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Biosorption of Mn(II) by ripped *Citrus paradisi* pulp waste

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ABSTRACT

The current exploration presents a primary study on the uptake of Mn(II) by ripped *Citrus paradisi* pulp waste (RCPW). The effects of various engineering parameters such as biosorbent dose, agitation, contact time, initial concentration, temperature, and different eluents were evaluated. Pseudo-second-order kinetic model fits well with the process, and uptake of Mn(II) by RCPW showed monolayer formation as enumerated by Langmuir's model. Increased temperature enhanced the biosorption capacity indicating endothermic nature of the phenomenon. Among HNO_3, H_2SO_4, HCl, and EDTA, 0.1 N NaOH was found to be the best desorbing agent.

Keywords: Batch study; Biosorption; Desorbent; Engineering parameters; Kinetic and equilibrium models

1. Introduction

It is a matter of immense regret that wild industrial expansion has posed detrimental effects on the delicate balance between human and environment. Especially, in the last century, hundreds of synthetic chemicals were manufactured to modernize various domestic and industrial needs. This resulted in uncontrolled release of hazardous chemicals into the atmosphere due to lack of knowledge about their lethal consequences. One such dilemma is related to the discharge of heavy metals into the aquatic reserves, resulting in terrible human diseases [1–6]. Manganese is generally found in trace concentration (0.02–130 μg/L) in fresh water [3]. According to WHO, the permissible limit for manganese in drinking water is 0.1 mg/L [1]. It is required in human body to maintain blood sugar, nerves, and immune system. Too much exposure of manganese causes neurological disorders such as manganism, hallucinations, excessive sleeping, DNA mutations, over flow of liver, and depression [1,3]. Manganese is generally found in effluents from industries such as dye, dry cell batteries, paint, steel alloy, glass, ceramics, ink, fertilizers, and coal fields [6]. It also occurs in metal mine drainage, especially in coal fields.

A list of conventional techniques can be identified for the removal/concentration of manganese from the aqueous media. It includes reverse osmosis, evaporation, sedimentation, adsorption, coagulation, and ion

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exchange [7–12]. Each of aforementioned technologies is hindered by the economic problem when applied for the remediation of dilute metal solutions. Over the last few decades, biosorption has been recognized as a potential alternative to cope up with economic barriers while dealing with lean solutions [13,14].

Removal of, metals or non-metal species by departed biomass has been recognized as biosorption. Literature witnesses the use of diverse types of biomass including bacteria, algae, fungi, agricultural waste, and biochemical industries residues [13]. All these biomass are cheaply available in the surroundings or can be generated through simple cultivation process. Low fixed and operating costs, regeneration of biomass, better selectivity, modest residence time, no byproduct formation, and deletion of lethal metals from wastewater, irrespective of its level of toxicity are some salient features of biosorption [15]. The application of dead biomass presents some advantages over other materials viz: (i) the metal elimination process does not limited by metal noxious restrictions; (ii) no requirements of any sort of ingredients for culture; and (iii) ease of metal desorption from biomass and its reuse [15].

Citrus paradisi is the botanical name of grape fruit. The pulp left after the extraction of juice was investigated for the removal of Mn(II). The objectives of the current investigation are to determine the effects of biosorbent dose, agitation, initial metal concentration, temperature, and eluent on the uptake of Mn(II). Pseudo-first and second-order models were used for kinetic modeling. Langmuir and Freundlich models were employed to interpret the mechanism of biosorption of Mn(II) into *C. paradisi* waste.

2. Materials and methods

2.1. Biosorbent preparation

In the present study, fresh ripped deep yellow grape fruit was selected to obtain biomass. *C. paradisi* (grape fruit) waste biomass used in this work was harvested from "Institute of Horticultural sciences, University of Agriculture, Faisalabad, Pakistan." The lignocellulosic fiber was derived from *C. paradisi* fruit by cold pressing and soaking it overnight in the distilled water to remove particulate material from its surface. It was first sun-dried and then oven-dried at 60°C for 72 h and used as biomass. One kilogram of biomass was sub-sampled for use in the experiments. In order to ensure that homogenous samples are collected, standard sampling techniques were applied. Dried biomass was ground by using food processor (Moulinex, France). The biomass was sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain adsorbent with homogenous known particle size. The fraction with <0.255–0.100 mm was selected for use in the sorption tests. The sieved sorbents were stored in $CaCl_2$ in ambulized form at 4°C.

2.2. Reagents

All chemicals used in these studies were pro-analysis grade and were purchased from Merck Company (Darmstadt, Germany), and they were of analytical grade including: $Mn(NO_3)_2{\cdot}4H_2O$, H_2SO_4, HCl, HNO_3, sodium hydroxide, EDTA, calcium chloride, and Mn(II) atomic absorption spectrometry standard solution (1,000 mg/L^1).

2.3. Batch biosorption studies

Stock Mn(II) solution (1,000 mg/mL) was prepared using DDW. Manganese solutions of different concentration were prepared by adequate dilution of the stock solution with DDW. In all sets of experiments, fixed volume of Mn(II) solutions (100 mL) was thoroughly mixed with biosorbent at 100 rpm and 30°C. The effect of different experimental parameters, such as biosorbent dose, initial metal concentration, shaking speed, temperature, and contact time was checked on sorption of Mn(II) by *C. paradisi* waste biomass. For adjusting the pH of the medium 0.1 N solutions of NaOH and HCl were used. In this study, 6.5 pH was maintained. The conical flasks were covered with aluminum foil and were placed on a rotating shaker with constant shaking. At the end of the experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman No. 40, ash less).

2.4. Determination of the Mn(II) contents in the solution

The concentration of Mn(II) in the solution before and after the equilibrium was determined by flame atomic absorption spectrometry, using a Perkin-Elmer A– Analyst 300 atomic absorption spectrometer equipped with an air-acetylene burner and controlled by Intel personal computer.

2.5. Metal uptake capacity

The Mn(II) uptake was calculated by the simple concentration difference method. The initial concentration C_i (mg/L) and metal concentrations at various time intervals C_e (mg/L), were determined and the metal uptake q_e (mg metal adsorbed/g adsorbent) was calculated from the mass balance equation as follows:

$$q_e = (C_i - C_e)V/100w$$

where V is the volume of the solution in mL and w is the mass of the sorbent in g.

% sorption is given as:

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

3. Results and discussion

3.1. Effect of biosorbent dose

Fig. 1 shows the effect of ripped *C. paradisi* pulp waste (RCPW) dose between 0.05 and 0.4 g on Mn(II) uptake. Similar trend has been observed elsewhere [7]. A sudden reduction in uptake of Mn(II) (from 34.74 to 5.61 mg/g) was observed when the biosorbent dose increased as mentioned above. This trend could be explained as biosorbent dose was directly linked with the number of available sorption sites on RCPW. For the given concentration of adsorbate, sufficient number of active sites should be present to carry out sequestration of metal optimally. Thus, increase of RCPW dose against fixed concentration of Mn(II) i.e. 100 mg/L, resulted in increase of vacant adsorption sites, hence, a lower uptake was observed on increasing the biomass dose beyond 0.05 g. Therefore, RCPW was used in 0.05 g in all experiments.

3.2. Effect of agitation

Agitation may ensure the proper interaction of biosorbent and metal, as biosorption phenomenon involves complex mass transfer steps [8]. Effect of agitation was investigated on the uptake of Mn(II) as depicted in Fig. 2. It was found that significant amount of Mn(II) was removed even at 0 rpm (40.1 mg/g). The uptake of Mn(II) was enhanced (43.56 mg/g) when rpm increased to 100 rpm. This may be interpreted in terms of reduction of convective resistance due to agitation. Further increase in rpm to 150 (39.18 mg/g) did not improve the uptake, which may be due to the desorption of Mn(II) from RCPW surface, due to weak bonding unable to withstand strong agitation.

3.3. Effect of contact time

To establish a suitable contact time between the biomass and Mn(II) synthetic solution, uptake of RCPW was determined in a series of experiments as a function of time varied from 15 to 1,440 min. Fig. 3 shows a smooth curve between uptake of Mn(II) onto RCPW. Five regions can be identified. In first step (0–60 min), there was a rapid increase in uptake of Mn(II) by RCPW from 0 to 25.34 mg/g followed by a relatively lower step (60–240 min) in which mild increase in Mn(II) uptake (25.34–33.48 mg/g) by RCPW was noticed. In the third step (240–720 min), a relatively lower enhancement in loading of RCPW by Mn(II) (33.48–37.3 mg/g) was observed. These steps can be interpreted at the start; binding groups present on the surface of RCPW were vacant due to which rapid uptake of Mn(II) was noted. However, with the passage of time due to decrease in number of available binding sites, uptake followed a decreasing trend. Nevertheless, a jump in uptake (37.3–40.22 mg/g) was observed when contact increased from 720 to 840 min. No further increment was observed when contact time varied from 840 to 1,440 min. This may indicate the removal of Mn(II) due to intraparticle diffusion and achievement of equilibrium. As an equilibrium time, 1,440 min (24 h) were chosen.

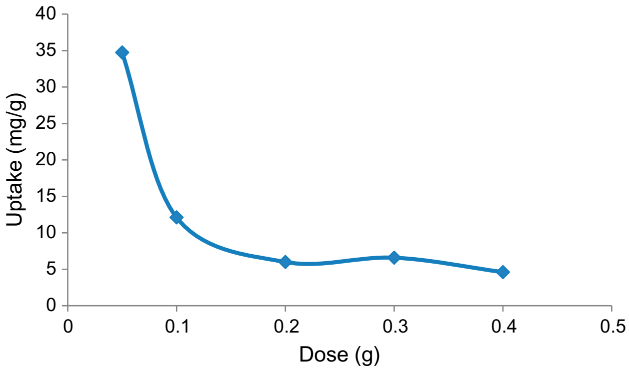

Fig. 1. Effect of RCPW dose on Mn(II) uptake.

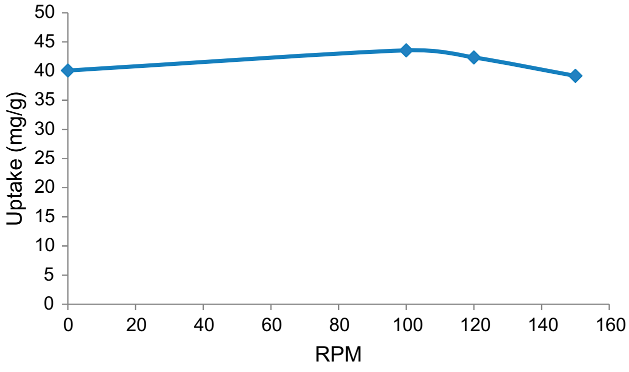

Fig. 2. Effect of RPM on the uptake of Mn(II) by RCPW.

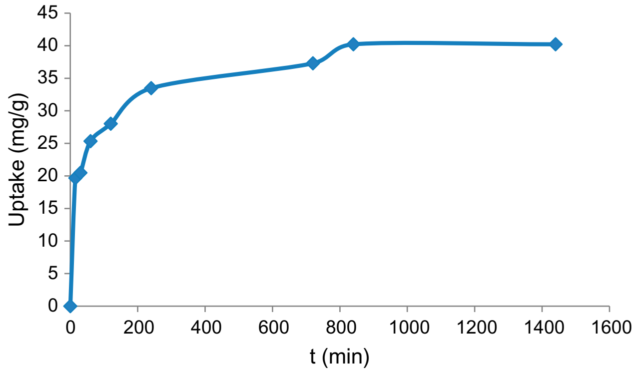

Fig. 3. Effect of contact time on uptake of Mn(II) by RCPW.

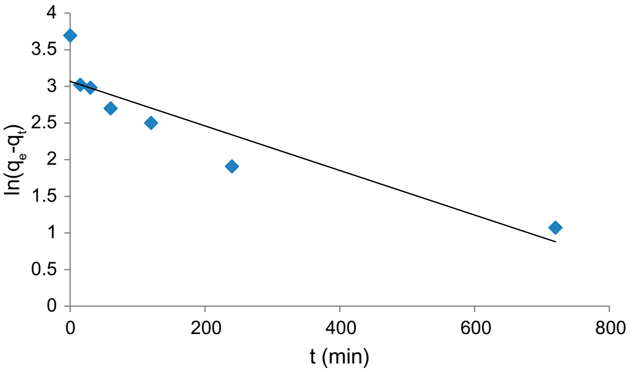

Fig. 4. Application of pseudo first order kinetic model on the uptake of Mn(II) by RCPW.

3.3.1. Kinetic modeling and mechanism

To explicate the time course of biosorption of metal upon a biomass, several authors have reported the use of multiple kinetic expressions [10,17,18]. Table 1 shows the kinetic model used in contemporary study. Pseudo-first-order kinetic model is an abundantly used rate expression. It is applied for liquid–solid systems in equilibrium with each other. It assumes that the rate of uptake of specie is directly proportional to vacant adsorption sites. A linear plot of $\ln(q_e{-}q)$ vs. time would indicate the applicability of this rate expression. Fig. 4 shows the use of pseudo-first-order kinetics for the biosorption of Mn(II) upon RCPW. R^2 for pseudo-first-order kinetic was 0.8412. Due to poor correlation with the experimental data it was concluded that biosorption of Mn(II) did not follow pseudo-first order-kinetic. Literature shows that pseudo-second-order kinetic satisfies most of the biosorption phenomenon [17,18]. It has been derived based on the assumption that the rate controlling step is chemisorption during biosorption phenomenon. Further, it assumes that the rate of fixation of ion on the biosorbent's active sites is directly proportional to the square of the vacant biosorption sites given in Table 1. The applicability of this model can be checked by plotting t/q_t vs. t. Fig. 5 illustrates that the time course of Mn(II) uptake by RCPW followed excellently pseudo-second-order rate expression with $R^2 = 0.9985$. The value of equilibrium uptake q_e estimated based on the slope of the graph, was 41.12 mg/g which was in close agreement with the experimentally observed (40.22 mg/g). However, there is a drawback of pseudo-second-order model that it does not satisfy the adsorption phenomenon at $t = 0$.

Particle size, porosity, and specific surface area of the biosorbent are few important structural properties which can affect the biosorption of Mn(II) onto RCPW [7,8,10]. Therefore, it was important to discuss the intraparticle diffusion. The resistance faced by the Mn(II) ion in bulk of the solution may be ignored on account of sufficient shaking, and dispersion of the biomass. Hence, diffusion of Mn(II) can be studied with respect to three processes viz. diffusion through the liquid film around RCPW, intraparticle diffusion through the biomass, and fixation of the Mn(II) on the active sites. Weber and Morris proposed a model given in Table 1. The relationship between q_t and t is shown in Fig. 6. It can be seen that plot can be divided into two linear portions indicating the existence of multiple steps in the biosorption of Mn(II) onto RCPW. First linear segment contributed to the diffusion through film, and second flat portion indicated the incidence of pore diffusion. Similar results have been shown in multiple papers [7,10,18]. Fig. 6 illustrates that pore diffusion is not the only rate controlling step as the plot did not pass through the origin [18].

Table 1
Different kinetic models

Kinetic model	Differential	Integral	Plot	References
Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs. t	[17]
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$	$\frac{t}{q_t}$ vs. t	[16]
Weber–Morris	–	$q_t = kt^{0.5}$	q_t vs. t	[17]

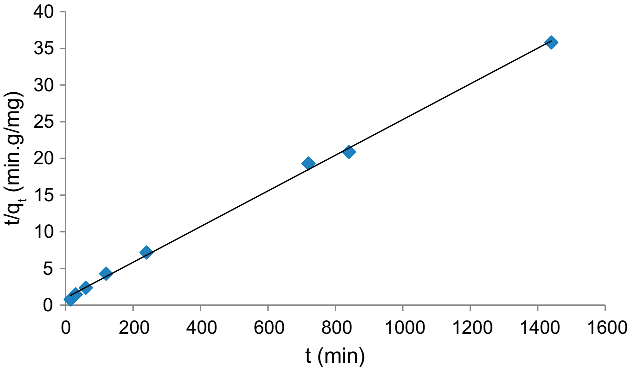

Fig. 5. Application of pseudo second order kinetics on the uptake of Mn(II) by RCPW.

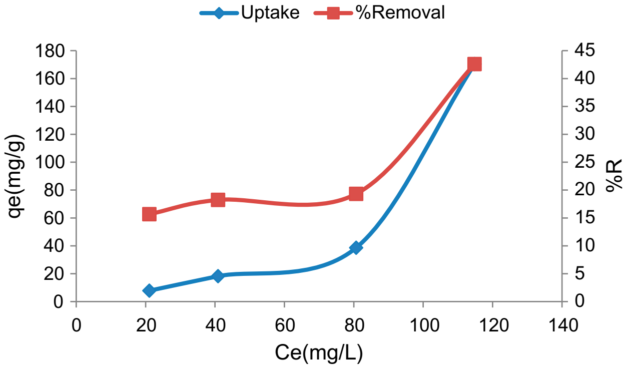

Fig. 7. Effect of initial concentration on the uptake of Mn(II) by RCPW.

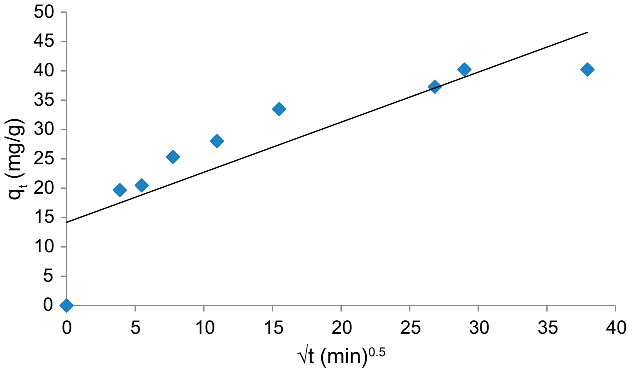

Fig. 6. Fitting of Weber–Morris model for uptake of Mn(II) by RCPW.

3.4. Effect of initial concentration

Performance of RCPW was investigated at different mass transfer driving forces by varying concentration of Mn(II) between 25 and 200 mg/L. Mn(II) uptake by RCPW enhanced from 7.84 to 170.4 mg/g when the concentration was increased as shown in Fig. 7. This can be explained as, greater number of Mn (II) species were adsorbed when its concentration was increased. Also, the percentage removal increased from 15.68 to 42.6% when initial concentration was increased in the above-mentioned range. Usually, increase in uptake results in decrease in percentage removal due to competition among the ions to occupy limited vacant adsorption sites [18]. Thus, it may be said that Fig. 7 highlighted the number of available sites that were sufficient, and there was no competition among the ions for adsorption.

3.4.1. Equilibrium modeling

To look into the nature of adsorption of Mn(II) on RCPW, Langmuir and Freundlich isotherms were studied as given in Table 2. Langmuir isotherm is a celebrated and extensively used model for the recognition of monolayer type adsorption. This isotherm supports indistinguishable fastening sites on the biosorbent [8,18]. Fig. 8 shows the application of Langmuir model on the adsorption of Mn(II) onto RCPW. A fairly high value of $R^2 = 0.9904$ was observed. The values of $q_{\max}$ and b were estimated from slope and intercept of Fig. 5 and were 41.16 mg/g and 0.007 L/mg, respectively. A comparison of various biosorbents used to remove Mn(II) with present study has been given in Table 3. It can be seen that RCPW showed fairly high value of uptake as compared to many biosorbents.

A salient feature of Langmuir's parameter b is that it helps to determine the feasibility of the biosorption process. This parameter is used to calculate separation factor (R_L) calculated by $1/(1 + C \times b)$ [19]. Fig. 9 shows that the value of R_L was less than 1 in all cases.

Table 2
Adsorption isotherms

Isotherm		Linearized form	Parameters	Plot	References
Langmuir	$q_e = q_{\max} \frac{bC_e}{1+bC_e}$	$\frac{q_e}{C_e} = bq_{\max} - bq_e$	$q_{\max}$, b	$\frac{q_e}{C_e}$ vs. q_e	[10]
Freundlich	$q_e = K_F C_e^{(1/n)}$	$\log(q_e) = \log(K_F) + (1/n)\log(C_e)$	K_F, n	$\log(C_e)$ vs. $\log(q_e)$	[8]

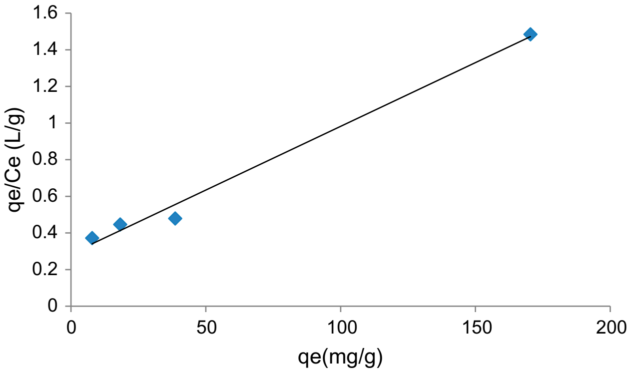

Fig. 8. Application of Langmuir's model on the biosorption of Mn(II) onto RCPW.

Table 3
Comparison of RCPW with other biosorbents for Mn(II) removal

Sr.#	Biosorbent	Biosorbent capacity (mg/g)	References
1	*Pseudomonas* sp.	109	[8]
2	Pecan nutshell	97.79	[9]
3	Thermally decomposed leaf	66	[7]
4	*S. xylosus*	59	[8]
5	Ripped *Citrus paradaisi* pulp waste	41.16	This study
6	*B. trispora*	40	[8]
7	Lignite	28.11	[6]
8	Decanicus	23.2	[10]
9	Stromboliensis	13.9	[10]
10	Black carrot	4.91	[5]

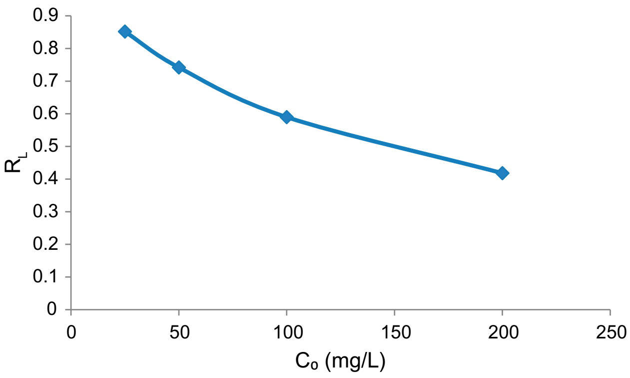

Fig. 9. Variation of separation factor with initial concentration of Mn(II).

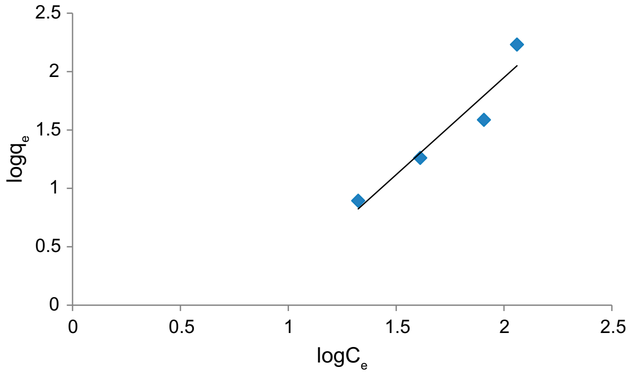

Fig. 10. Application of Freundlich's isotherm for the biosorption of Mn(II) onto RCPW.

Thus, it may be concluded that the biosorption of Mn(II) upon RCPW is feasible under the experimental conditions [19]. In addition to Langmuir isotherm, Freundlich model was also applied as shown in Fig. 10. The value of R^2 (0.9143) was much lower than that of Langmuir's. Hence, it may be said that the process of Mn(II) removal by RCPW was uniform and resulted in formation of monolayer on the biomass.

3.5. Effect of temperature

A series of experiments were performed to investigate the effect of temperature on the uptake of Mn(II) by RCPW from 30 to 50˚C as shown in Fig. 11. It was found that uptake of Mn(II) increased from 29.3 to 33.74 mg/g, when temperature increased from 30 to 45˚C. This showed the endothermic nature of Mn(II) biosorption onto RCPW. However, when temperature was increased from 45 to 50˚C a decrease in uptake of Mn(II) was observed. This may be interpreted as the increase in temperature beyond 45˚C damaged the binding sites resulting in lower uptake. Another

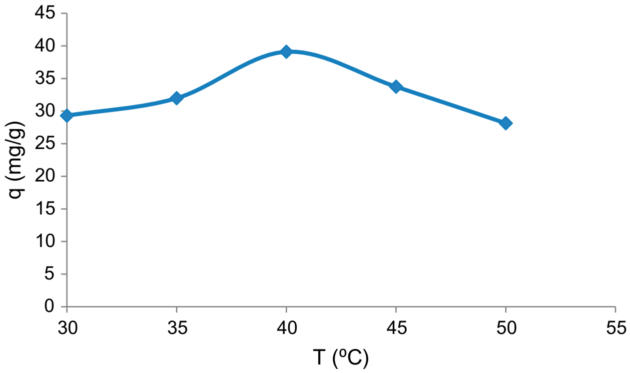

Fig. 11. Effect of temperature on the uptake of Mn(II) by RCPW.

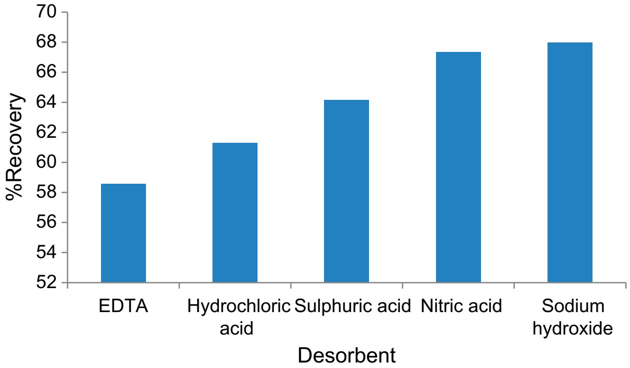

Fig. 12. Effect of desorbent on the percentage recovery of Mn(II) from RCPW.

possibility could be the damaging of biosorbent pores due to which uptake of Mn(II) due to pore diffusion was affected. Hence, a lower uptake was detected. Similar pattern has been observed elsewhere [8].

3.6. Effect of desorbent

The attractive feature to use biosorption for removal of heavy metals from dilute solution is the reuse of biomass. Different eluents have been tested by the researchers [14,20]. In this investigation, HCl, H_2SO_4, HNO_3, EDTA, and NaOH were used as desorbent. All the eluents were 0.1 N in concentration and the results of study is as shown in Fig. 12. All the biosorbents recovered more than 50% Mn(II) adsorbed on RCPW. Nitric acid and sodium hydroxide showed close values of percentage recovery. EDTA and Sodium hydroxide showed the minimum and maximum percentage recoveries, respectively. Order of eluents in their increasing percentage recovery were EDTA < HCl < H_2SO_4 < HNO_3 < NaOH.

4. Conclusion

Current study shows that RCPW is a promising biosorbent for the sequestration of Mn(II) from dilute solution. As per Langmuir model, its capacity was 62.0 mg/g which makes RCPW a good biosorbent when compared with other biomaterials as shown in Table 3. Application of pseudo-second-order kinetic and pore diffusion model showed that rate of biosorption of Mn(II) onto RCPW was second-order and govern by film diffusion as well as intraparticle diffusion. A comprehensive analysis on the effect of various engineering parameters revealed that biosorption of Mn(II) by RCPW was optimum at 6.5 pH, 0.05 g dose, 100 rpm, 30°C. It was possible to recover Mn(II) by the application of different acidic, basic, and complexing agents but 0.1 N NaOH showed best recovery.

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