

Parameter	**WR**				**PWR**			
	K_{AB} (L/mg min)	**N_o (mg/L)**	**R^2**	**MSE**	**K_{AB} (L/mg min)**	**N_o (mg/L)**	**R^2**	**MSE**
1 ml	0.022	8798	0.913	7.6	0.025	8814	0.921	8.2
2 ml	0.017	9345	0.891	11.7	0.019	9542	0.916	7.7
3 ml	0.009	9812	0.876	13.5	0.015	9920	0.909	8.5
1 cm	0.022	8798	0.913	7.6	0.025	8814	0.921	8.2
2 cm	0.029	8231	0.923	7.3	0.031	8526	0.928	8.3

3 cm	0.037	7865	0.934	6.9	0.039	8198	0.933	6.8
50 mg L^{-1}	0.037	7865	0.934	6.9	0.039	8198	0.933	6.8
100 mg L^{-1}	0.030	8671	0.926	7.5	0.035	8757	0.921	7.2
150 mg L^{-1}	0.027	9487	0.919	7.9	0.031	9533	0.913	7.6

Thomas model

Table-5 shows the constants of Thomas model fitted to various parameters. It is observed that the K_{Th} and q_o had an opposite trend for all the parameters of WR and PWR. The adsorption capacity was found to increase with the increasing bed heights and this is due to the ambient environment for Cd^{2+} ions at higher bed depths having enough time for adsorption. On the other end with the rise in flow rate and feed concentration, the adsorption capacity reduced and this is due to week adsorption and Cd^{2+} ions not finding suffice time for interaction. Further, higher flow rates and concentrations decrease the liquid - solid contact time [Na and Li 2023]. The correlation coefficients were found to be best fitting of the model to the data obtained for WR and PWR. Further, the Mean squared error (MSE) analysis of the data suggest that the regression error is less compared for the experimental data suggesting that the best fit of the model. The best fit correlation coefficients suggest the rate limiting step is not dependent on mass transfers.

Table-5 Constants of Thomas model for the removal of Cd^{2+} by WR and PWR

Parameter	**WR**				**PWR**			
	K_{Th} (ml/min mg)	**q_o (mg/g)**	**R^2**	**MSE**	**K_{Th} (ml/min mg)**	**q_o (mg/g)**	**R^2**	**MSE**
1 ml	0.0018	26.9	0.982	2.3	0.0019	29.9	0.991	1.5
2 ml	0.0021	22.1	0.971	2.7	0.0024	28.1	0.989	1.7
3 ml	0.0023	20.8	0.976	2.5	0.0025	27.8	0.989	1.8
1 cm	0.0018	26.9	0.982	2.3	0.0019	29.9	0.991	1.5

2 cm	0.0017	53.9	0.978	2.5	0.0015	69.6	0.982	2.1
3 cm	0.0013	95.2	0.989	1.9	0.0014	104.2	0.983	1.7
50 mg L^{-1}	0.0013	95.2	0.989	1.9	0.0014	104.2	0.983	1.7
100 mg L^{-1}	0.0020	78.4	0.990	1.7	0.0025	89.6	0.991	1.4
150 mg L^{-1}	0.0024	70.7	0.986	2.0	0.0029	71.1	0.990	1.3

Yoon-Nelson model

Table-6 shows the parameters and fitting constants of Yoon-Nelson model obtained for Cd^{2+} ions removal by WR and PWR. The data tend to fit well to the Yoon-Nelson model in addition to the Thomas model. The τ values and K_{YN} had opposite trend for all the investigated parameters of both the adsorbents. The τ rose with the rise in bed depths and this is due to increased interaction of Cd^{2+} ions with the adsorbents WR and PWR at higher depths provided more sites for interaction. The τ declined with rise in flow rate and feed concentration and this suggest the Cd^{2+} ions do not have enough sites to interact due to competition and quick saturation of bed. The trend observed indicates that more adsorption takes place when solid-liquid interface are enhanced.

Table-6 Constants of Yoon Nelson model for the removal of Cd^{2+} by WR and PWR

Parameter	**WR**				**PWR**			
	K_{YN} (min^{-1})	**τ (min)**	**R^2**	**MSE**	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**	**MSE**
1 ml	0.917	47.5	0.992	1.2	0.923	51.3	0.991	1.1
2 ml	0.943	43.3	0.991	1.1	0.946	49.2	0.986	1.5
3 ml	0.958	39.8	0.987	1.5	0.972	44.7	0.989	1.6
1 cm	0.917	47.5	0.992	1.2	0.923	51.3	0.991	1.1
2 cm	0.907	55.6	0.987	1.4	0.911	68.6	0.988	1.5
3 cm	0.889	61.0	0.990	1.2	0.895	77.2	0.993	1.1

50 mg L^{-1}	0.889	61.0	0.990	1.2	0.895	77.2	0.993	1.1
100 mg L^{-1}	0.912	57.5	0.986	1.5	0.935	59.7	0.991	1.3
150 mg L^{-1}	0.932	51.2	0.991	1.2	0.941	53.3	0.990	1.2

Desorption and regeneration

Revival of adsorbents adds value to an adsorption process in terms of economic viability. In the present investigation, WR and PWR were assessed for desorption and regeneration abilities. To evaluate the desorption and regeneration efficiencies, the columns were packed with Cd^{2+} ions loaded WR and PWR to bed height of 3 cm and from the top of the column desorbing agents were allowed. The eluent was collected at the bottom of the column and tested for the concentration of Cd^{2+} ions in an Atomic Absorption Spectrophotometer. Two desorbing agents such as 0.1 M HCl and 0.1 M Acetic acid were selected for the desorption investigations. The results of the study are represented in Fig. 8. It was noted that the HCl exhibited higher desorption and regeneration efficiency compared to the Acetic acid for both WR and PWR. A maximum of 95.6 and 96.1 % of desorption efficiency was achieved respectively for WR and PWR. In the case of Acetic acid, the efficiencies were found to be 79.8 and 84.3 % for WR and PWR respectively. The higher efficiencies exhibited by the HCl is due to the high dissociation constant of HCl which provides rapid H^+ ions with higher acidity of the solution. While acetic acid is a weak acid and gives out H^+ ions at a slower rate and thus sufficient H^+ ions are not available at solid-liquid interface for the desorption process. These observations suggest that HCl is a better desorbing agent for WR and PWR and thus the adsorbents can be reused for next cycles of adsorption of Cd^{2+} ions in continuous process.

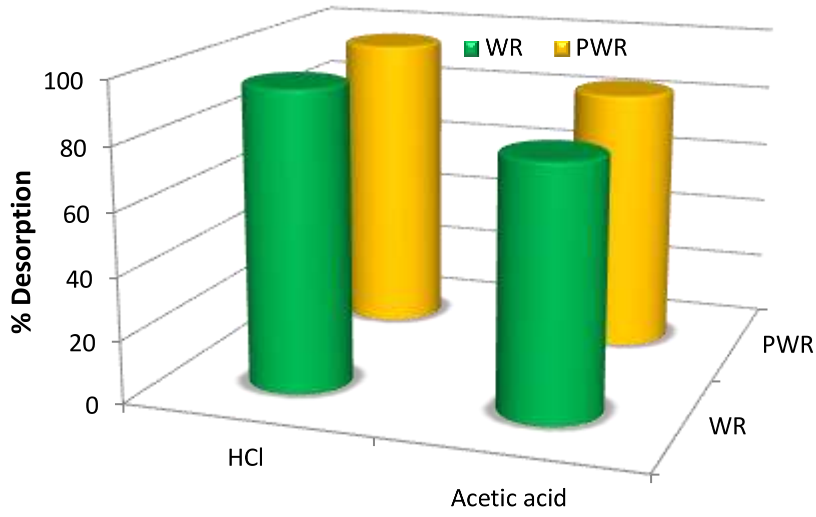


Fig.8 Desorption efficiency of WR and PWR

Conclusion

Comparative investigation of native and protonated watermelon rind for the removal of Cd^{2+} ions in continuous process was executed in this study. The WR and PWR was surface characterised with analytical techniques to understand the adsorption process. Continuous parameters were optimised and found that low flow rates and initial concentration and higher bed heights favoured the maximum adsorption process for both the adsorbents. The loading capacities were found to be high for protonated watermelon rind compared to native one and this is due to the elimination of K^+ and Mg^{2+} ions from the surface during the protonation step. Further the loading capacities of WR and PWR are high compared to several adsorbents. Yoon-Nelson and Thomas models were best fit models that explained the data satisfactorily with high correlation coefficients and better MSE values compared to Adams-Bohart model. Regeneration close to 96 % of the WR and PWR was successfully achieved with 0.1 M HCl as desorbing agent. These results suggest that WR and PWR are prolific adsorbents for the removal of Cd^{2+} ions from aqueous solution. Further, the WR and PWR can be explored for the continuous removal of other inorganic contaminants and emerging contaminants from aqueous solution and also the WR can be activated with varying activating agents and employ in the adsorption process.

Conflicts of interest

Authors declare no conflicts of interest

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