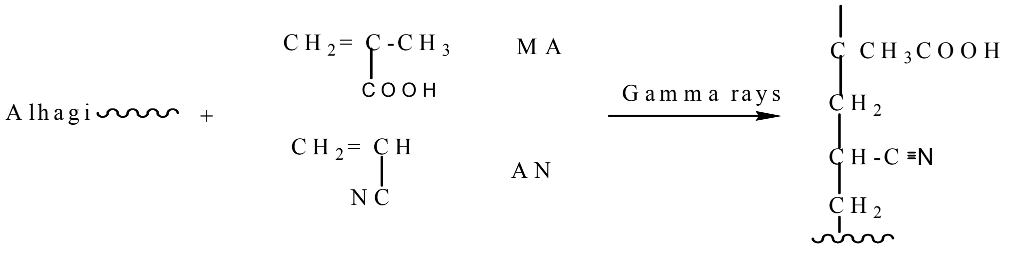
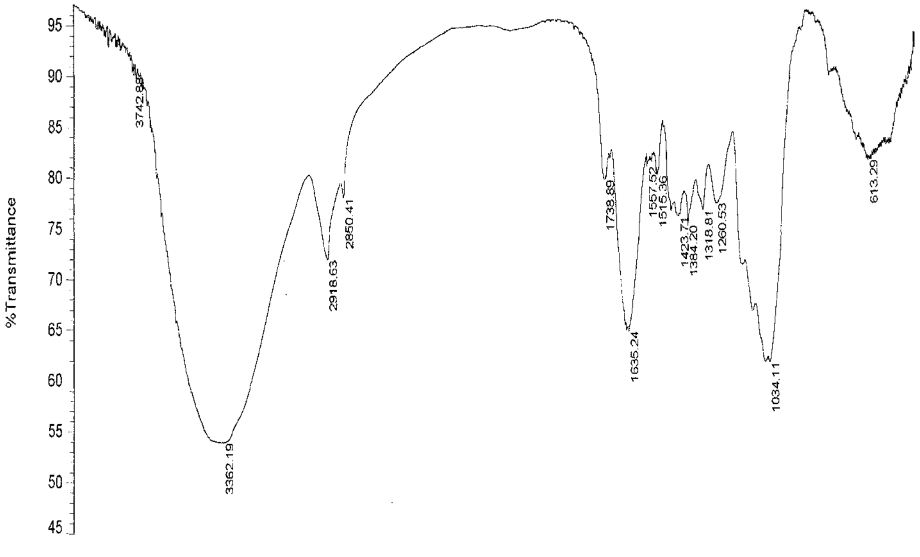
3. Results and Discussion

3. 1. FT-IR spectroscopy

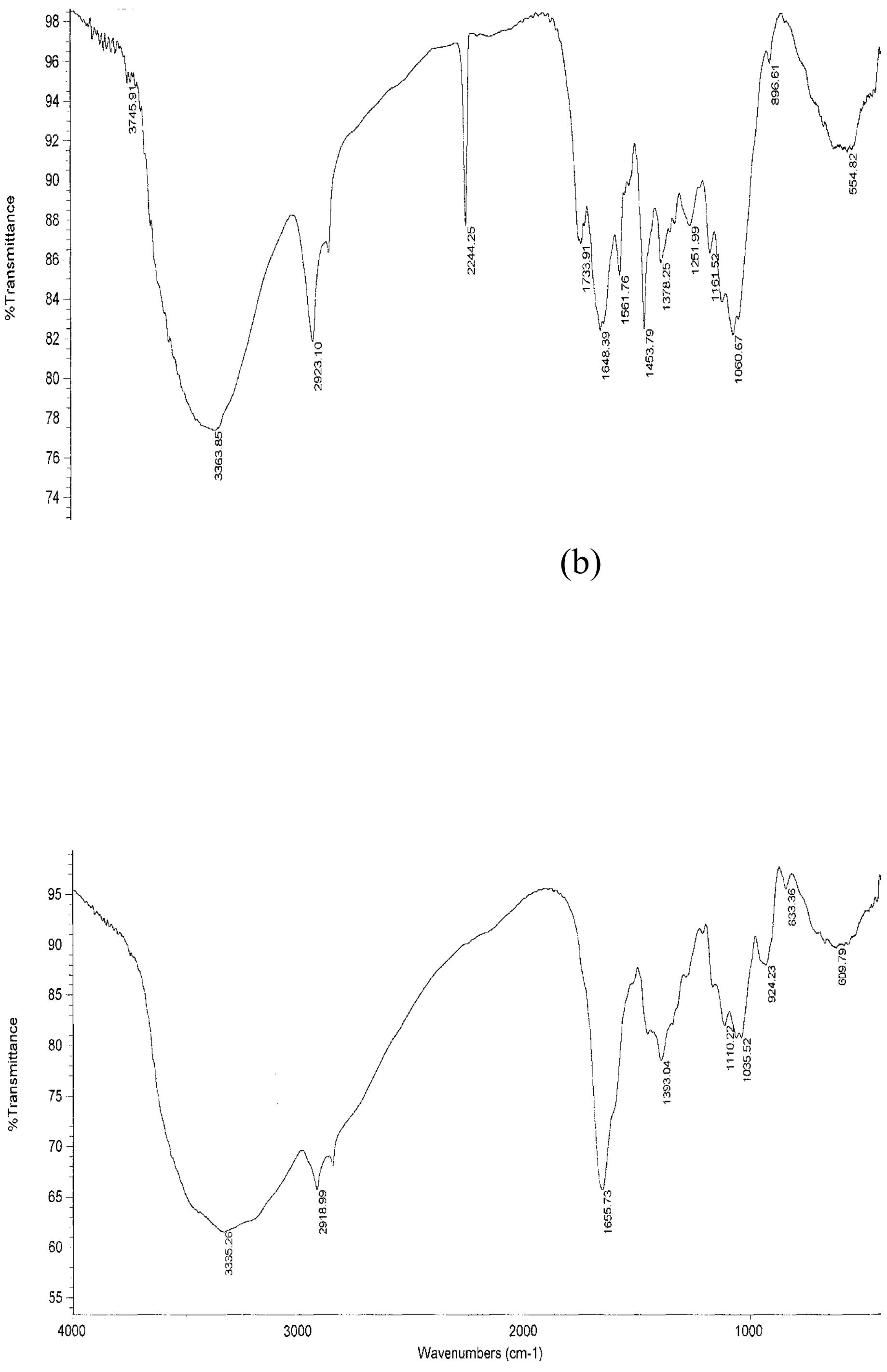
Fig. 1 shows the FT-IR spectra of native Alhagi residues (1a), grafted Alhagi residues (1b) and amidoximated Alhagi residues (1c). The FT-IR spectra in Fig. 1b shows the appearance of a new absorption peak (sharp peak) at 2244.25cm^{-1}, which is attributed to the cyanide (-CN) groups. This testifies to the existence of a grafting reaction of Alhagi residues with AN as shown in Scheme 1. Fig. 1a also shows one peak at 1635.24 cm^{-1} corresponds to the carbonyl group. This peak is shifted to one peak at 1648.39cm^{-1}corresponds to carbonyl of carboxyl indicating the grafting of Alhagi residues by MAA (Scheme 8). The FT-IR spectra in Fig. 1c shows that the disappearance of the cyanide peak and appearance of new absorption peak at 1655.73 cm^{-1} corresponding to the stretching vibration of the C=N bond.



Scheme 8: Reaction mechanism of grafting of (MAA/AN) onto Alhagi residues using γ-radiation.



(a)

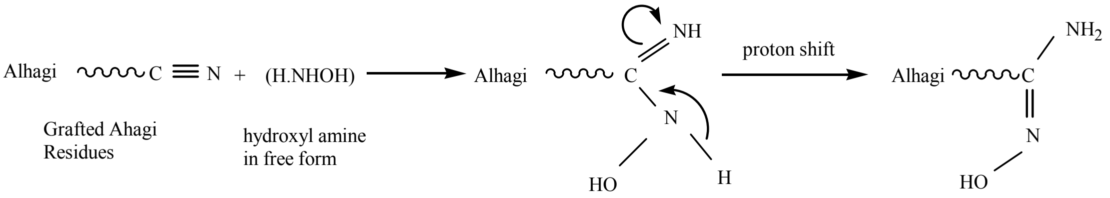


(b)

(c)

Figure 1: FT- IR spectra of (a) Alhagi residues, (b) grafted Alhagi residues and (c) amidoximated Alhagi residues.

These results clearly show the conversion of the original cyanide groups to amidoxime groups through the treatment with hydroxylamine. The reaction mechanism of conversion of cyanide groups of grafted Alhagi residues to amidoxime groups via reaction with hydroxylamine hydrochloride in alkaline solution was shown in scheme 9.

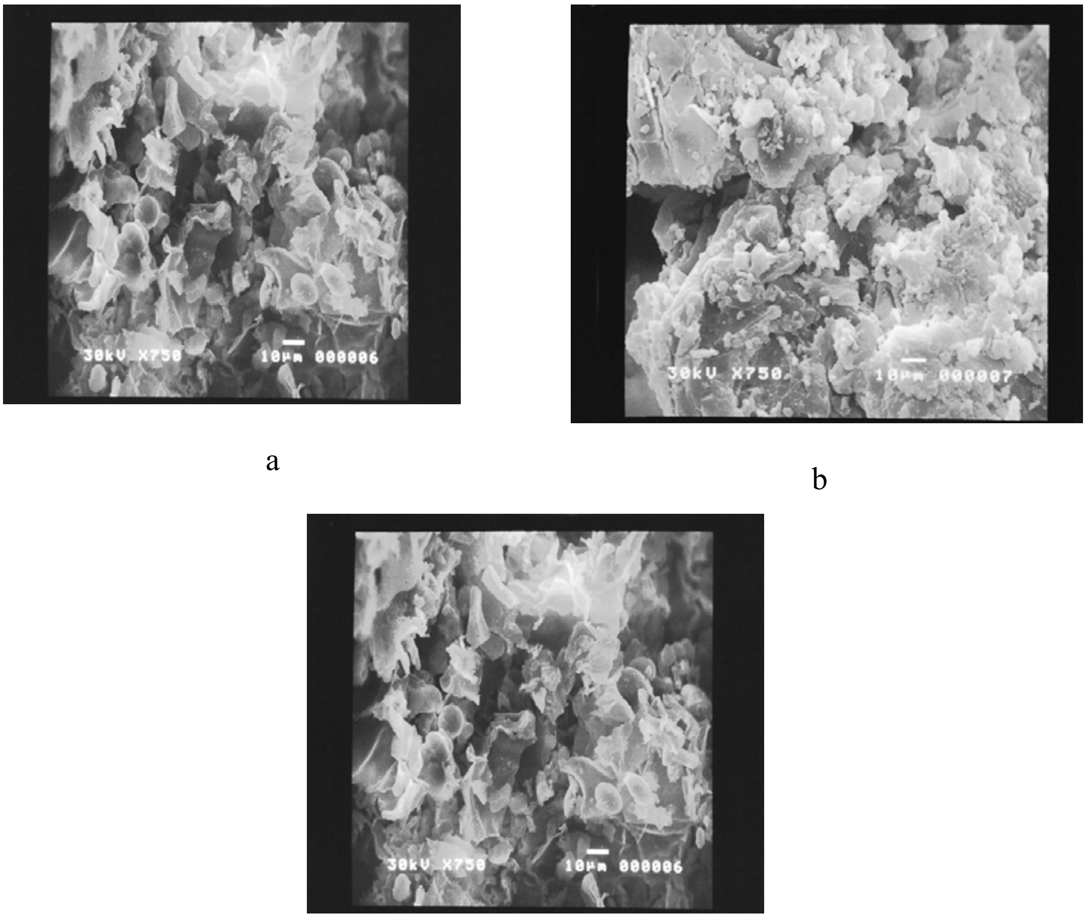


Scheme 9: Reaction mechanism of conversion nitrile groups in grafted Alhagi residues to amidoxime groups to obtain amidoximated Alhagi residues.

3. 2. Surface morphology

Figure 2 depicts the surface morphology of (a) the ungrafted Alhagi residues, (b) the poly (AN/MAA)–Alhagi residues and (c) amidoximated Alhagi residues.

Comparison of Figures 2(a) and 2(b) shows that grafting process led to a pronounced swelling of Alhagi residues, with the diameter of each individual granule appearing somewhat greater than that shown for the ungrafted Alhagi. Figure 2(c) shows further swelling of amidoximated poly (MAA/AN)–grafted Alhagi residues resulted from treatment of grafted Alhagi residues with hydroxyl amine in alkaline medium.



a

b

C

Fig. 2: SEM of Ahagi (a), grafted Alhagi (b) and amidoximated Alhagi (c).

3. 3. Factors affecting grafting reaction

3. 3. 1. Effect of irradiation dose

Table 7 shows the graft yield % as a function of radiation dose and monomer composition. It is clear from this table that the graft yield % increase by increasing radiation dose from 5 to 10 kGy and then remained constant for higher radiation doses (15-20 kGy).

Enhancement in the graft yield % by increasing radiation dose from 5 to 10 kGy is probably due to increased initiation. On the other hand, a higher radiation dose above 10 kGy cause a levelling off of the graft yield % due to an increase in the number of cellulose radical of Alhagi residues prior to MAA/AN addition. Furthermore, homopolymer formation at higher radiation dose which competes with the grafting reaction for available monomers could lead to the levelling of the graft yield % in the grafted products.

3. 3. 2. Effect of comonomer concentration and composition

Table 7 also shows the graft yield % versus comonomer composition when MAA/AN was grafted on Alhagi residues using gamma radiation as initiation system. Obviously, the graft yield % increases by increasing comonomer composition up to 60/40(MAA/AN, wt/wt) and then decreased.

The significant enhancement in graft yield % by increasing the comonomer composition could be attributed to greater availability of MAA/AN molecules in the vicinity of cellulose molecules in Alhagi particles. It is understandable that cellulose hydroxyls in Alhagi (sites for grafting) are immobile and therefore, their reaction would depend upon availability of MAA/AN molecules in the proximity of these hydroxyl groups.

The decrement in graft yield % by increasing comonomer composition above 60/40 (MAA/AN) could be attributed to the decrease in hydrophilicity of the polymer matrix. This indicates that the reactivity of AN towards grafting of Alhagi is less than MAA.

Table 7: Effect of co-monomer ratio at different radiation dose on graft yield % of poly (MAA/AN)-grafted Alhagi residues

MAA: AN Ratio	Graft Yield %			
	RD[*] (5 kGy)	RD (10 kGy)	RD (15 kGy)	RD (20 kGy)
20:80	12	28	28	28
30:70	17	36	36	36
40:60	22	45	45	45
50:50	28	50	50	50
60:40	45	70	70	70
70:30	38	60	60	60
80:20	32	55	55	55

[*] RD is radiation dose (KGy)

3. 4. Factors affecting the adsorption of Zn(II) ions onto amidoximated Alhagi residues

3. 4. 1. Effect of cation type

The effect of type of cation on adsorption capacity was investigated using different metal cations such as Hg(II), Pb(II) and Zn(II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at 30°C.

The data indicate that the adsorption capacity values depend on the metal cations used.

The adsorption capacity for these heavy metal ions follows the following order:

Zn (II) > Hg (II)> Pb (II)

The difference in adsorption capacity of these metals ions on amidoximated poly (MAA/AN)-grafted Alhagi residues could be attributed to the difference in solubility constants of the formed complexes [108].

For this reason, amidoximated poly (MAA/AN)-grafted Alhagi residues was Utilized for the removal of Zn (II) from aqueous solution in this study.

According to the values of adsorption capacities as shown in Table 8, Zn metal was selected as adsorbate in this study.

Table 8: Effect of cation type on their adsorption capacity onto amidoximated poly (MAA/AN) –grafted Alhagi residues at 30°C.

Metal Cations Used	q_e(mg/g)
Hg(II)	146
Pb(II)	170
Zn(II)	200

Adsorption Conditions: Metal cations conc., 300mg/l ; pH,4; agitation time ,2h; adsorption temperature,30°C; particle size range, 50-125µm.

3. 4. 2. Effect of pH

Figure 3 shows the adsorption capacity of Zn (II) ions onto amidoximated Alhagi residues as a function of the pH of the adsorbate at fixed adsorbent concentration, fixed agitation time and fixed adsorbate concentration at 30°C. It is clear from this figure that the adsorption capacity of amidoximated Alhagi residues towards Zn (II) ions increased on increasing the pH value from 3 to 5 and then decreased with a further increase in pH. Under highly acidic conditions (pH = 2), the adsorption capacity towards Zn(II) ions was a minimum because the metal ion binding sites on the adsorbent were mainly occupied by H_3O^+ ions, which restricted the approach of Zn(II) cations as a result of repulsive forces. However, as the pH value of the solution increased, the number of associated H_3O^+ ions diminished, exposing an increasing proportion of the negatively charged adsorbent surface and thereby allowing an increasing number of positively charged Zn (II) ions to be adsorbed. The decrease in the adsorption capacity of amidoximated Alhagi residues towards Zn (II) ions at pH > 5 may be attributed to a decrease in the positive charge associated with the zinc species. At pH values above 5, no further adsorption occurred due to the precipitation of Zn (II) ions as $Zn(OH)_2$.

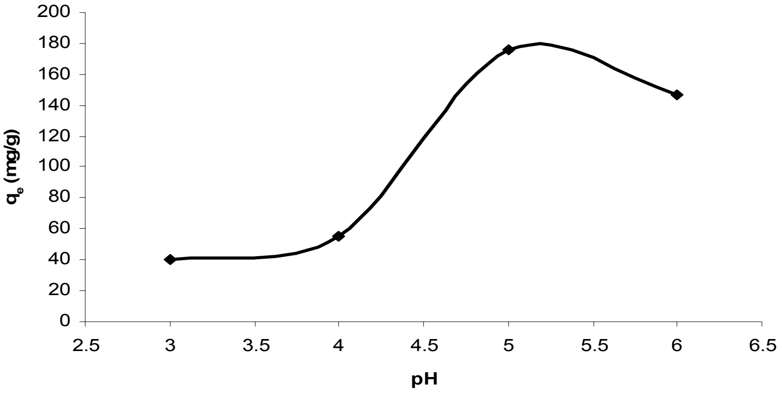


Fig. 3: Effect of pH on adsorption capacity of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues.

3. 4. 3. Effect of adsorbent dose

The dependence of adsorption capacity of Zn (II) ions by amidoximated Alhagi residues on the adsorbent dose was studied by varying the adsorbent dose over the range 0.5–8.0 g/ℓ at 30°C (Figure 4). It is clear from Fig. 4 that the adsorption capacity of Zn (II) ions by amidoximated Alhagi residues decreased from 126.6 mg/g to 28.4 mg/g on increasing the adsorbent dose from 0.5 g/ℓ to 8.0 g/ℓ. The decrement in adsorption capacity of Zn (II) with increasing adsorbent dose is mainly due to overlapping of the adsorption sites as a result of the overcrowding of adsorbent particles and also due to the competition among Zn (II) ions for the sites on the adsorbent surface [109].

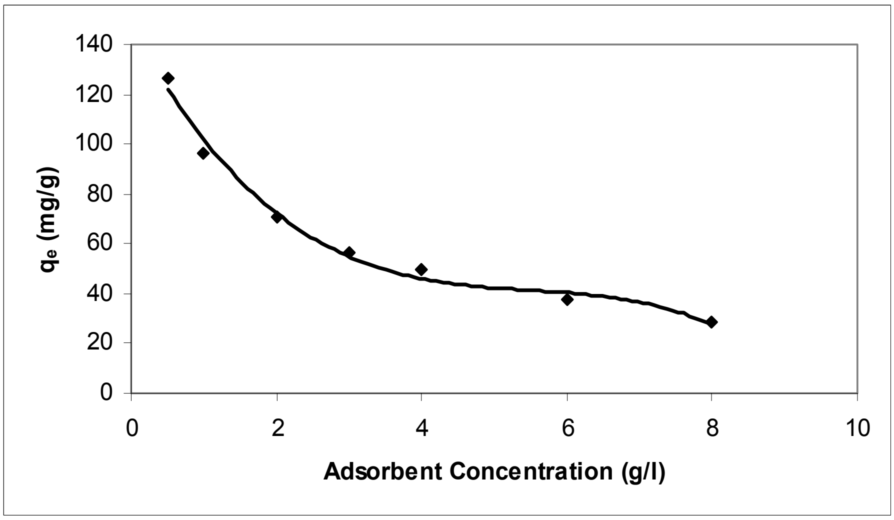


Fig. 4: Effect of adsorbent dose on adsorption capacity of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues.

3. 5. Effect of adsorbate solution

3. 5. 1. Adsorption isotherms

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. By plotting the solid-phase concentration against the liquid-phase concentration, it is possible to depict the equilibrium adsorption isotherm graphically.

Figure 5 shows the adsorption isotherm of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures (30, 40 and 50^{o}C). In order to optimize the design of an adsorption system to remove heavy metal ions from effluents, it is important to establish the most appropriate correlation for the equilibration curve. There are many theories associated with adsorption equilibration. Two isotherm equations have been tested in this study, viz. that of Langmuir and of Freundlich.

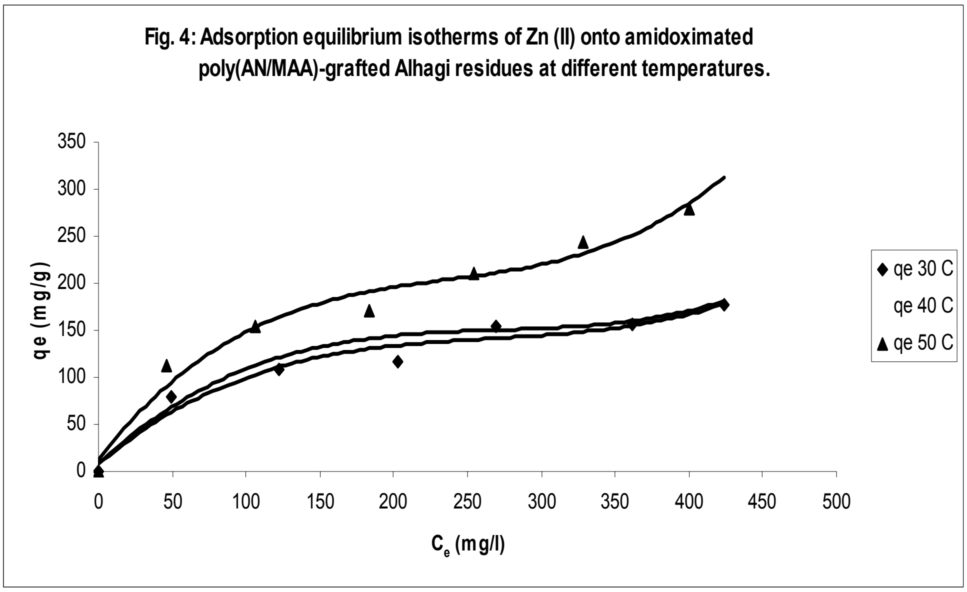


Fig. 5: Adsorption equilibrium isotherms of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures.

The Langmuir treatment is based on the assumption that maximum adsorption corresponds to the formation of a saturated monolayer of adsorbate molecules on the adsorbent surface, that the adsorption energy is constant and there is no transmigration of the adsorbate in the surface plane. The Langmuir model [110] may be represented as follows:

$$q_e = \frac{k_L C_e}{1 + a_L C_e} \qquad (5)$$

where C_e is the equilibrium concentration of Zn (II) ions (mg/ℓ) and q_e is the amount of zinc adsorbed (mg/g), while constants k_L and a_L are the Langmuir constant (ℓ/g) and Langmuir isotherm constant (ℓ/mg), respectively. It is possible to represent equation (5) in a linearized form as shown in equation (6):

$$\frac{C_e}{q_e} = \frac{1}{k_L} + \frac{a_L}{k_L} C_e \qquad (6)$$

This equation predicts that a plot of C_e / q_e versus C_e should give a straight line for three temperatures (see Figure 6) with a slope of a_L/K_L and intercept of $1/K_L$.

The linearized Langmuir model was applied to the experimental data arising from the adsorption of Zn (II) ions onto amidoximated Alhagi residues. The Langmuir constants of adsorption of Zn (II) onto amidoximated Alhagi residues at three temperatures are listed in Table 9. The relationship between K_L and Q_{max} is given by the following equation:

$$k_L = Q_{\max} . b \qquad (7)$$

where b is the Langmuir constant (ℓ/mg) related to the energy of adsorption.

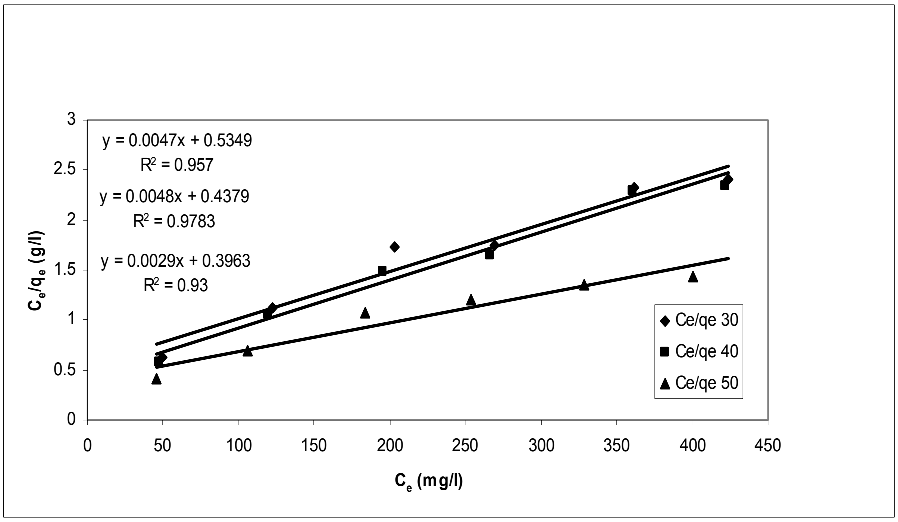


Fig. 6: Langmuir adsorption plots of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures.

Table 9: Langmuir adsorption plots of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures

pH	Temp. (◦C)	Q_{max} (mg/g)	b (l/mg)	R^2
5	30	212.7659	0.0087866	0.957
	40	208.3333	0.010961	0.9783
	50	344.8275	0.0073176	0.93

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by Equation (8):

$$R_L = \frac{1}{(1 + bC_o)} \qquad (8)$$

where C_0 is the initial concentration of Zn (II) ions (mg/g) employed. According to Hall *et al.* [111]. The values of R_L obtained at three temperatures in the present study are listed in Table 5.

It is clear from the data in Table 10 that the values of R_L in the present study lay between 0.165 to 0.561, 0.137 to 0.506 and 0.192 to 0.606 for 30, 40 and 50 ^{o}C, respectively, indicating that the adsorption of Zn(II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures were favourable.

Table 10: R_L values based on Langmuir equation of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures

Initial conc., C_o of Zn (II) (mg/l)	R_L values		
	Temp. (^{0}C)		
	30	40	50
88.98295	0.5612	0.50625	0.60564
176. 1312	0.3925	0.3412	0.4369
261.4448	0.30328	0.25868	0.34327
346.7583	0.2417	0.2083	0.2827
439.4107	0.2057	0.1719	0.2372
511.8813	0.18189	0.15127	0.2107
576.0958	0.165	0.1367	0.1917

The maximum adsorption capacity, Q_{max}, of Zn(II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues were 212.8, 208.3 and 344.8 mg/g for

30, 40 and 50 ^{o}C, respectively compared with a negligible value (not shown) for the poly(MAA/AN)–grafted Alhagi residues. The enhancement of the adsorption capacity of Zn (II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues could be attributed to the presence of –COOH groups resulted from grafting of Alhagi with MAA and amidoxime group resulted from treatment of –CN groups in the grafted sample by hydroxylamine hydrochloride as well as chelation between the election-donating oxygen- and nitrogen-containing groups in amidoximated poly (MAA/AN)-grafted Alhagi residues and the electron-accepting Zn(II) ions. The fact that the value of the correlation coefficient, R^2, was > 0.92 for three temperatures indicate that the adsorption of Zn (II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues was well fitted by the Langmuir isotherm.

The value of the correlation coefficient, R^2, for all temperatures used is over than 0.92, indicate that the adsorption of Zn (II) by amidoximated poly (MAA/AN)-grafted Alhagi residues fits well on the Langmuir isotherm (obeys the Langmuir isotherm).

The adsorption capacity Q_{max} increased with increasing temperature, i.e. temperature has favourable effect on adsorption process. The increase in adsorption capacity of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at higher temperature may be attributed to chemo-sorption rather than physo-sorption due to presence of ionic bonds between cations in Zn (II) ions in solution and anionic groups in amidoximated poly (MAA/AN)-grafted Alhagi residues (ion exchange mechanism).

The Freundlich model [112] was also applied to the adsorption of Zn (II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures. This model can be used for non-ideal adsorption that involves heterogeneous sorption. The Freundlich equation is basically empirical and can be represented as shown in Equation (9):

$$q_e = k_F C_e^{1/n} \tag{9}$$

while equation (9), in turn, can be linearized to give:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{10}$$

where q_e is the amount of Zn(II) ions adsorbed on the surface of amidoximated poly (MAA/AN)-grafted Alhagi residues (mg/g), C_e is the equilibrium concentration of Zn(II) ions (mg/ℓ). K_F is a system constant related to the bonding energy. It represents the quantity of zinc adsorbed onto the surface of the adsorbent (i.e., the adsorption capacity). The slope of the equation, (1/n), is a measure of adsorption intensity or surface heterogeneity. The system becomes more heterogeneous as the value of (1/n) gets close to zero [113]. A value of (1/n) below one indicates favourability of the adsorption. The Freundlich plot derived from the experimental data obtained in the present work for the adsorption of Zn(II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues at three temperatures(30, 40 and 50 °C) is shown in Figure 7, while the corresponding values of the Freundlich constants are listed in Table 11.

In general, as the value of K_F increases, the adsorption capacity of the adsorbent towards a given metal ion increases. Values of 1/n were 0.348906, 0.405515 and 0.366502 at temperatures of 30, 40 and 50 °C, respectively, indicating the favourable adsorption of Zn (II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues. The plots of log q_e versus log C_e should be linear with a slope and intercept corresponding to 1/n and log K_F, respectively.

It is clear from Table 11 that the value of 1/n and R^2 for three plots showing that the adsorption of Zn (II) ions onto the amidoximated poly (MAA/AN)-grafted Alhagi residues is favourable. Hence, the data for the adsorption of Zn (II) ions onto amidoximated poly (MAA/AN)-grafted Alhagi residues were also well fitted by the Freundlich isotherm.

The adsorption capacity, K_F of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at three temperatures (30, 40 and 50 °C) were 21.4684, 22.9245 and 18.5182 mg/g at temperatures of 30, 40 and 50 °C, respectively, as shown in Table 11.

The Freundlich equation is better obeyed by the system than the Langmuir one, as is evident by the values of correlation coefficients, R^2 shown in Tables 9 and 11.

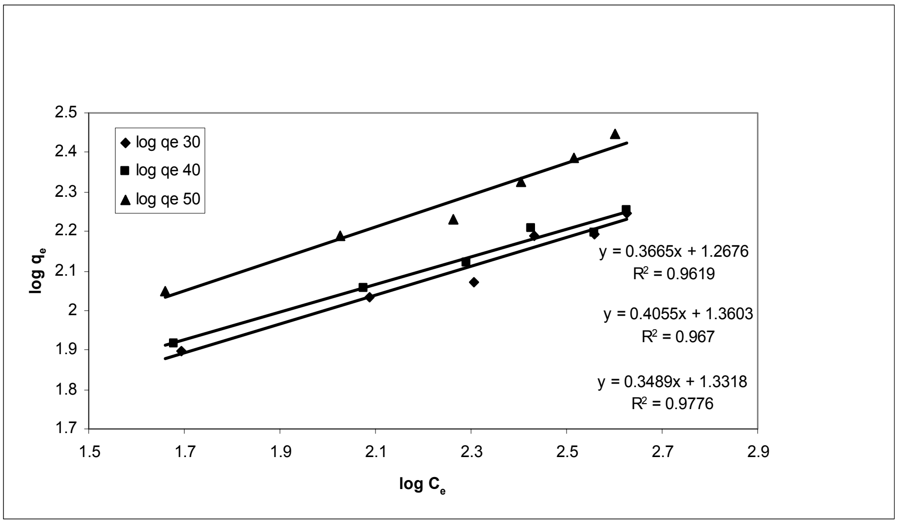


Fig. 7: Freundlich adsorption plots of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures.

Table 11: Freundlich constants of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures

pH	Temperature (C)	K_F (mg/g)	1/n	R^2
5	30	21.4684	0.348906	0.9776
	40	22.9245	0.405515	0.967
	50	18.5182	0.366502	0.9619

3. 6. Effect of contact time

Fig. 8 shows the effect of contact time and adsorbate concentrations (300, 400, and 500 mg/l) on adsorption capacity of Zn (II) by amidoximated poly (MAA/AN)-grafted Alhagi residues. The adsorption capacity (mg/g) increases by increasing the agitation time and concentration of adsorbate and remained nearly constant after equilibrium time. The equilibrium time increases by increasing the concentration of adsorbate. The equilibrium times are 15, 30 and 45 min for adsorbate concentration of 300, 400 and 500 mg/l, respectively. It is clear that the adsorption capacity of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues depends on concentration of adsorbate. The contact time required for Zn (II) removal with amidoximated poly (MAA/AN)-grafted Alhagi residues is very minimal. This is one of the parameters for economical wastewater treatment plant applications.

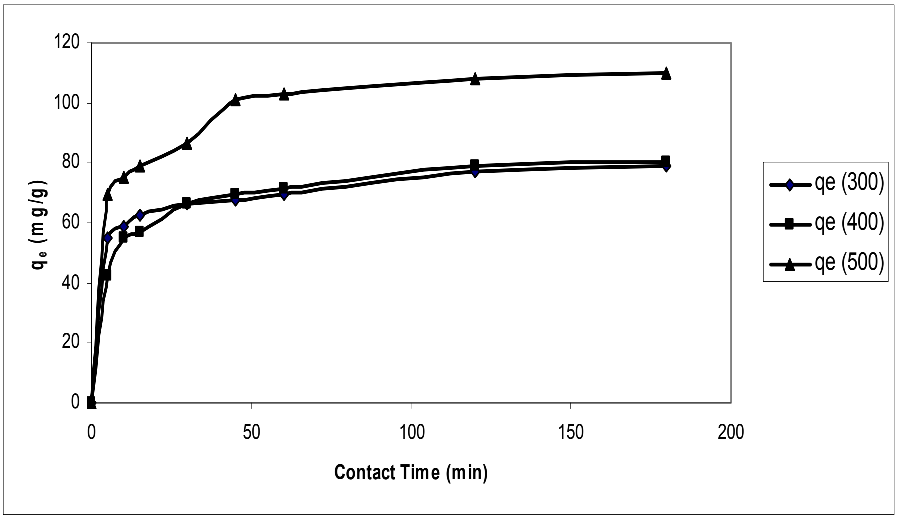


Fig. 8: Effect of contact time and concentration of adsorbate on adsorption capacity of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues.

3. 6. 1. Adsorption Kinetics

A pseudo first-order kinetic process was used for reversible reaction with an equilibrium being established between liquid and solid phases, the first-order rate expression of Lagergren [114] is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.203} t \qquad (11)$$

where q_e and q_t are the amounts of metal ion adsorbed on the adsorbent at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of first-order of adsorption (min^{-1}).

The plot of log (q_e-q_t) versus t (Eq. 11) for 300, 400 and 500 mg/l for Zn (II) amidoximated poly (MAA/AN)-grafted Alhagi residues show that the correlation coefficient, R^2 for all plots are very low (figure not shown). This indicates that the first order rate expression is not so valid to the present study.

Another widely used kinetic expression is the pseudo second-order rate expression derived by Ho and McKay [115] where adsorption capacity was assumed to be proportional to the number of active sites occupied on the adsorbent. The pseudo second-kinetic rate law can be expressed as:

$$\frac{t}{q_t} = \frac{1}{(k_2.q_e{}^2)} + \frac{t}{q_e} \tag{12}$$

where k_2 is the second- order rate constant of adsorption and there is no need to know any parameter beforehand. If the second order kinetic (Eq. 10) is applicable, the plot of t/ qe versus t shows a linear relationship. The linear plots of t / q_t versus t show a good agreement of experimental data with the second-order kinetic model of 300, 400 and 500 mg/l of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues (Fig. 9).

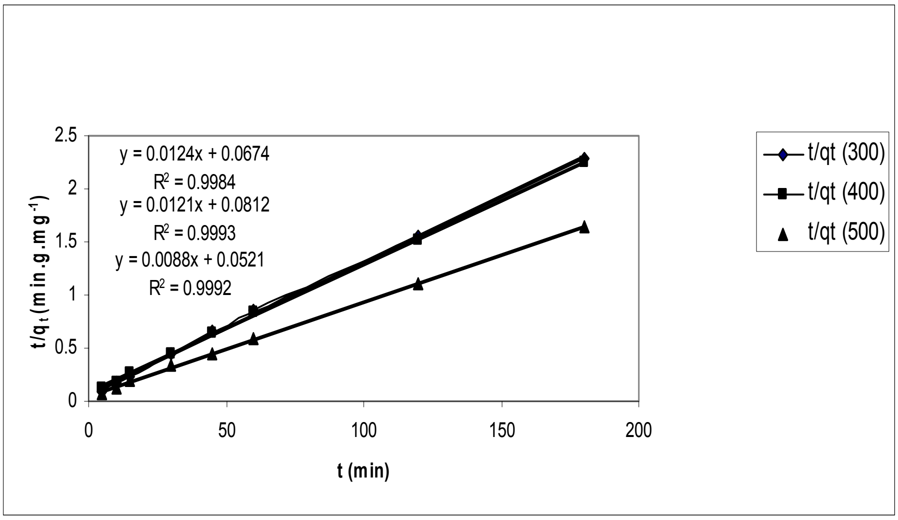


Fig. 9: Pseudo second order kinetic reaction of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different concentrations of adsorbate.

The correlation coefficients are equal 0.9984, 0.9993 and 0.9992 for the concentrations 300, 400 and 500 mg/l, respectively. This indicate that the adsorption of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues follow second order kinetics. The experimental and calculated adsorption capacity for three concentrations of Zn (II) as well as second-order rate constant, k_2 are presented in Table 12.

Table 12: Pseudo-second order adsorption rate constant and the calculated and experimental q_e of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at 30 ^oC.

Adsorbent	Initial concentration of Zn(II) (mg/l)	Experimental q_e (mg/g)	Calculated q_e (mg/g)	Adsorption rate constant k_2 (g/mg. min)	R^2
Amidoximated Alhagi residues	300	77	80.6451	0.0022813	0.9984
	400	79	82.6446	0.001803	0.9993
	500	108	113.6363	0.001486	0.9992

The intra-particle diffusion model [116] can be written by the following equation:

$$q_t = k_p t^{1/2} + C \tag{13}$$

where k_p is the intra-particle diffusion rate constant (mg. g^{-1}. min^{-1}) and q_t is the amount of solute adsorbed per unit mass of adsorbent. The data of solid- phase metal concentration against time t at the initial concentrations of 300, 400 and 500 mg/l of Zn (II) were further processed for testing the rate of diffusion (as the rate controlling step) in the adsorption process. Adsorption process incorporates the transport of adsorbate from the bulk solution to the interior surface of the pores in amidoximated poly (MAA/AN)-grafted Alhagi residues.

The rate parameter for intra-particle diffusion, k_p for the three concentrations of Zn (II) are measured according to Eq. 13.

The plots of q_t versus $t^{1/2}$ for the concentrations of 300, 400 and 500 mg/l of Zn (II) are shown in Figure 10. Due to the mass transfer effect, the shape of q_t versus $t^{1/2}$ plot is curved at a small limit times. The plots for three concentrations of metal ions have the same features, the initial portion (curved) followed by linear portion and plateau. The initial curved portion is attributed to the bulk diffusion and the linear portion to the intra-particle diffusion.

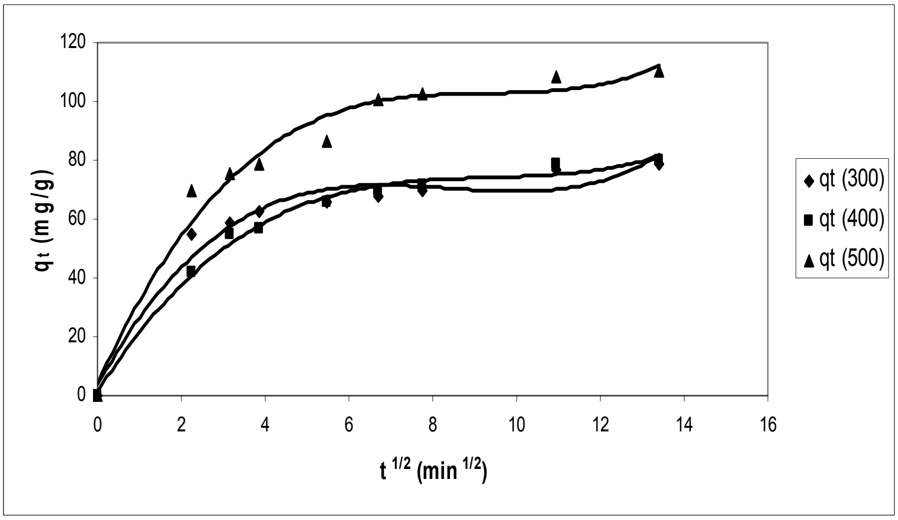


Fig. 10: Intra-particle diffusion of Zn (II) onto amidoximated poly (MAA/AN)- grafted Alhagi residues at different concentrations of adsorbate.

If intra-particle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion is also involved [117].

It can be seen from Fig. 11 that the regression was linear, but the plot did not pass through the origin, suggesting that the adsorption involved intra-particle diffusion, but that was not the only rate-controlling step. Other mechanisms may control the adsorption rate. The values of k_p (mg. g^{-1}. min^{-1}) obtained from the slope of the straight lines (Figure 11) are listed in Table 13. The values of R^2 for the three plots are listed also in Table 13.

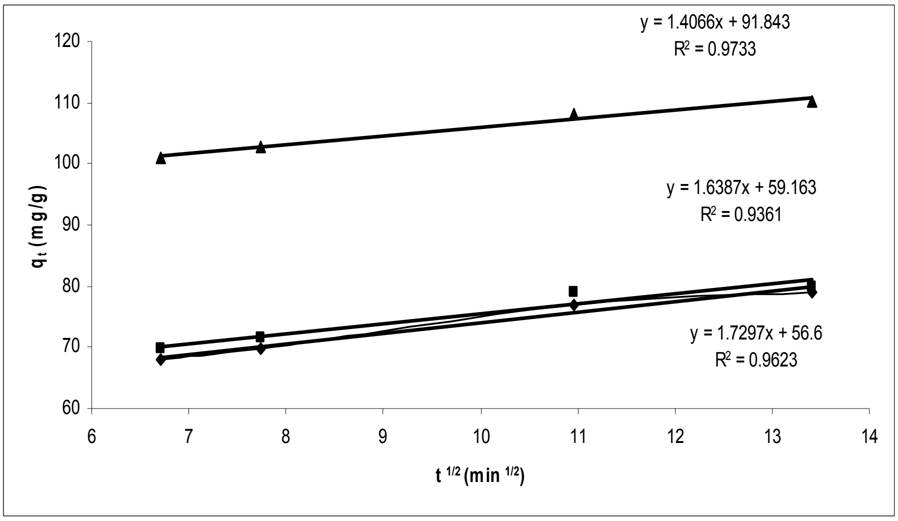


Fig. 11: Test of intra-particle diffusion model of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different concentrations of adsorbate.

Table 13: Rate parameters of intra-particle diffusion at different initial concentrations of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at 30 °C.

Adsorbent	Initial concentration of Zn (II) (mg/l)	k_p (mg/g. min$^{1/2}$)	R^2
Amidoximated Alhagi residues	300	1.7297	0.9623
	400	1.6387	0.9361
	500	1.4066	0.9733

3. 6. 2. Mechanism of removal

The removal of Zn (II) ions on the surface of amidoximated poly (MAA/AN)-grafted Alhagi residues were attributed to three mechanisms as follows:

1. Ion exchange mechanism between the anionic nature of carboxyl groups in amidoximated poly (MAA/AN)-grafted Alhagi residues resulted from treatment Alhagi residues with MAA in presence of gamma radiation and the cationic nature of Zn(II) ions in solution(predominant mechanism as indicated under in section 3.5.1.),
2. Chelation between the electron-donating oxygen- and nitrogen-containing groups in amidoximated poly (MAA/AN)-grafted Alhagi residues and electron-accepting in Zn (II) ions.
3. Intra-particle diffusion model which involve four steps: (a) migration of adsorbate from the bulk of the solution to the surface of the adsorbent, (b) diffusion of the adsorbate through the boundary layer to the surface of the adsorbent, (c) adsorption at active sites on the surface of amidoximated poly (MAA/AN)-grafted Alhagi residues, and (d) intra-particle diffusion of zinc ions into the interior pores of amidoximated poly (MAA/AN)-grafted Alhagi residues.

3. 7. Thermodynamic Parameters

The original concepts of thermodynamics assumed that in an isolated system, where energy cannot be gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Thermodynamic parameters such as standard free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated using the following equations [118-120] as follows:

The standard free energy ($\Delta G°$) was calculated from Eq. 14:

$$\Delta G^{o} = -RT \ln b \qquad (14)$$

where b is the Langmuir constant, R is universal gas constant, 8.31441 J/mol K, and T is absolute temperature (K).

The Langmuir constant, b can be used in the Van't Hoff equation to determine the enthalpy change, ΔH° of adsorption as a function of temperature as follows:

$$\ln \frac{b_2}{b_1} = -\frac{\Delta H^{o}}{R} * \frac{(T_2 - T_1)}{T_2 . T_1} \qquad (15)$$

where b_1 and b_2 are the Langmuir constants at 30, 40 °C , respectively.

The negative values of ΔG°(Table 14) indicate spontaneous nature of adsorption of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues.

Table 14: Thermodynamic parameters of adsorption Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at different temperatures

Adsorbent	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/ K mol)
Amidoximated Alhagi residues	303	-22.14	-17.40	0.015
	313	-28.52		
			33.93	0.166
	323	-19.66		

Negative values of ΔH° (between 30 and 40 ºC (Table 9) suggest the exothermic nature of adsorption and positive values of ΔH° in the range 40-50ºC suggest the endothermic nature of adsorption of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues in this range.

The entropy change (ΔS°) was calculated from Eq. 16:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (16)$$

The positive value of ΔS° shows in the range shows the increase in randomness at the solid/ solution interface during the adsorption of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues.

4. Conclusions

Alhagi residues were grafted with (AN/MAA) by γ-irradiation. Factors affecting the radiation reaction, i.e. the radiation dosage and comonomer composition were investigated. The grafted samples were characterized by FT-IR spectroscopy and scanning electron microscopy as well as by estimation of carboxyl and nitrogen contents.

Utilization of the so-obtained amidoximated poly (MAA/AN)-grafted Alhagi residues for the removal of Zn (II) ions from aqueous solution was examined.

The results indicated that, adsorption capacity of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues were affected by pH, adsorbent dose, agitation time, initial metal ions concentration and temperature. The Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues at 30, 40 and 50 °C. The results obtained showed that the adsorption equilibrium data are fitted well on Langmuir and Freundlich models in the range studied of concentrations. The negative values of ΔG° indicate the spontaneous nature adsorption process.

The negative values of ΔH° in the range 30-40 ^{o}C (303- 313 K) indicate the adsorption process was exothermic and positive values of ΔH° in the range 40-50 ^{o}C (313-33 K) suggest the endothermic nature of adsorption of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues in this range. The positive values of ΔS° shows the increase in randomness at the solid/ solution interface during the adsorption of Zn (II) onto amidoximated poly (MAA/AN)-grafted Alhagi residues.