Chromium (VI) Ion Adsorption onto Maleic Acid Red Onion Skin Extract Resin (MRER) in Aqueous Solution

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Abstract. Feasibility studies on the thermodynamics of Cr (VI) ions adsorption in aqueous medium by maleic acid red onion skin extract resin (MRER) was undertaken. The acetone extract of red onion skin was used in the synthesis of MRER. The regression analysis of the models at different temperatures and concentrations was found to closely fit the experimental data in the order: Freundlich > Langmuir > Temkin. Investigation of the thermodynamics of adsorption reaction revealed values for the change in enthalpy (- 34.05414 kJ/mol), Gibbs free energy (-18.001, -17.362, -17.860, -15.809 and -16.154 kJ/mol) and entropy (-52.7839 J/K/mol), which reflected the process spontaneity, exothermic nature and feasible affinity of the interacting metal ions at the adsorption sites. Dubinin-Radushkevich (DR) isotherm was applied in studying the sorption pathway, and it was observed that physisorption is the dominant pathway. Kinetic study showed that pseudo-second order best describe the experimental data with respect to its highest correlation coefficient (R^2) values.

Keywords: maleic acid, adsorption capacity, chromium (VI) ion, Freundlich isotherm, pseudo-second order, *Allium cepa*

Introduction

Allium cepa (globally called onion) is cultivated worldwide. It is regarded as one of the oldest and most frequently cultivated edible plant and among one of the richest source of phenols and flavonoids (Slimestad *et al*., 2007). *A. cepa* is a vegetable with long history of medicinal use. The fleshy bulb which grows below the ground (usually used as spice) and other parts of the plant have found importance in traditional medicine (Downes *et al*., 2010; Abayomi and Terry, 2009). *A. cepa* generates large quantities of waste (for example, 450,000 tonnes of onion is generated yearly in European Union) which necessitated its management (Salak *et al*., 2013). Its waste evolves pungent smell and enhances the growth of phytopathogen; thus it cannot be used for fodder and land fill disposal (Roldan *et al*., 2008). However, it contains large moisture content, thus making it disposal by combustion expensive (Salak *et al*., 2013). Oancea *et al*. (2013) and Hwang *et al*. (2008) worked on the peel of *A. cepa* and the results of their study showed that it contains large amount of flavonols, flavones and anthocyanidins. Quercetin is the common flavonol aglycone but it usually exists as glycosides, quercetin-3,4-diglucoside and quercetin-4-glucoside (most

abundant making up to 80-85% of the total flavonoid) (Lindahl *et al*., 2013).

Heavy metals are chemical elements that possess a relatively high density (Bailey *et al*., 1999). Presence of these metallic elements in undesirable forms in the environment is known as heavy metal pollution (Bose and Hemantaranjan, 2005). Heavy metals are toxic to living organisms at excessive concentrations, density greater than 5 g/cm^3 and atomic weight higher than 23 in their elemental form (Bose and Hemantaranjan, 2005). Most of the heavy metals are known to be toxic and half of these, including chromium, cadmium, silver, zinc, selenium, nickel, mercury, lead, copper and cobalt are released into the environment in quantities that pose risk to human health (Misra and Mani, 2009).

Heavy metal contamination exist in aqueous waste streams from diverse industries such as metal plating manufacturing, batteries, as well as agricultural sources where fertilizers and fungicidal sprays are intensively used. Pollution of marine ecosystem and terrestrial surroundings by heavy metals has escalated, resulting to some of the world's environmental and public health problems. This is due to the fact that these metals are persistent, very difficult to break down into smaller biodegradable fractions and bio-accumulate (Ralkwar *et al*., 2008). Heavy metals are non-biodegradable, thus

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builds up in important organs when ingested and get accumulated through the food web leading to poisoning of the living organisms (Cha *et al.*, 1997).

Chromium belongs to the group of refractory metals, which comprises all metals with a higher melting point than platinum (1,772 °C). Naturally occurring chromium is composed of three stable isotopes ^{52}Cr, ^{53}Cr and ^{54}Cr with ^{52}Cr being the most abundant (83.8%). Chromium is mined as chromite, $FeCr_2O_4$, the single commercially viable ore. Chromium exhibits a wide range of oxidation states from -4 to +6, where +3 state is the most stable energetically. The +3 and +6 states are most commonly observed in chromium compounds. The main field of application of chromium is Ferrochrome with 95.2%. Other applications have only low-volume uses: foundry 2.4%, chemicals 1.6%, refractory 0.8%. Water-insoluble Cr (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of Cr (VI) have been known for a long time. Cr (VI) has not been established as a carcinogen when in solution, although it may cause allergic contact dermatitis (ACD). Cr (VI) compounds are widely-used in industrial chemicals and are recognized human carcinogens. Chronic occupational exposure to hexavalent chromium causes DNA damage, respiratory diseases and lung cancer in electroplating workers (Misra and Mani, 2009).

The reduction of the pollutants to an acceptable level is necessary when toxic metals are present in aquatic systems. Methods have been introduced for elimination of these metals from aqueous media which include chemical precipitation, ion exchange, electrodialysis, solvent extractions, coagulation, evaporation and adsorption (Mohamadi *et al.*, 2015; Garba and Afidah, 2014; Garba *et al.*, 2014, Mohan *et al.*, 2008). Adsorption method has been considered the most flexible and easy for removing heavy metals from waste waters (Garba *et al.*, 2015; Cao *et al.*, 2014) due to much less sludge disposal problems.

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the convectional adsorbents, from environmental and the economical point of view. Different adsorbents were described in the past for uptake of heavy metal ion; however new adsorbents with great availability, high adsorption capacity as well as economic suitability are still required. Chemically synthesized plant waste, as well as its extracts have been studied as adsorbent for

heavy metal elimination; some of which include: peanut and walnut shells (Johns *et al.*, 1998), pineapple peel (Mohammed, 2014), pomegranate peel (Masoud, 2013), rice straw (Gao *et al.*, 2008), rice husk (Kumar and Bandopadhayay, 2006), maple sawdust (Yu *et al.*, 2001), soybean hull (Marshall and Wartellely, 2003), corn cob (Nada *et al.*, 2009), flax and cotton fibre (Marshall *et al.*, 2007), orange mesocarp (Ibezim-Ezeani 2012; Ogali *et al.*, 2008), cellulose (Thanh and Nhung, 2009), plantain peel (Zaharaddeen *et al.*, 2016), banana peel, orange peel, maize tassel, onion and garlic skins (Ibezim-Ezeani and Ikodiya, 2017; Kumara, 2013; Avisha *et al.*, 2012; Zvinowanda *et al.*, 2009).

This research is aimed to evaluate the effectiveness and capacity of modified red onion skin extract for the uptake of chromium (VI) metal ions from aqueous medium through adsorption of ions, thus producing low cost resin that is green chemistry oriented.

Materials and Methods

Sample collection and preparation. The onion skin was collected at mile 1 market in Port Harcourt, Rivers State, Nigeria. The samples were preserved in a clean plastic bag which was then transported to the laboratory for the research. The onion skin was hand sorted and washed with distilled water to remove debris. The sample was aired for three days at 29 °C to dry. The dried red onion skin was crushed into a fine powder with an electric milling machine, sieved to 150 µm particles sizes and stored in an airtight bottle prior to extraction process at 29 °C.

Extraction procedure. Extraction of pulverized red onion skin (235 kg) was carried out using Soxhlet extractor and acetone as the extracting solvent. The desired extract was recovered from the extract-solvent mixture using a rotatory evaporator.

Preparation of maleic acid red onion skin extract resin (MRER). Red onion skin extract (15 g) was placed in 100 mL of deionized water at 29 °C on magnetic hot plate stirrer for 30 min. Maleic acid (2.88 g) was added to the stirred mixture and the temperature of the mixture raised to 50 °C. Iodine (0.75 g) was introduced into the mixture and heating continued with the temperature of the water bath maintained at 50 °C for 2 h (Ikodiya *et al.*, 2016). The reaction system was then removed from the heating source and allowed to cool to 29 °C. A saturated solution of 30 mL sodium thiosulphate was added to the mixture and the brownish

colour of the iodine disappeared. The mixture was filtered and the residue washed with deionized water (100 mL, thrice). The resulting residue was oven dried for 4 h at 60 °C and preserved in an air tight container at 29 °C.

Adsorption capacity studies. Adsorption studies were carried out in batch equilibrium experiments to determine the adsorption capacity, effects of temperature, time and pH on the adsorption reaction. The experiment involves shaking 0.2 g of MRER in 20 mL of 60 mg/L of Cr (VI) ion solution in a mechanical shaker at 100 rpm with corked plastic bottle at 29 °C. The mixture was equilibrated for an hour and filtered with Whatman No.1 filterpaper.The filtrate was analysed with AAS (700 series) to ascertain the amount of metal ion adsorbed by MRER. The above experiment was repeated at agitation time (10 to 60 mins) and temperature (29 to 70 °C).

The effect of pH on the metal ion adsorbed was resolved by placing 0.2 g of MRER in 20 mL of 60 mg/L Cr (VI) ion solution at varied pH values (2, 4, 6, 8, 10 and 12). The adjustment of the pH was done by adding drops of 0.1 M HCl or NaOH into the metal solution. The solution in the corked plastic bottles were equilibrated at 29 °C for an hour and then filtered. The metal ion concentration in the filtrate was evaluated using AAS and the percentage ion adsorbed determined.

Analysis of metal ion adsorption capacity. The percentage amount of metal ion adsorbed was obtained by the difference between the initial metal ion concentration and that of the supernatant. Percentage Cr (VI) ion adsorbed by MRER was calculated using the following by equation.

$$\text{Metal ion adsorbed (\%)} = 100 \times (\frac{C_o\text{-}C_e}{C_o}) \ldots\ldots\ldots\ldots 1$$

The adsorption capacity (q_e) of MRER was ascertained by the mass balance from initial to equilibrium composition using the relationship in equation (2) and the values plotted against those of initial metal ion concentration.

$$q_e = V/M \times (C_o - C_e) \ldots\ldots\ldots\ldots\ldots\ldots 2$$

where:

C_o and C_e are the initial and final equilibrium metal ion concentration in solution (mg/L), respectively; V is the volume of the initial metal ion solution (L) and m is mass of MRER used (g).

Instrumentation: Scanning electron microscope (SEM coater model Q15ORES) was used to determine the morphology of the onion skin extract and that of the maleic acid red onion skin extract resin (MRER).

Results and Discussion

Adsorption studies. *Effect of pH:* Successful uptake of heavy metals in aqueous media relies on the establishment of a suitable pH range. The rate at which ions are adsorbed depends on the pH value of the media which directly influences the surface charge of adsorbing material, concentration of the metal ions on the active groups of the adsorbing material, rate of ionization and speciation of metal ions (Kannan and Murugavel, 2007).

The effect of pH on the metal ion adsorption with MRER is presented in Fig. 1. It was observed that at pH value of 2, the percentage metal ion adsorbed was 73.02% and this drastically increased to 98.25% at pH of 4. pH value of 4, 6 and 8 gave similar percentage ion adsorption of 98.25, 98.62 and 98.98%, respectively, while pH 10 gave the highest percentage metal ion adsorption of 99.97% (optimum pH). This suggests that the rate of metal ion adsorption would depend on the relative concentration of the exchangeable hydrogen, as well as the hydrogen ion concentration of the medium (Igwe *et al*., 2005). From the experimental results, it suggest that protons occupy almost all the active points at low pH value, thereby preventing the attraction of the metal ions to these points which in effect led to relatively lower percentage of metal ion adsorption. However, there might also be the possibility of competition between the protons and Cr (VI) ions resulting in lower adsorption of Cr (VI) ions (Hamead and Ahmand, 2009).

At high pH values of solution, there is a reduction in hydrogen (proton) concentration at the active points, causing the active points to be negatively charged as a result of the occurrence of hydroxide ions in the medium. This effect led to an increase in electrostatic interaction between the active points and the metal ions, thus favoring greater percentage of metal ion adsorption. Furthermore, when metal is in solution, it possesses a positive charge and will be attracted to the active point that is negatively charged at high pH, favoring metal ion adsorption. An increase in adsorption of metals with increase in pH values of solution was recorded in the
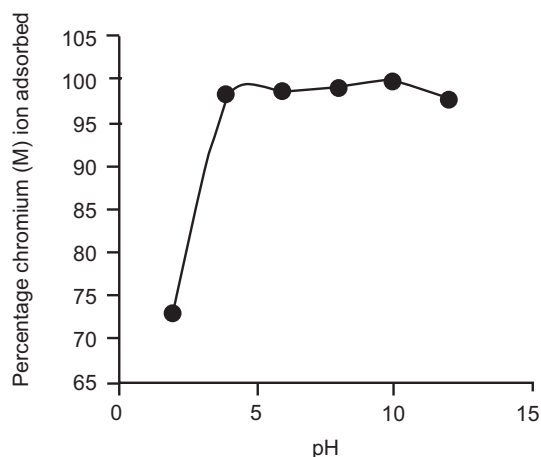
Fig. 1. Plot of percentage Cr (VI) ion adsorbed against pH.

research by Lakhveer *et al*. (2012); Shim *et al*. (2007) and Kadiavelu and Namasivayam (2003).

Effect of temperature. The effect of temperature on the adsorption of Cr (VI) ions onto MRER was investigated for 60 mg/L of initial metal ion concentrations at 29, 40, 50, 60 and 70 °C. It was observed that by increasing the temperature from 29 to 40 °C, the percentage removal of Cr (VI) ions increased from 78.83 to 97.65%. This showed that the adsorption process was endothermic in nature at this stage.

Further increase of the temperature from 40 °C to 50, 60 and 70 °C, showed that the percentage amount reduced gradually to 95.23, 94.93 and 90.73%, respectively; implying that exothermic reaction occured at these temperatures and that interaction between the adsorbate and adsorbents reduced. This could also be as a result of decrease in the surface area of the adsorbent due to temperature increase and its impact on the structural alignment of the adsorbent (Fig. 2).

Effect of agitation time. The result for the time dependent experiment on the adsorption of chromium (VI) ions at 29 °C is displayed in Fig. 3.

Agitation time effect on metal ion uptake was carried out by varying the agitation time (10 to 60 mins). The rate at which MRER adsorbed Cr (VI) ions increases steadily as the time variation increased. However, at 40 mins, the rate of metal ion uptake was maximum (98.37%), which was observed to be the optimum adsorption time for the experiment. Further increase in agitation led to reduction in Cr (VI) ions. It could be
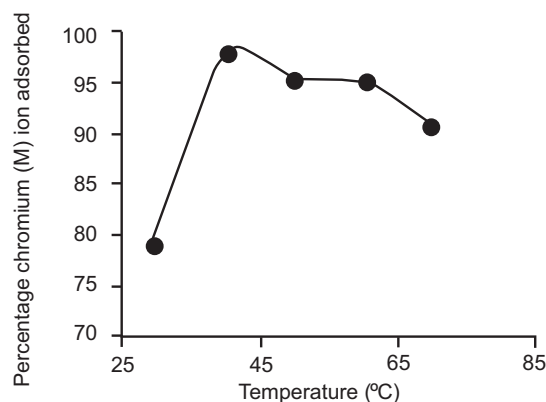

Fig. 2. Plot of percentage Cr (VI) ion adsorbed against temperature.
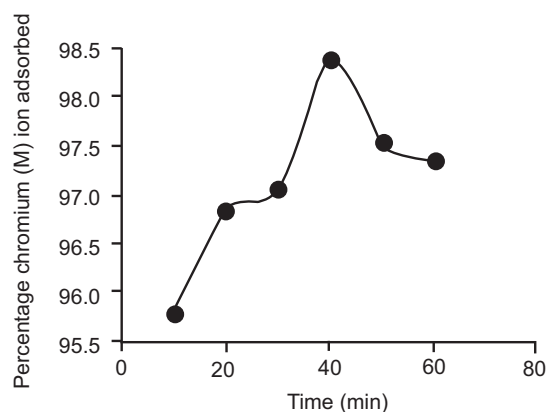

Fig. 3. Plot of percentage Cr (VI) ion adsorbed against time.

that available pores of MRER have been occupied by Cr (VI) ions before 40 mins.

Adsorption isotherm model. Adsorption isotherms describe the type of interaction that exist between sorbate and sorbents during an adsorption process when equilibrium state is attained (Shokoohi *et al*., 2009). Isotherm which describes the experimental data well was investigated by applying the equilibrium data evaluated at temperatures 29 to 70 °C to the linearized forms of Langmuir, Freundlich and Temkin models, (Ibezim-Ezeani and Anusiem, 2011; Langmuir, 1918; Freundlich, 1906)

Langmuir model assumes that sorption occurs in a homogeneous layer and can occur only at fixed sites and thus holding only one sorbate molecule at a time (monolayer). Hence, all sites are energetically equal

and transmigration of sorbate in the plane of the layer do not occur (Boukhiar *et al*., 2008).

$$q_e = \frac{1}{X_m b} + \frac{C_e}{X_m} \quad \text{..} \quad 3$$

Freundlich isotherm applies to sorption on heterogeneous layer. It assumes that the ratio of the amount of solute adhere unto a certain mass of sorbent to the solute concentration in solution is not constant at varied concentration (Oubagaranadin *et al*., 2007).

$$\text{In } q_e = \text{In } K_F + \frac{1}{n} \text{ In } C_e \quad \text{.......................................} \quad 4$$

Temkin isotherm assumes that decrease in the heat of sorption is linear and the sorption is characterized by a uniform distribution of binding strength (Buasri *et al*., 2012).

$$q_e = \frac{RT}{b_T} \text{ In } K_T + \frac{RT}{b_T} \text{ In } C_e \quad \text{...................................} \quad 5$$

where:

b, K_T and K_F are Langmuir, Temkin and Freundlich isotherm constants, respectively. 1/n is the activity strength of adsorption in the sorption process having values between zero and one. X_m, R, T are the monolayer adsorption capacity, universal gas constant and temperature, respectively. C_e is the equilibrium concentration of the solute in the solution (mol/L), q_e is the amount of solute adsorbed (mol/g) and b_T is related to the adsorption rate. The results for the adsorption isotherm models are presented in Fig. 3-6.

The correlation coefficient (R^2) values for the isotherm models explored in this study are presented in Table 1. Freundlich isotherm model gave the highest R^2 values for the study and thus fitted the experimental data from the sorption process.

Table. 1 Comparison of coefficient of determination (R^2) for the Isotherms

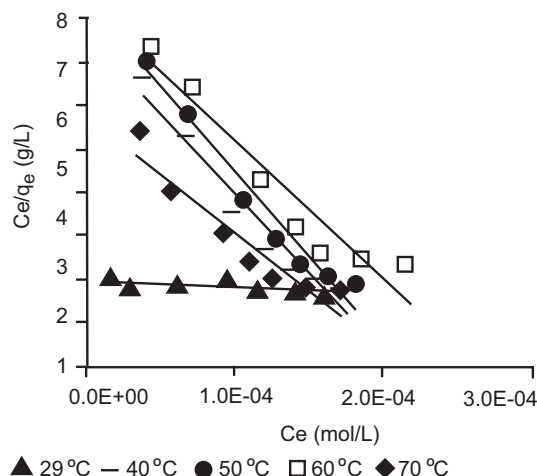| Temp(°C)	Langmuir	Freundlich	Temkin
29	0.7095	0.9863	0.9396
40	0.9186	0.9954	0.8547
50	0.9010	0.9629	0.7659
60	0.8953	0.9886	0.8509
70	0.8852	0.9824	0.8454

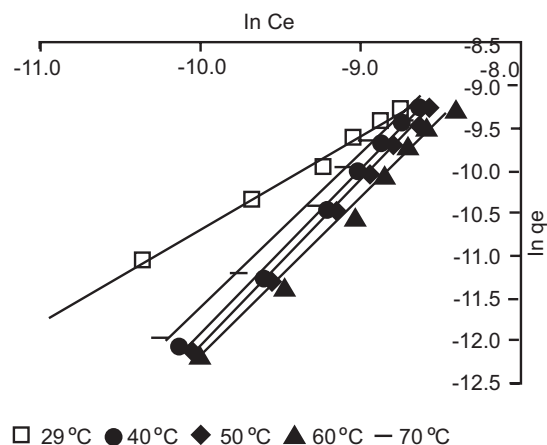**Fig. 4.** Langmiur isotherms at different temperatures.

Fig. 5. Freundlich isotherms at different temperatures.

Furthermore, it implied that MRER possess a heterogenic surface with respect to Freundlich isotherm. In addition, n, 1/n, K_F and ΔG at different temperatures studied were evaluated and their values are presented in Table 2.

Plot of In KF versus 1/T produces a linear plot (Fig. 7); ΔH and ΔS were deduced from the slope and intercept using equations (6), while equation (7) was applied for resolving ΔG.

$$\text{In } K_F = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \text{...} \quad 6$$

$$\Delta G = \text{-RT In } K_F \quad \text{...} \quad 7$$
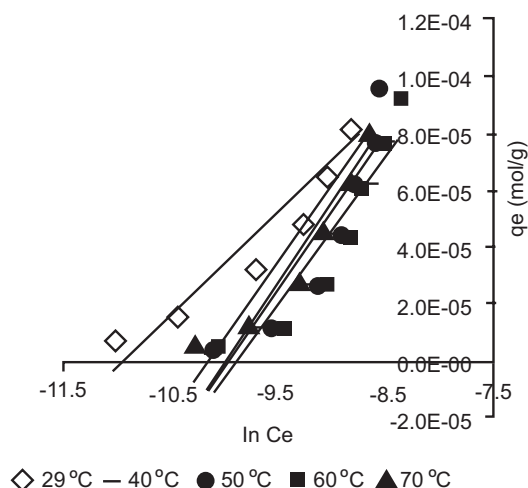
Fig. 6. Temkin isotherms at different temperatures.

Table 2. Freundlich constants and DG values at different temperatures.

	Freundlich constant			
Temp (°C)	n	1/n	K_F mol/g	ΔG kJ/mol
29	0.536	1.863	1299.19	-18.001
40	0.541	1.846	789.97	-17.362
50	0.542	1.844	772.70	-17.860
60	0.562	1.776	301.87	-15.809
70	0.581	1.720	288.47	-16.154
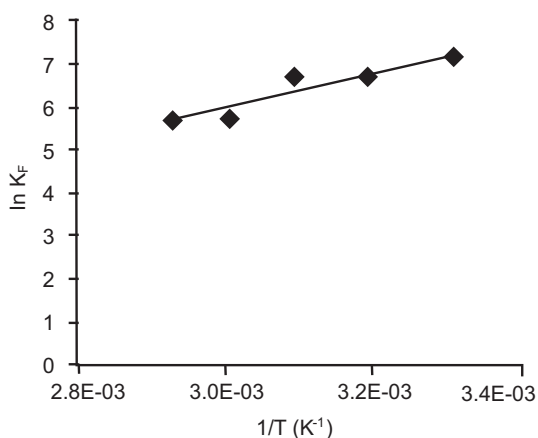
Fig. 7. Plot of In K_F against 1/T.

The ΔH and ΔS values as calculated from the slope and intercept of the graph in Fig. 7 are -34.05414 kJ/mol, and -52.7839 J/K/mol, respectively. The ΔG values evaluated at different temperatures are shown in Table 2. The negative ΔH values imply that exothermic sorption process occurred, while the negative ΔS value indicates reduction in disorderliness of reaction system during the sorption of Cr (VI) ions. Also, negative ΔG values signify the feasibility of the adsorption process at different temperatures studied.

Adsorption mechanism studies. The most likely mechanism (physisorption, particle diffusion or ion exchange) in which reaction followed for removal of Cr (VI) ions from an aqueous solution was investigated with the use of Dubinin-Radushkevich (DR) isotherm at different temperatures. The linear form of DR isotherm model is displayed in equation 8:

$$\text{In } q_e = \text{In } q_D - B_D\varepsilon^2 \text{ .... 8}$$

where:

q_D= maximum ion adsorption capacity (mol/g)
B_D =DR model constant (KJ/mol)
ε = Polanyi potential which is equivalent to RT In (1 + 1/Ce), R (J/mol/K) is the universal gas constant and T (K) is temperature. B_D is related to the mean free energy E, of sorption per mole of metal ion through equation 9:

$$E = \frac{1}{\sqrt{2B_D}} \text{ .... 9}$$

Plot of In q_e against ε^2 (Fig. 8) gave linear graph.

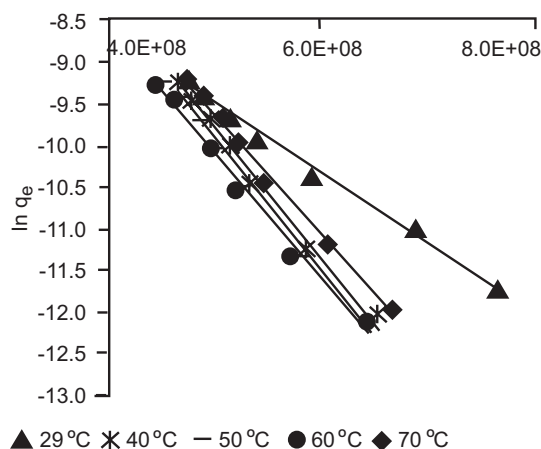The slope and intercept were used to deduce the values of B_D and q_D while the values of E were calculated by

Fig. 8. Plot of Dubinin-Radushkevich isotherm model at varying temperature.

Table. 3 Dubinin-Radushkevich constants, linear equations and R^2 values

Temp (°C)	Linear equation	B_D (mol^2/J^2)	q_D (mol/g)	E (kJ/mol)	R^2
29	y= -1.563E-08× - 1.6097	1.563E-08	0.1999	5.66	0.9905
40	y= -1.560E-08× - 1.9859	1.560E-08	0.1373	5.66	0.9928
50	y= -1.557E-08× - 2.1298	1.557E-08	0.1189	5.67	0.9579
60	y= -1.520E-08× - 2.5007	1.520E-08	0.0820	5.74	0.9948
70	y= -1.436E-08× - 2.4761	1.436E-08	0.0841	5.90	0.9794

inserting the value of B_D into equation (9). Table 3 contains the E values at different temperatures studied. However, it was observed that the E values were less than 8kJ/mol, which suggest that physisorption is the pathway which the reaction process followed.

Adsorption kinetic study. The kinetics of Cr (VI) ion adsorption by MRER was investigated by varying the concentration of ions adsorbed at different tempretures and time intervals. The kinetic data were analysed by applying pseudo-first order, pseudo-second order, Elovich and Intraparticle diffusion models to achieve a more reliable result and good understanding of the adsorption dynamic behaviour. Linear equations of the models are presented below.

$$Log\ (q_e\text{-}q_t) = Log\ q_e - \frac{k}{2.303}\ t \dots\dots\dots\dots\dots\ 10$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e^2}} + \frac{1}{q_e}\ t \dots\dots\dots\dots\dots\ 11$$

$$q_t = \frac{1}{\beta}\ \ln(\alpha\beta) + \frac{1}{\beta}\ \ln(t) \dots\dots\dots\dots\dots\ 12$$

$$q_t = K_p t^{1/2} + C \dots\dots\dots\dots\dots\ 13$$

The plots which were evaluated from the linear equations and from the experimental data are presented in Fig. 9-12. The corresponding R^2 values are presented in Table 4.

From the analysis, its was observed that the values of R^2 for pseudo-second order model are higher than those of other models. Therefore, the kinetic adsorption data fits well to the pseudo-second order model. The pseudo-second order rate constant (k_2) and q_e were determined from the slope and intercept of the plots. A plot of In k_2 against 1/T at various temperatures was plotted
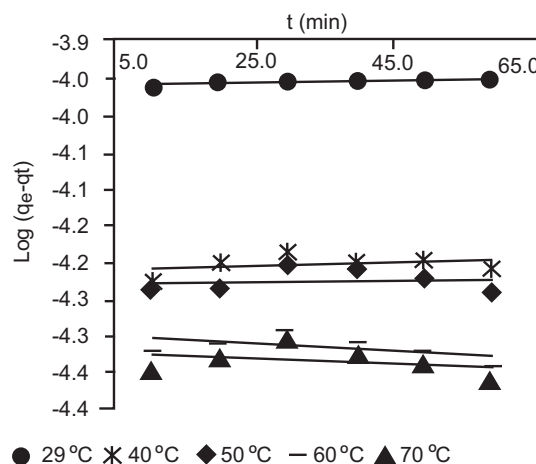
Fig. 9. Plot of first order kinetic model at varying temperature.
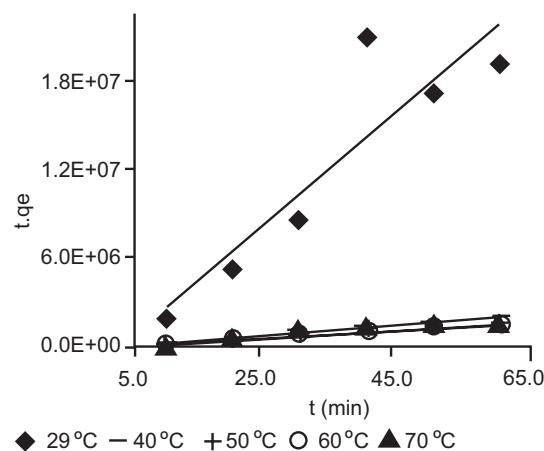
Fig. 10. Plot of second order kinetic model at varying temperature.

(Fig. 13) and from the plot, the pre exponential factor (A) and activation energy (Ea) was determined with regards to the slope and intercept. The pre exponential factor was observed to be 3.2554×105 g/mol/min while the activation energy was 796.290 kJ/mol.
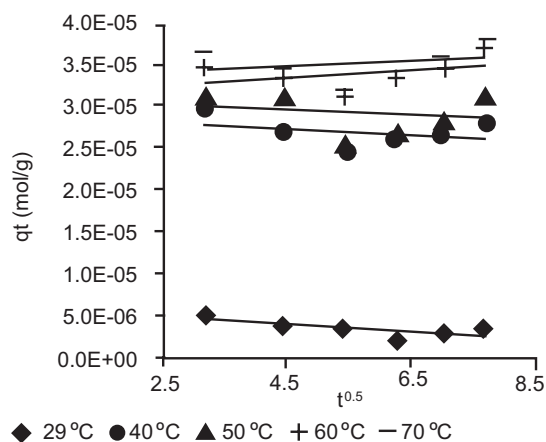
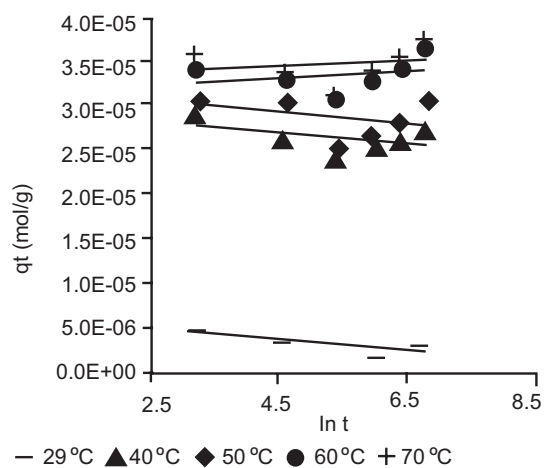**Fig. 11.** Plot of intraparticle diffusion kinetic model at varying temperature.

Fig. 12. Plot of Elovich kinetic model at varying temperature.

Table 4. Comparison of coefficient of determination (R^2) for the Isotherms

Temp (°C)	Pseudo-first order	Pseudo-second order	Intraparticle diffusion	Elovich
302	0.4868	0.8130	0.5775	0.6568
313	0.0834	0.9832	0.1523	0.2504
323	0.0231	0.9773	0.0592	0.1090
333	0.2497	0.9773	0.1514	0.0781
343	0.1481	0.9857	0.0710	0.0221

Scanning electron microscope gives details of the surface properties and morphology of the samples. Particle size used for this analysis was 400 μm for all samples. Figure 14(a-c) displays the SEM images for unmodified and
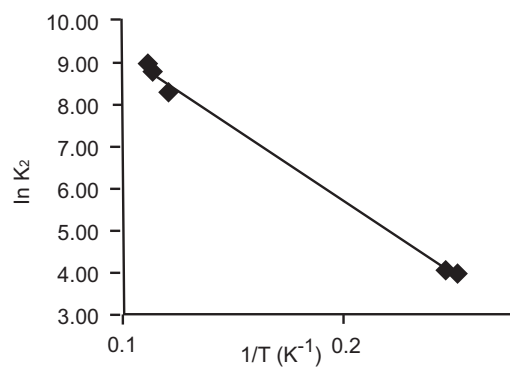

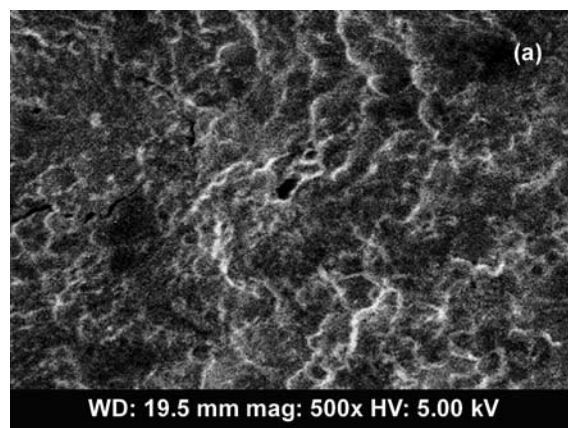**Fig. 13.** Plot of In K_2 against 1/T.

Fig. 14(a). SEM image of unmodified red onion skin extract..
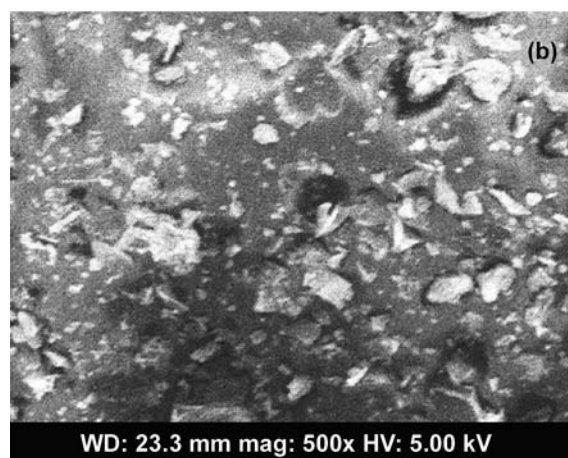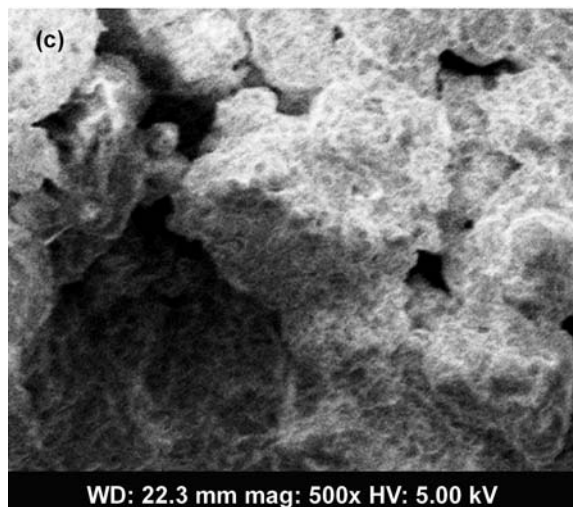

Fig. 14(b). SEM image of MRER.

Fig. 14(c). SEM image of MRER after adsorption of 60 mg/L Cr (VI) ions.

maleic acid modified red onion skin extract resins. Figure 14(a) shows that the unmodified red onion skin extract possess smooth surface structure which implies that it has a smaller surface area and its pores where adsorption of metal ions could take place are few. Figure 14(b), showed that the surface structure of the adsorbents changed on modification with maleic acid. It can be observed that the surface property of MRER (Fig 14 b) possess irregular shapes implying that the resin have large surface area as compared to the unmodified extract resin and has more pore spaces for adsorption of metal ion. Figure 14(c) showed MRER after adsorption of metal ions. Observation shows that some of its pores have closed up due to the fact that the pores now contain metal ions thus, making it relatively smooth as compared to the unadsorbed MRER.

Conclusion

Chemical treatment of red onion skin extract with maleic acid, increased its efficiency towards adsorption of Cr (VI) ion from aqueous solution. The adsorption capacity studies showed that agitation time, pH and temperature affected the rate at which Cr (VI) ion was adsorbed from aqueous solution by MRER. Thermodynamics studies conducted at temperatures 29 to 70 °C showed that Freundlich isotherm model gave best fit for the experimental data; indicating that MRER possesses a heterogeneous surface; while from the kinetic studies, it was observed that pseudo-second order kinetic best

described the kinetic reaction. However, the adsorption process was observed to be feasible with respect to the negative ΔG (kJ/mol) values at all temperatures following the sequence: -18.001 (29 °C), -17.362 (40 °C), -17.860 (50 °C), -15.809 (60 °C) and -16.154 (70 °C).The results obtained from fitting the experimental data into the Dubinin-Raduskevich isotherm model showed that the major sorption pathway for the sorption process is physisorption. The SEM analyses of MRER revealed that the synthesized resin possesses larger and more active pore spaces than the unmodified red onion skin extract sample making it possible for adsorption of metal ion in aqueous solution. The synthesized adsorbent can be further used for removal of other heavy metals.

Acknowledgement

Conflict of Interest. The authors declare no conflict of interest

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