

Evaluating the Effect of Thermal Activation on Separation Process of Insoluble Fraction of Gasoline using Red Mud

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Abstract

Contamination of water resources with petroleum products is a serious environmental problem. The current study was carried out to investigate the effect of using raw and heat activated red mud (RM) as adsorbent to remove insoluble fraction of gasoline from aqueous solution. Some parameters such as pH, contact time, adsorbent dose and initial concentration were optimized in adsorption process to obtain the highest removal efficiency. Maximum removal of gasoline by raw and heat activated red mud at pH 8 and 7 were 90% and 92% respectively, during the contact time of 30 minutes, adsorbent dose of 50 g/L and 1% initial concentration of gasoline were the same for both adsorbents. Study of isotherm for raw and heat activated red mud showed high consistency with Langmuir and Freundlich isotherms, respectively. The kinetics of adsorption process was described by a pseudo-second-order model for both adsorbents. Experimental adsorption capacity of raw and heat activated red mud was achieved 0.7 and 0.66, respectively. According to the results, the adsorbents used in this study, have an appropriate efficiency for removal of the insoluble fraction of gasoline from aqueous solution.

Keywords

Adsorption;
Aqueous solution;
Heat activation;
Kinetics, Gasoline;
Red mud.

1. Introduction

Oil pollution of the aquatic environment is an environmental problem that usually occurs through extraction, transportation, refining and storage of crude oil. The significance of the problem is due to the toxicity of hydrocarbon compounds in oil which causes many health

issues and environmental problems. It is estimated that 10 to 20 mega tons of oil is annually spilled onto the surface waters, whereas a ton of it can cover about 12 Km² of the surface [1]. Water surface covered by petroleum derivation reduce oxygen transfer between surface water and atmosphere, moreover the evaporation of toxic volatile constituents of oil spills cause atmospheric pollution.

Different techniques consist of physical, chemical and biological have already been used for the removal of petroleum from water [2-3-4]. Among

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these methods, adsorption attracted many attentions among the scientific community since it showed a very high efficiency if designed properly. Recently, many researches were conducted to replace the expensive sorbents such as activated carbon with accessible techniques for the removal of various contaminants from aqueous solutions. Different types of adsorbents including sugarcane bagasse [5], rice husk [6], activated carbon, bentonite, deposited carbon [7] and organoclay have been employed for the removal of petroleum pollutants and water remediation. Red mud is a by-product of the Bayer process in the aluminum industries with a high alkalinity that treated as a waste. It is estimated that 1 to 2 tons of red mud are generated for 1 ton alumina production [8]. Worldwide, 120 million tons of red mud is produced annually [9].

The present study was carried out to investigate the effect of using raw and heat activated red mud as adsorbents to remove the insoluble fraction of gasoline from aqueous solution. The effect of various parameters such as pH, contact time, adsorbent dose and initial concentration on the adsorption process were studied. The obtained data from the experiments were fitted to different isotherm and kinetic models to determine the mechanism of adsorption.

2. Methods and Materials

Glass containers used in experiments were soaked in dilute HCl solution for 24 hours and

then were rinsed with distilled water for 5 times. Solutions in the experiments were prepared with distilled water. Tests were triplicated and the average was used for the data analysis. The maximum error of 5% was calculated.

Red mud used in this research was obtained from Jajarm Alumina Industries, Iran. The chemical composition of red mud was determined by X-ray diffraction (XRD) analysis as shown in Fig. 1. The results of XRD analysis showed that calcite, kaolinite, iron oxide, iron hydroxide, manganocalcite and montmorillonite compounds exist in the red mud structure. In order to determine raw red mud's morphology and main oxides present in it, SEM and XRF analysis were done and results are presented in Fig. 2 and Table 1, respectively.

From XRF analysis, it is observed that Ca and Fe oxides had the most frequencies. SEM analysis showed adsorbents pores and its structure with 50000 fold magnification. Raw red mud was washed 5 times with distilled water to remove the possible contaminants from the surface and to reduce alkalinity. The washed red mud was dried and passed through sieve No. 100 (opening size of 0.149 mm). Unleaded gasoline used in the experiments was purchased from Tehran Shahid Tondgouyan Petroleum Refinery, Iran. All other chemicals used in this research were obtained from the Merk chemical Co. 0.1 M NaOH and 0.1 M HCL were used in order to adjust the pH of the solutions.

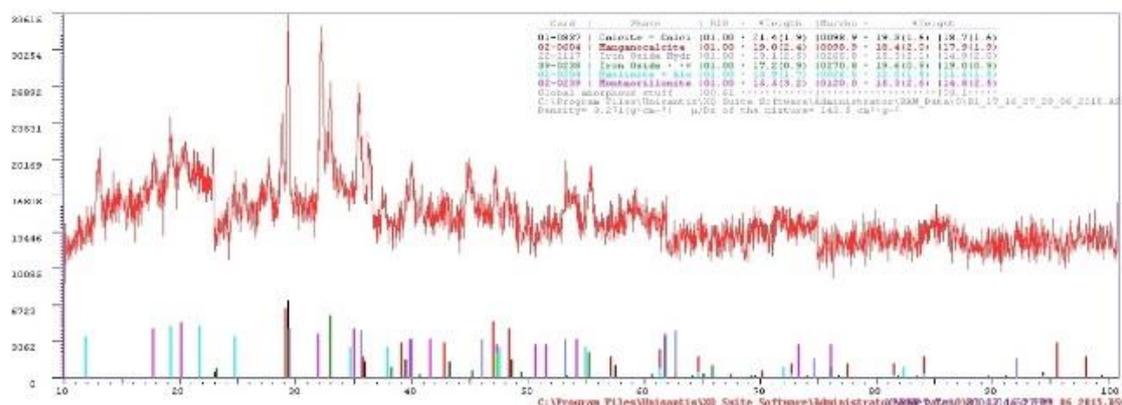


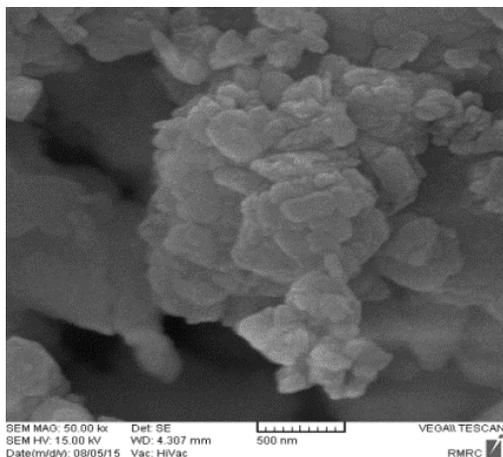
Figure 1. XRD patterns of red mud

Table 1. Main oxides present in raw red mud (XRF results)

Main oxides			
SiO ₂	13	MnO	0.06
Al ₂ O ₃	13.98	CaO	24.25
Na ₂ O	4.2	P ₂ O ₅	0.16
MgO	2.01	Fe ₂ O ₃	22.17
K ₂ O	0.42	SO ₃	1.63
TiO ₂	7.17	LOI	9.55

2.1. Modification of adsorbent

In order to modify the red mud, the samples in porcelain dishes were heated at temperatures 200, 500, 700, 800, 900, and 1000 °C for 0.5, 1, and 2 hours in a furnace [10]. The modified red mud was then cooled at ambient temperature and passed through sieve No. 100.

**Figure 2.** SEM photograph of raw red mud

2.2. Sorption procedure

In order to reduce the error, two steps were taken. First, the gasoline was stabilized at room temperature for 24h to remove the volatile hydrocarbons [7]. Second, the amount of adsorbed hydrocarbon on the glassware during the adsorption experiments were assessed by applying 250 mL of solution at different concentration of gasoline in water to the glassware that were subjected to agitation for 60 minutes. Finally, the samples were vacuum filtered and then were poured in a separating funnel. The water and insoluble part of gasoline were separated and the remaining oil was measured. The results showed a 1% difference between the initial and final volume of gasoline, which is acceptable in the experimental procedures.

Batch experiments were performed under the condition of 5% gasoline, contact time of 90 minutes and 10 gr of adsorbent in 200 mL of sample. After completing the tests and achieve equilibrium, samples were centrifuged at 3500 rpm for 20 minutes. The adsorbent and the supernatant were separated using a vacuum Buchner funnel. Supernatant was poured in a separating funnel where the soluble and insoluble portions of gasoline were separated. The remaining volume of insoluble portion of gasoline was measured. Gasoline removal efficiency was calculated according to the following equation:

$$R(\%) = (V_i - V_e/V_i) \times 100 \quad (1)$$

where R is removal efficiency of insoluble portion of gasoline, V_i and V_e are volumes of insoluble portion of gasoline at the beginning and the end of the experiment, respectively.

At each stage of the experiment, one of the investigated parameters including pH, contact time, initial concentration of gasoline and adsorbent dose was changed and the maximum gasoline removal resulted from each stage was used in the next stage to investigate the effect of other parameters.

3. Results and discussion

3.1. Effect of heat treatment

The results of the experiments carried out using activated red mud by heating at temperatures of 200, 500, 700, 800, 900, 1000°C and at times of 0.5, 1 and 2 hours were presented in Fig. 3 in which RM represents red mud. The number following RM and the hashes show the temperature and the duration of heat treatment respectively. All experiments were conducted at initial pH of 7. The results of adsorption studies using heat modified red mud showed a significant reduction in the amount of gasoline content in the solution.

According to the present study, gasoline removal by the red mud calcined at 200, 500, 700, 800, 900, 1000 °C for 30 minutes was 65, 52, 60, 68, 48, 55%, respectively. The results showed gasoline removal by the RM calcined at 700 °C for 0.5 h, had the highest removal rate (68%). It is also seen that the efficiency of gasoline removal does not show a linear trend with the treatment temperature nor with the time. One can interpret that treating the red mud at 700 °C increases the ac-

tive sites and surface area of the adsorbent which increase the adsorbent structure stability [11], that consequently increase the adsorption efficiency. The results show consistency with the previous findings that the decomposition and reduction of adsorbent surface varies with the temperature of treatment [6].

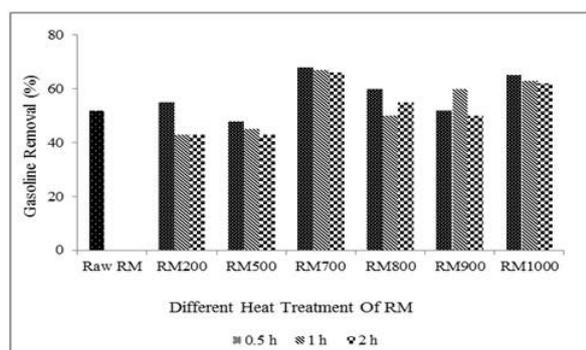


Figure 3. Effect of heat activation on the removal of insoluble fraction of gasoline (pH=7, time= 90 min, adsorbent mass to volume solution= 1:20, initial gasoline concentration= 5%)

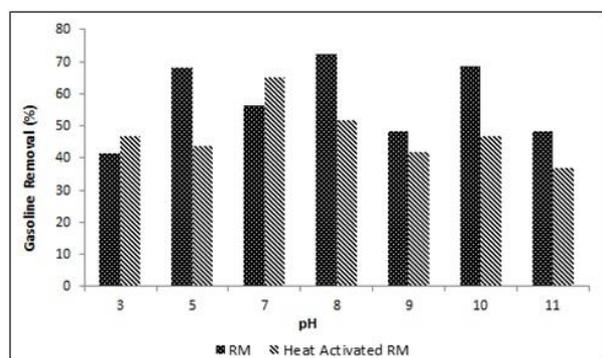


Figure 4. Effect of different pH on the removal of insoluble fraction of gasoline by the raw and heat activated red mud (time= 90 min, adsorbent mass to volume solution= 1:20, initial gasoline concentration= 5%)

3.2. Effect of initial pH of solution

Solution pH is one of the most important variables affecting the adsorbent surface charge, degree of ionization and speciation of adsorbate and adsorption properties. Fig. 4 presents the results of gasoline removal experiments by raw and heat activated red mud at 700 °C for 30 minutes in the initial pH of 3, 5, 7, 8, 9, 10, 11 and gasoline of 5% concentration.

As the present study results indicate, this parameter normally does not follow any particular

trend in hydrocarbons adsorption [5, 12]. Maximum removal of gasoline for raw and heat activated red mud was obtained at pH 8 and 7, respectively.

3.3. Effect of contact time

The effect of contact time on gasoline removal from aqueous solution by adsorbents at the times of 5, 15, 30, 90 min, initial pH of 8 and 7 for raw and heat activated red mud were evaluated. According to Fig. 5, gasoline sorption by raw and heat activated red mud occurs immediately after the contact, then continues to the slower rate until the equilibrium.

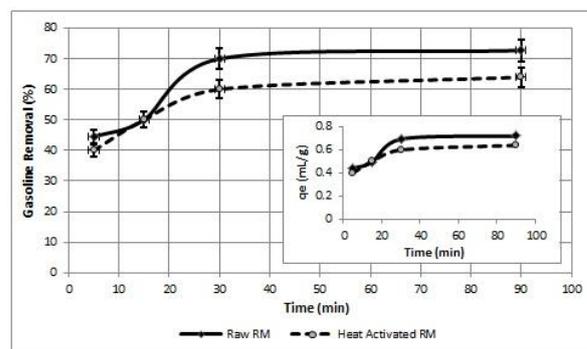


Figure 5. Effect of different contact time on the removal of insoluble fraction of gasoline by the raw and heat activated red mud (pH= 8 for raw RM, pH= 7 for heat activated RM, adsorbent mass to volume solution= 1:20, initial gasoline concentration= 5%)

In this study, the equilibrium achieved in less than one hour. The rapid pace of adsorption at the beginning of the experiment could be due to the presence of empty active sites for adsorption on the surface of adsorbent. In the following step, decrease in adsorption rate is because of the occupation and exhaustion of the active sites as mentioned for other adsorbents by [13]. In this study, for both raw and heat activated red mud, optimal contact time of 30 min was selected to investigate the effect of adsorbent dose and initial gasoline concentration on the sorption efficiency.

3.4. Effect of adsorbent dose

The effect of adsorbent dose on the removal of gasoline from water was investigated. The doses of 5, 10, 20, 50, 100 g/L (mass of adsor-

gent/volume of the solution) were applied to the solutions with an initial pH of 8 and 7 for raw and heat activated red mud respectively, 5% gasoline concentration, and contact time of 30 min. Fig. 6 shows the enhancement of the removal of gasoline by increasing the adsorbent dosage. Increasing the adsorbent mass and consequently the larger adsorption sites in the solution due to greater surface area for adsorption, elevates the number of functional active groups in adsorption by increasing the number of active adsorption sites [14], thus, the removal efficiency will increase. It should be noted that increasing the amount of adsorbent is partly responsible for the increase in gasoline removal. At high doses of adsorbent, hydrocarbons do not cover the active sites at the adsorbent surface, thus adsorption capacity is reduced.

In other words, the reduction in adsorption capacity in higher doses of adsorbent (more than 50 g/L) is due to insufficient hydrocarbons in compared to the number of adsorbent active sites. This phenomenon was reported for other adsorption processes as well [13, 15]. In this experimental study, for raw and heat activated red mud when the dosage is 50 g/L, both adsorbent capacity (0.65 mL/g and 0.63 mL/g, respectively) and gasoline removal percentage (67.5% and 62%, respectively) reached to an equilibrium that occurred at relatively high rate of removal; therefore, a dose of 50 g/L was selected for further studies.

3.5. Effect of initial concentration of gasoline

The amount of gasoline adsorption is dominated by the initial concentration of gasoline in an aqueous solution. 1, 2, 5, 10, 20% of the initial concentration of gasoline were tested. Fig. 7 illustrates the effect of initial concentration of gasoline on gasoline removal percentage and adsorbent capacity.

At low concentrations of hydrocarbons (1%, 2%), the ratio of hydrocarbons to the surface area available for adsorption is small, so the adsorption process is independent of the initial concentration of hydrocarbons. At higher initial concentrations (20%), available active sites for adsorption, compared to the amount of hydrocarbons present, are lower. Therefore, hydrocarbon adsorption depends on its initial concentration in the solution. The same conclusion was drawn for

bio-sorption of cadmium [16]. In other words, increasing adsorbent capacity can be due to increase in the concentration gradient while the reduction in the removal rate can also be due to insufficient number of active sites [14]. It is evident from the results that the percentage removal of gasoline by raw and heat activated red mud decreased from 90% to 16% and 30% respectively, for initial concentration of gasoline in the range of 1-20%.

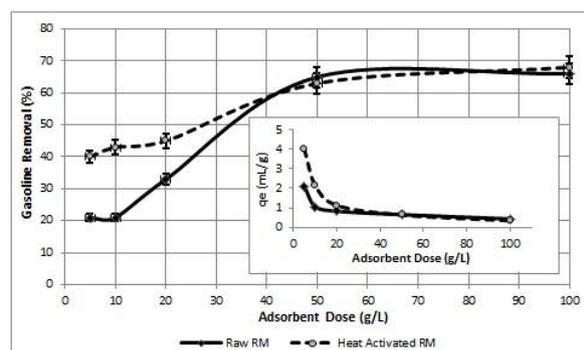


Figure 6. Effect of different adsorbent dose on the removal of insoluble fraction of gasoline by the raw and heat activated red mud (pH=8 for raw RM, pH=7 for heat activated RM, time = 30 min, initial gasoline concentration=5%)

3.6. Adsorption Isotherms

Adsorption Isotherm investigation is important because it describes the adsorption mechanisms. Several isotherm models are used in the study of adsorption with both mathematical and empirical basis. Since the adsorbent used in this research was not previously undergone a comprehensive study, finding the relationship between the concentration of gasoline in the solid and liquid phases has particular importance. Therefore the results of gasoline adsorption by red mud in equilibrium were tested against different isotherms to find the most consistent isotherm with the experimental data. In the present study, the Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906) and D-R (Dubinin and Radushkevich, 1947) isotherm models were tested according to the experimental data.

3.7. Langmuir isotherm

The Langmuir model assumes monolayer adsorption onto a homogeneous surface containing fi-

nite number of similar adsorption sites without migration of adsorbed molecules on the surface [16]. The Langmuir model is represented as:

$$q_e = q_{max} \times b \times C_e / (1 + bC_e) \quad (2)$$

where q_e is the adsorbent capacity at equilibrium (mL/g), q_{max} is the maximum monolayer adsorbent capacity (ml/g), C_e is the equilibrium concentration of the adsorbate (mL/L), and b is the Langmuir sorption constant (L/mL) relating the free energy of sorption. A dimensionless constant (R_l) has been also defined as:

$$R_l = 1 / (1 + bC_0) \quad (3)$$

where b is the Langmuir constant and C_0 refers to the initial concentration of the adsorbate. R_l value between 0 and 1 indicates favorable adsorption, $R_l > 1$ represents unfavorable adsorption, $R_l = 1$ shows a linear adsorption, and $R_l = 0$ shows an irreversible adsorption [17]. The dimensionless constant R_l for raw and heat activated red mud ranged from 0.01 to 0.2 and 0.07 to 0.61 respectively, that represents adsorption process is desirable. Table 2 shows the coefficients and constants of the Langmuir isotherm. The correlation coefficients (R^2) and maximum adsorption capacity for raw and heat activated red mud was 0.99, 0.91 and 0.64 and 0.6 (mL/g), respectively, which shows an efficient adsorption process.

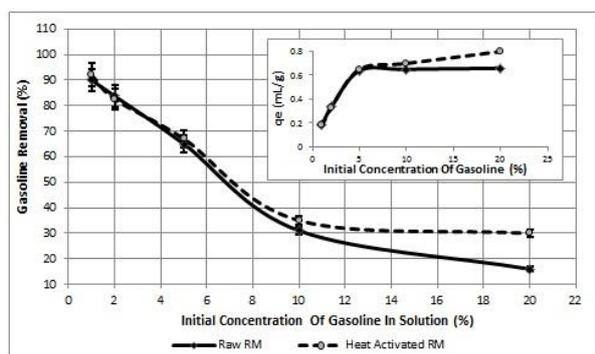


Figure 7. Effect of different gasoline initial concentration on the removal of insoluble fraction of gasoline by the raw and heat activated red mud (pH=8 for raw RM, pH=7 for heat activated RM, time = 30 min, adsorbent dose= 50 g/L for both adsorbents)

3.8. Freundlich isotherm

Freundlich empirical isotherm model that is based on the multilayer adsorption on heteroge-

neous surfaces assumes that stronger binding sites are occupied first, and that the binding strength is related to the concentration of gasoline at equilibrium [18]. It is also assumed that by increasing in the concentration of contaminants in the solution, the gradient of the pollutant on the adsorbent surface will increase. The Freundlich isotherm model can be expressed as:

$$\ln(q_e) = \ln(k_f) + 1/n \ln(C_e) \quad (4)$$

where n and k_f are Freundlich constants, C_e is the equilibrium concentration of the adsorbate (mL/L), and q_e is the adsorbent capacity at equilibrium (mL/g). k_f is the distribution coefficient which related to the adsorption capacity and n describes the intensity of adsorption. The value of n depends on the number of ions bonded to the adsorbent surface. If the value is between 1 and 10, it means that adsorption is remarkable. The values of n close to 1 indicate the little importance of the heterogeneity of sorbent surface. The closer the value of n to 10, the more important the heterogeneity [19]. According to the results showed in Table 2, the values of n for raw and heat activated red mud were 4.11 and 2.83, respectively. These values indicate that the adsorption process was satisfactory and adsorbent surface heterogeneity does not have a significant impact on the process. The correlation coefficients (R^2) for raw and heat activated red mud was 0.86 and 0.95, respectively.

3.9. D_R isotherm

To determine whether physical or chemical adsorption process, D_R isotherm model shown in Equations 5 and 6 were utilized:

$$\ln q_e = \ln q_{max} - K_{DR} \varepsilon^2 \quad (5)$$

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

where q_e is the adsorbent capacity at equilibrium (mL/g), q_{max} is the maximum adsorbent capacity (ml/g), C_e is the equilibrium concentration of the adsorbate (mL/L), K_{DR} is the isotherm constant expressing the adsorption energy (mol^2/j^2), ε is the Polanyi potential, T is the absolute temperature (K), and R is the gas constant [j/(mol.K)]. The mean energy of adsorption (E) is obtained from the following equation:

$$E = 1 / \sqrt{2k_{DR}} \quad (7)$$

The value of E between 8 and 16 kJ/mol indicates chemical reaction is dominant, and if $E < 8$ kJ/mol, a physical adsorption is dominant [20]. The D-R isotherm constants are shown in Table 2. Mean energy of adsorption for raw and heat acti-

vated red mud was 1.18 and 1, respectively, which shows that the dominant process in adsorption is physical. The mean energy of the adsorbents was almost the same which revealed the same mechanism of the adsorption.

Table 2. Adsorption isotherm constants for raw and heat activated red mud

adsorbent	Langmuir Isotherm				Freundlich Isotherm			D-R Isotherm			
	q_{max}	b	R_L	R^2	K_f	n	R^2	q_{max}	K_{DR}	E	R^2
	mL/g	L/m			$(\frac{mL}{g})$			mL/g	mol^2/J^2	KJ/mol	
		L			$/(\frac{mL}{L})^n$						
Raw RM	0.64	0.38	0.01-0.20	0.99	0.22	4.11	0.86	0.56	4×10^{-7}	1.11	0.87
Heat activated RM	0.606	0.063	0.07-0.61	0.91	0.09	2.83	0.95	0.35	5×10^{-7}	1	0.71

3.10. Final remarks on isotherm studies

The adsorption isotherms are important to estimate adsorbent capacity in the process. Raw red mud was best described by Langmuir model ($R^2 = 0.99$) in compared with Freundlich ($R^2 = 0.86$) and D-R ($R^2 = 0.87$) models. It means that monolayer adsorption was occurred on the finite number of sites and homogeneous surface of adsorbent. In this type of adsorption, chemical reactions between adsorbate molecules and adsorbent surface did not happen and molecules were not migrated [16]. For heat activated red mud, Freundlich model ($R^2 = 0.95$) has more compliance than Langmuir ($R^2 = 0.91$) and D-R ($R^2 = 0.71$) models. It indicates that Freundlich isotherm is more suitable for describing the adsorption equilibrium. In this case, multilayer adsorption was occurred on the heterogeneous surface of adsorbent which could be due to the heat modification of red mud. In this kind of process, adsorbent capacity is increased by increasing gasoline concentration in the solution [15].

3.11. Adsorption Kinetic studies

Kinetic parameters in order to predict the reaction rate, design and modeling of adsorption processes are important. In this study, zero order kinetic, pseudo first order kinetic and pseudo second order kinetic were utilized to assess the adsorption kinetic of insoluble portion of gasoline from aqueous solution.

3.12. Zero order Kinetic

The linear form of Zero-order kinetic model is represented as:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (8)$$

where α is the initial adsorption rate (g/mL.min), β is the desorption constant (g/mL), and q_t is the adsorbent capacity at time t (mL/g). The values of kinetic constants are shown in Table 3. The correlation coefficients (R^2) for raw and heat activated red mud was 0.86 and 0.94, respectively.

3.13. Pseudo First order kinetic

The pseudo first order kinetic model describes a rate of adsorption that is proportional to the number of unoccupied binding sites in the adsorbent. The linear form of pseudo first order model is represented as:

$$\log(q_t + q_e) = -\frac{k_1 t}{2.303} + \log(q_e) \quad (9)$$

where q_e and q_t are adsorbent capacity at equilibrium and at time t (mL/g), k_1 is the rate constant of pseudo first order sorption (min^{-1}). The values of k_1 and q_e are shown in Table 3. The correlation coefficient (R^2) for raw and heat activated red mud was 0.97 and 0.93, respectively.

3.14. Pseudo Second Order Kinetic

The pseudo second-order equation is generally expressed as:

$$t/q_t = 1/K_2q_e^2 + 1/q_e t \quad (10)$$

where q_e and q_t are adsorbent capacity at equilibrium and at time t (mL/g), k_1 is the rate constant of pseudo second order sorption (g/mL.

min). The value of kinetic constants is shown in Table 3. It is observed that the correlation coefficient (R^2) for both sorbents was greater than 0.99.

Table 3. Kinetic model constants for raw and heat activated red mud.

adsorbent	Zero order Kinetic			Pseudo First order kinetic			Pseudo Second Order Kinetic		
	α	β	R^2	K_1	q_e	R^2	K_2	q_e	R^2
	(g/mL.min)	(g/mL)		(min ⁻¹)	(mL/g)		(g/mL.min)	(mL/g)	
Raw RM	1.14	9.12	0.86	0.09	0.62	0.97	0.996	0.76	0.25
Heat activated RM	1.99	11.57	0.94	0.07	0.64	0.93	0.999	0.66	0.37
Experimental q_e for raw and heat activated red mud= 0.7 and 0.66, respectively									

3.15. Final remarks on Kinetic studies

Zero order, pseudo first order and pseudo second order kinetic models were investigated to simulate the behavior of gasoline adsorption from aqueous solution by raw and heat activated red mud. Pseudo-second-order kinetic model with a correlation coefficient of more than 0.99 was the best model for assessment of gasoline adsorption by both adsorbents.

In addition, the equilibrium adsorption capacity obtained from experimental data (0.7 and 0.66 for raw and heat activated red mud, respectively) for two sorbents had more compliance with theoretical adsorption capacity resulting from the pseudo-second-order model (0.76 and 0.66 for raw and heat activated red mud, respectively). These information are important to design of a fixed-bed adsorption column to determine adsorbent capacity.

4. Conclusion

In this study, the feasibility of gasoline adsorption by raw and heat activated red mud was investigated. The effect of parameters such as initial pH, contact time, adsorbent dose, pollutant concentration and adsorbent modification on the adsorption of the insoluble fraction of gasoline was evaluated. The modified adsorbent by heating at different temperature and times, led to the selection of red mud heated at 700°C for 30 minutes for further testing due to its better performance. During the experimental studies, it was found that adsorption of insoluble fraction of gasoline is independent from pH. For both adsorbents, equilibrium was reached in 30 minutes. Maximum

removal of gasoline by raw and heat modified red mud at adsorbent dose of 50 g/L were 90% and 92% respectively at 1% initial concentration of gasoline. Results of isotherm studies for raw and heat modified red mud showed high consistency with Langmuir and Freundlich isotherms with correlation coefficients of 0.99 and 0.95, respectively. The kinetics of adsorption process was described by a pseudo-second-order model with R^2 equals to 0.99 for both adsorbents. The free energy of adsorption for two adsorbents was less than 8 kJ/mol, which indicates physical adsorption was dominant.

It is notable that used red mud was solid waste which should be disposed. Using this by-product had no cost. Electrical energy was used for activation of the adsorbent, was very low and economical. Due to a suitable pH range, short adsorption equilibrium time, acceptable adsorption capacity, low cost of adsorbents and easy accessibility, both adsorbents were suitable to remove the insoluble fraction of gasoline from aqueous solution.

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