ADSORPTION OF DIRECT RED 23 BY MICROWAVE ACTIVATED LD SLAG

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ABSTRACT

The main objective of this work is the removal of Direct Red 23one of toxic dyes mainly present in industrial wastewater by using LD slag, an industrial solid waste abundantly available from the steel industries, as a good quality low cost adsorbent and thereby presenting a solution for both treating a problematic wastewater and turning industrial waste into a valuable material. The raw LD slag has been modified by acid treatment followed by microwave heating. The composition of different oxides e.g. CaO, Fe_2O_3*,* SiO_2 *etc. present in both raw and modified LD slag has been determined through XRF technique. The adsorbent has been further characterized by using BET apparatus, SEM images and XRD patterns. Batch experiments have been conducted for adsorption equilibrium study of microwave activated LD slag for removal of Direct Red 23 from aqueous solution at three different temperatures (303, 313, and 323 K) as depicted in the figure. The experimental data have been shown in the figure below. The typical isotherm models such as Langmuir and Freundlich models have been fitted to the experimental data. Adsorption kinetic and thermodynamic studies have been performed for understanding the adsorption process better. The effect of pH on the adsorption process has also been investigated.*

KEYWORDS

LD slag; Microwave Activation; Adsorption; Direct Red 23.

1. INTRODUCTION

The Presence of different type dyes in the water is one of the major reasons for water pollution due to their various harmful effects. Direct red 23 is a dye which is mainly discharged into water bodies by the effluent of textile industries [1]. Direct red 23 (Chemical Formula: $C_{35}H_{25}N_7Na_2O_{10}S_2$) is an anionic dye having diazo group (-N=N-) and sulphonate group. Direct red 23 can harm our human body as it is carcinogenic in nature [2]. Therefore, direct red 23 should be removed from the industrial effluent fully before it gets discharged into water stream. Removal of direct red 23 from the industrial effluent (i.e. waste water) is a crucial task to perform. Several processes have been developed to remove direct red 23 from the industrial wastewater including advanced oxidation process such as photocatalytic degradation [3], membrane filtration [4] and adsorption [5].

Adsorption can be considered as one of the best methods to eliminate dyes from the waste water due to its cost effectiveness. In solid liquid adsorption process, solute gets accumulated at the surface or interface of the adsorbent particles which have large surface area and pore volume. Activated carbon is one such type of adsorbent which is widely used due to their good adsorption capacities for the removal of dyes. However, the use of adsorption by activated carbon is highly expensive and it requires a costly regeneration system. So, many researchers started to search for alternative adsorbents which are of low cost and easily available. In recent years, research interest has been highly intensified in the development of good adsorbents from industrial solid waste or by-product which is abundant in the industry, for the removal of dyes present in the industrial wastewater. Thus, the solution for both treating polluted wastewater and reducing the disposal cost of by-products can be served. The typical examples of such adsorbents are fly ash [6], red mud [7], and slag [8] etc.

LD slag (Linz Donawitz (LD) converter slag), a solid waste of steel making industries generated from pig iron refining processing using LD converters [9]. It consists of mainly calcium oxide, iron oxide along with silica. During the last few decades, the disposal of LD slag has become a significant issue for the steel industries due to (a) its generation in enormous quantity associated with high disposal costs, (b) reduction in the amount of available landfill space and (c) unsuitableness in cement making due to its high iron oxide content. Few researchers have successfully utilized the basic oxygen furnace slag for removal of dyes like reactive blue 19 (RB19), reactive black 5 (RB5) and reactive red 120 (RR120) [10]. LD slag, being similar in nature, can be proposed as a good adsorbent for direct red 23 removal due to its unique porous structure, with a sufficient surface area. The focus of the present work is to explore the suitability of LD slag as a low cost adsorbent for removal of direct red 23 by investigating the various adsorbent activation techniques and adsorption characteristics.

2. Material and Method

2.1. Preparation of modified LD slag

The LD slag, used in this study, was collected from the TATA Steel, Jamshedpur, India. The slag was ground by ball mill and then sieved to pass through 72 mesh sieves (0.2 mm). The LD slag was treated with 0.6 N hydrochloric acid and was washed with distilled water for five times and dried at room temperature for 24 h. A domestic microwave oven having a frequency of 2.45 GHz, has been used for heating the LD slag uniformly for the activation of the adsorbent [11]. The oven was controlled at 240 W for 10 min by setting a timer. Direct red 23 was considered as the adsorbate in this study. Artificial wastewater was synthesized by dissolving specified weight of direct red 23 in deionized water. The experiments were conducted at different initial direct red 23 concentrations (20–160 mg/L). Deionized water was used to prepare all the reagents and solutions.

2.2. Characterization of modified LD slag

The physical and chemical characteristics of both raw and modified LD slags were carried out by the following techniques. The specific surface area was determined by the nitrogen physical adsorption-desorption technique by BET apparatus (Quantachrome, AUTOSORB-1, USA). The pore volume and pore size of the adsorbents were measured by the liquid N_2 adsorption at 77 K. Powder XR diffraction (PXRD) patterns of the adsorbent samples were obtained from Panalytical X'Pert^3 Powder X-ray Diffractometer in the spectrum (2θ) range from 10^0 to 80^0using Cu-Kα radiation at wavelength (λ) of 1.54 Å. Its composition was determined using X-ray fluorescence spectroscopy technique (AXIOS, PANalytical). The images of the surface textures of the modified LD slag samples were viewed in Zeiss Merlin (Gemini) scanning electron microscope.

2.3. Adsorption experiments

Adsorption of direct red 23 with LD slag was measured for various initial concentrations (20-160 mg/L) at an adsorbent dose of 0.5 g in 100 ml of aqueous solution in a set of 250 mL stoppered Erlenmeyer flasks using batch method in a shaker. The contact time was about 24 hours. The samples were filtered and the residual concentration of direct red 23 in the solutions were determined using direct photometric method of by a double beam UV–vis-spectrophotometer

(Perkin-Elmer, Lambda25) at a wavelength of 504 nm. Adsorption uptake at equilibrium, Q_e (in mg/g), was determined by [12],

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (in mg/L) are the initial and equilibrium liquid-phase direct red 23 concentrations, respectively. V (in L) is the volume of the solution and W (in g) is the mass of adsorbent.

3. RESULT & DISCUSSION

3.1. Characterization of modified LD slag

Composition of the raw LD slag by XRF technique is presented in Table 1. The main components of the steel slag were calcium oxides and iron oxides followed by silica and alumina. Other oxides commonly found in slag materials are P_2O_5 and MgO etc. Detailed of the characteristics properties of modified LD slag including external surface area, total pore volume and average pore diameter were summarized in Table 2. From the present observation, it can be clearly observed that the BET surface area of modified LD slag increased significantly compared to that of raw LD slag, as additional pores were developed because of microwave heating.

Table 1. Compositions of raw and modified LD slag obtained by XRF technique.

Type of slag	CaO (%)	Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	P_2O_5 (%)	MgO (%)	Other oxides (%)
Raw LD slag	55.119	27.732	9.999	1.140	1.469	1.774	2.767
Modified LD slag	30.006	50.304	13.863	0.011	2.155	2.232	1.429

Table 2. Surface area of raw and modified LD slag obtained by BET apparatus

Type of slag	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (Å)
Modified LD lag	81.18	0.124	61.55
Raw LD slag	14.51	0.054	65.92

The morphological structure of LD slag can be seen from the SEM photographs depicted in Figure 1. It is observed that the LD slag particles are smaller in size and porous structure. External surface of the LD slag particles became rough after treating with HCl resulting a high increase in pore volume[10]. Microwave heating of the acid treated LD slag further enhanced the widening of the existing micropores. At the specified microwave power and radiation time, cavities are observed over the LD slag surface due to the evaporation of the HCl derived compounds which were previously occupying the space of the active sites. The combined effect of internal and volumetric heating by the microwave oven is mainly responsible for the formation of an orderly microporous surface of the modified LD slag [13]. PXRD patterns for both raw and modified LD slags in Figure 2. show that the modified LD slag is amorphous in nature whereas the raw LD slag is crystalline in nature having several major peaks.

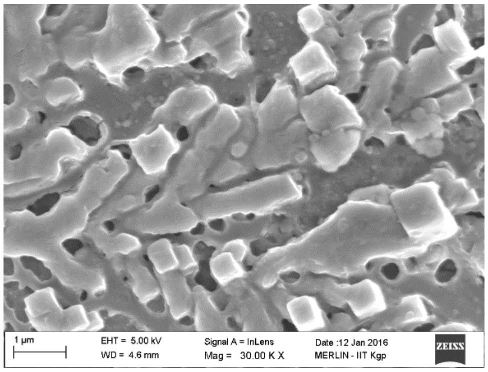


Figure 1. SEM image of modified LD slag

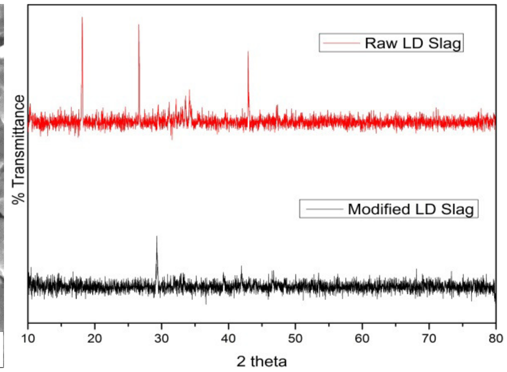


Figure 2. XRD pattern of raw and modified LD slag

3.2. Adsorption isotherm studies

The amount of direct red 23 adsorbed onto the modified LD slag was determined at the equilibrium. The adsorption data at 303 K was plotted as a function of the equilibrium concentration of direct red 23 in Figure 3. Different isotherm models have been used to correlate the experimental equilibrium adsorption data.

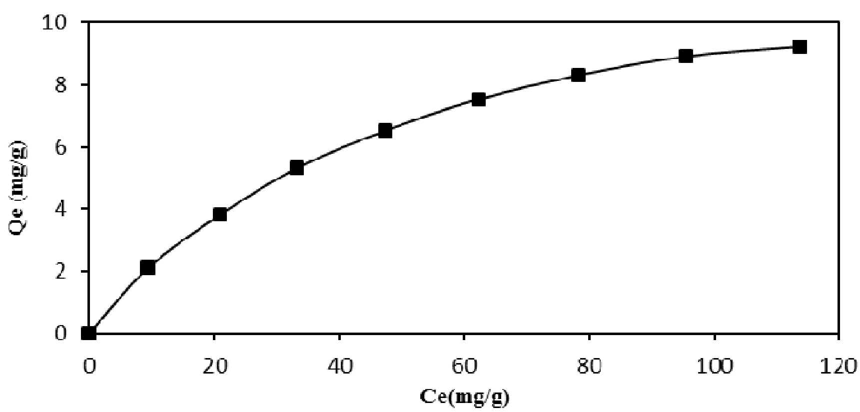


Figure 3. Adsorption equilibrium curve of direct red 23 on modified LD slag.

Langmuir model is based on the assumptions of homogenous adsorption sites and absence of interactions between adsorbed components. Langmuir equation is expressed as [14]:

$$Q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (2)$$

This can be written as,

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{K_L Q_0 C_e} \quad (3)$$

where Q_0 (mg/g) is the maximum monolayer adsorption capacity and K_L (L/mg) the energy of adsorption.

Freundlich model is an empirical model assuming a heterogeneous adsorbent surface and exponentially increasing adsorption capacity of the adsorbate. It is shown as [15]:

$$Q_e - K_F r C_e^{1/n} \quad (4)$$

This can be written as,

$$\log Q_e - \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F (L/mg) and n are Freundlich isotherm constants.

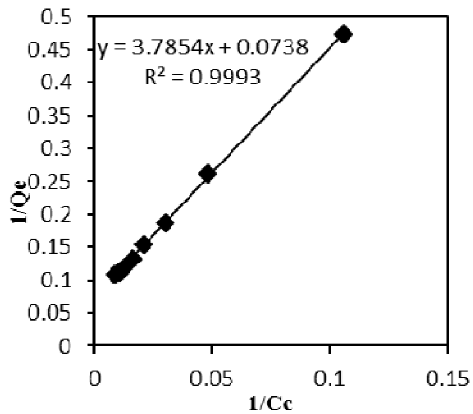


Figure 4. Langmuir Isotherm of direct red 23 adsorption on modified LD slag

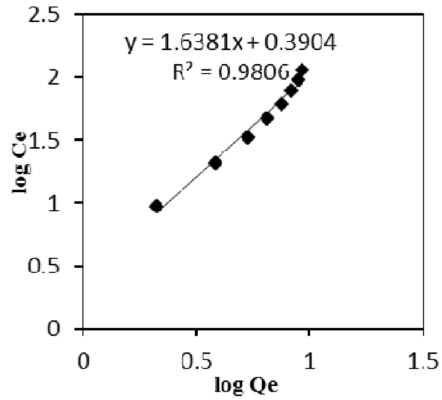


Figure 5. Freundlich Isotherm of direct red 23 adsorption on modified LD slag

The maximum adsorption capacity increases upto 9.24 mg/g for the initial direct red 23 concentration of 160 mg/L. The plots of linearized Langmuir model and Freundlich model are shown in Figure 4 & Figure 5 respectively. The results of the isotherm fittings are presented in Table 3. Based on the correlation coefficient, linearized Langmuir model equation shows better fit than the Freundlich Equation. Moreover, the linearized model of Langmuir gives better correlation coefficient (0.9993). Therefore, it can be opined that the adsorption process of direct red 23 by LD slag is a monolayer adsorption [16].

Table 3. Various parameters of Langmuir and Freundlich adsorption isotherm models.

Langmuir			Freundlich		
Q_0 (mg/g)	K_L(L/mg)	R^2	K_F (mg/g) $(L/mg)^{1/n}$	n	R^2
13.55	0.0194	0.9993	1.477	0.6104	0.9806

Acid treatment and microwave heating of the LD slag improves the surface structure of the LD slag with increase in BET surface to 81.18 m^2/g, enhances the opening of channels by formation of more micro pores in the material and increases the adsorption capacity of direct red 23 in comparison with the raw LD slag.

3.3. Effects of pH on adsorption

The effect of initial pH on adsorption of direct red 23 was studied from pH of 2 to 12 at 303 K and constant initial direct red 23 concentration of 100mg/l, adsorbent dose of 5 g/l and contact time of 24 h. Figure 6 shows the effect of pH on the adsorption of direct red 23 onto modified LD slag. It is seen that adsorption uptake of direct red 23 reduced with increase of the pH ranging from 2 to 12 (decreased from 7.63 mg/g to 5.10 mg/g), mainly because of the electrostatic interaction between the dye molecules and positive charge surface. High adsorption of direct red at acidic condition is due to presence of excess H^+ ions which enhances adsorption.

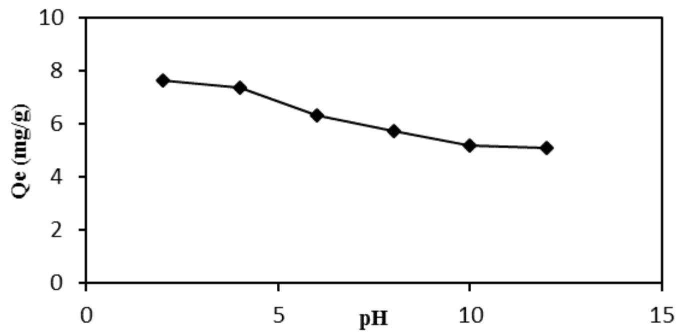


Figure 6. Effect of pH on direct red 23 adsorption on modified LD slag.

3.4. Adsorption kinetic study

The adsorption capacity Q_t (in mg/g) at contact time t, was calculated using [17],

$$Q_t = \frac{(C_i - C_t)V}{W} \tag{6}$$

where C_i is the initial dye concentration (mg/L), C_t is the dye concentration in the aqueous solution at time t (mg/L), V is the volume of the solution (L), and W is the weight of the adsorbent (g). The adsorption capacity for different initial dye concentartion at 303 K as a function of time has been plotted in Figure 7.

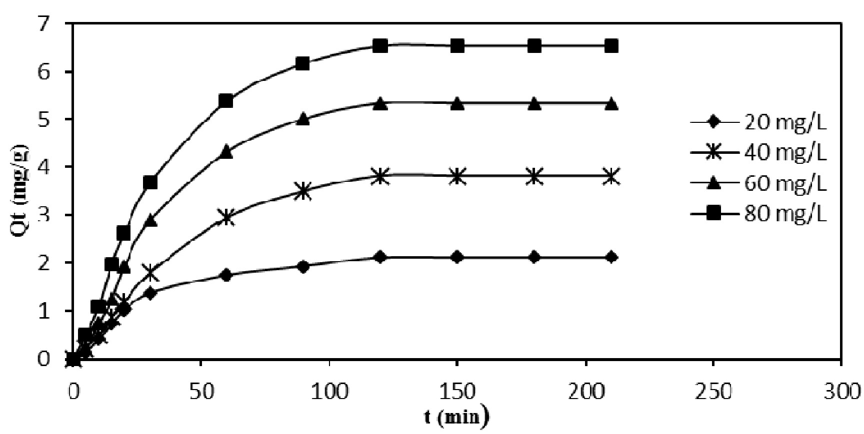


Figure 7. Effect of agitation time on direct red 23 adsorption on modified LD slag at various initial concentrations

The adsorption rate data are correlated with pseudo-first-order and pseudo-second-order models to find the appropriate kinetics [18]. The adsorption kinetics of modified LD slag represented by pseudo-first-order model is given in Eq. (7) [19].

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{7}$$

This can be rewritten as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{8}$$

where Q_e and Q_t are the adsorption uptakes in mg/g at equilibrium and at any time t (min), respectively. The constant k_1 (1/min) is the adsorption rate constant of pseudo-first-order model. Similarly, the pseudo-second-order kinetic model used to explain adsorption kinetics of modified LD slag is given in Eq. (9) [20].

$$Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \tag{9}$$

This can be rewritten as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{10}$$

where, the constant k_2 (g/mg min) is the adsorption rate constant of pseudo-second-order adsorption. The kinetic parameters including rate constant, correlation coefficient values and both theoretical and experimental adsorption uptakes for both pseudo-first-order model and pseudo-second-order model of the adsorption process are calculated at the initial direct red 23 concentration of 40 mg/L from the Fig 8 & 9 respectively. All the kinetic parameters of both the models are compared in Table 4.

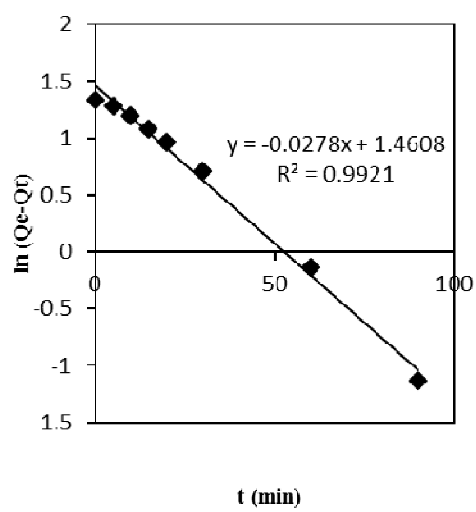
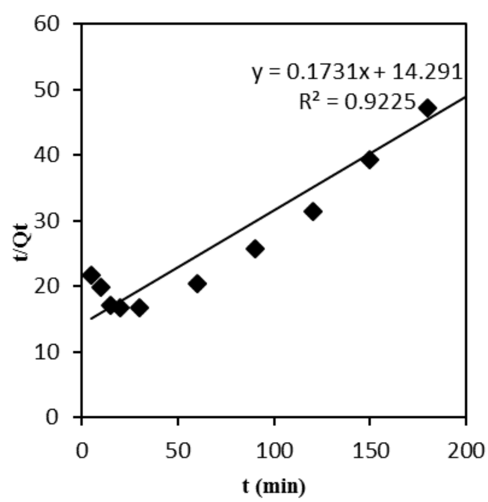


Figure 8. Pseudo-first-order model of direct red 23 adsorption kinetics LD slag



Fiure. 9. Pseudo-second-order model of direct red 23 adsorption kinetics LD slag

Table 4. Parameters of kinetic models for direct red 23 adsorption on modified LD slag.

Kinetic model	$Q_{e,exp}$ (mg/g)	$Q_{e,cal}$ (mg/g)	K_1/K_2 (min^{-1})	R^2
Pseudo-first-order model	3.81	4.309	0.0278	0.9921
Pseudo-second-order model	3.81	5.777	0.0029	0.9225

The results clearly reveal that pseudo-first-order model fitted the experimental data quite well in comparison with pseudo-second-order model. In case of pseudo-first-order model, the correlation coefficient value tends to become unity and the experimental and theoretical adsorption uptakes are more consistent. Therefore, the pseudo-first-order kinetic model is the appropriate model to describe the adsorption kinetics of direct red 23 onto modified LD slag.

3.5. Adsorption thermodynamics

The spontaneity of the adsorption process can be well understood considering both energy and entropy factors [21]. To determine the thermodynamic parameters, the changes in standard enthalpy (ΔH_0), standard entropy (ΔS_0), and standard free energy (ΔG_0) due to transfer of unit mole of solute from solution onto the solid–liquid interface, adsorption studies of modified LD slag were carried out at 303, 313, 323 K keeping initial dye concentration constant and contact time at 24 hour. The equilibrium data of direct red 23 adsorption at the above mentioned temperatures is plotted in Figure 10. The thermodynamic parameters, ΔG_0, ΔH_0, and ΔS_0 can be determined by using Eqs. (11) and (12):

$$\Delta G_0 = -RT\, lnK_L \quad (11)$$

$$\ln K_L = \frac{\Delta G_0}{RT} = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \quad (12)$$

where K_L is the Langmuir isotherm constant, R (8.314 J/mol K) is the universal gas constant, and T (K) is the absolute solution temperature.

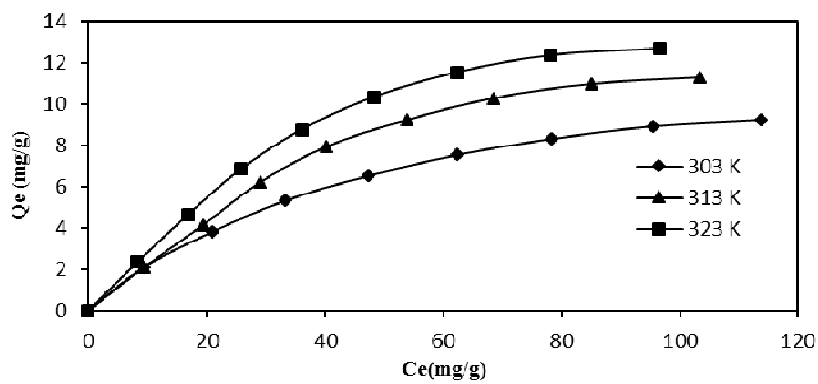


Figure 10. Effect of various temperatures on direct red 23 adsorption on modified LD slag at equilibrium.

In this study, the values of $\ln K_L$ are plotted against 1/T as shown in Figure 11, where ΔH_0 and ΔS_0 values are obtained from the slope and intercept of the plot. The thermodynamic parameters are documented in Table 5.

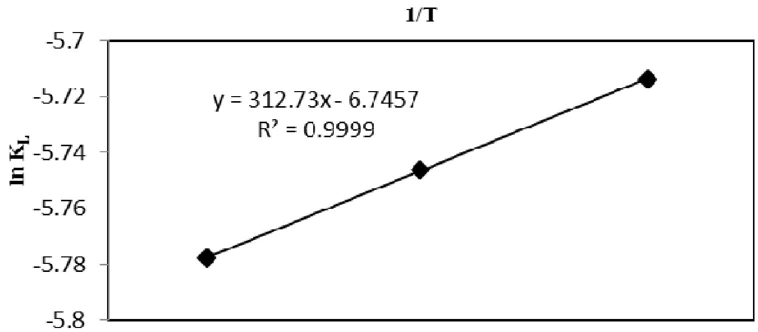


Figure 11. Plot of lnK_L versus reciprocal of temperature.

Table 5. Thermodynamic parameters of the adsorption process.

ΔH_0(kJ/mol)	ΔS_0(kJ/mol K)	ΔG_0 (kJ/mol)			K_L (L/ mg)		
		303 K	313 K	323 K	303 K	313 K	323 K
-2.6	-0.0056	-14.393	-14.953	-15.515	0.0194	0.0087	0.0103

Negative ΔG_0 values at all temperatures; clearly state that the adsorption process is a feasible process and it's spontaneous in nature [22]. Negative value of ΔH_0 indicates exothermic nature of the adsorption process. Typically, the magnitude of ΔH_0value for physical adsorption is in the range 2.1 to 20.9 kJ/ mol, and that of chemical adsorption from 80 to 200 kJ/ mol [23]. In this study, the calculated ΔH_0 value (-2.6 kJ/mol) indicates the physical adsorption of direct red 23 onto modified LD slag. The negative value of ΔS_0 (−0.0056 kJ/mol K) proposes that the fixation of the dye molecule at the solid-liquid interface turns less random [24]. In present study, the negative ΔS_0value may tell us that modified LD slag surface has affinity to adsorb water molecules over dye molecules. Henceforth, the adsorption of direct red 23 onto modified LD slag is an enthalpy driven process.

4. CONCLUSION

In this work, modified LD slag has been developed successfully as a low cost adsorbent for the removal of the direct red 23 by treating with dilute HCl (0.6 N) followed by heating in a domestic microwave oven for 10 min at 240 W. A batch adsorption experiment with this adsorbent shows the maximum monolayer adsorption uptake as 12.68 mg/g for direct red 23 at 323 K. From the results of the experiment, it is clearly understood that the adsorption capacity of modified LD slag decreased with increasing pH value. Adsorption equilibrium data fits the Langmuir isotherm model confirming monolayer adsorption. The adsorption kinetics follows the pseudo-first-order model. Thermodynamic analysis of the adsorption of direct red 23 onto modified LD slag shows that the process is spontaneous in nature and it's an enthalpy driven process.

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