Microwave Activated LD Slag for Phenolic Wastewater Treatment: Multi-parameter Optimization, Isotherms, Kinetics and Thermodynamics

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LD slag, a by-product of steel making industries, has been modified as low cost adsorbent for removing phenol through adsorption. The modified LD slag has been prepared by acid treatment followed by microwave heating activation. Box Behnken design (BBD) in response surface methodology has been applied to understand the effect of operating variables e.g. acid concentration (0.2-1 N of HCl), microwave radiation time (2-10 min) and power (240-1200 W), in the modification of adsorbent. Optimum conditions of the parameters are obtained with the help of Design Expert 7.0 (Stat-Ease Inc., USA) software. The adsorbent has been characterized by using XRF technique, BET apparatus and SEM images. The BET surface area of the modified LD slag is obtained as 81.18 m2/g. Batch experiments have been conducted at different temperatures (298 K, 308 K, 318 K). Langmuir model fits the experimental data with the maximum adsorption uptake of phenol, onto modified LD slag, as 3.4 mg/g at 298 K. The adsorption kinetics is fitted well to pseudo-second-order model. Thermodynamic analysis proves that the adsorption process is spontaneous in nature and it's an enthalpy driven process.

1. Introduction

Water pollution is a very serious environmental issue across the globe. Presence of phenol in water is one of the major reasons for water pollution due to its various harmful effects. Several processes have been developed to remove phenol from the industrial wastewater including advanced oxidation (Esplugas et al., 2002), membrane filtration (Rzeszutek and Chow, 1998), biological degradation (Annachhatre and Gheewala, 1996), electrochemical oxidation (Rodgers et al., 1999), photo catalytic degradation (Guo et al., 2006), and adsorption (Yousef et al., 2011).

Adsorption can be considered as one of the best methods to eliminate phenol from the waste water due to its cost effectiveness. Activated carbon is one such type of adsorbent which is widely used due to their good adsorption capacities for the removal of phenol. 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 phenol 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 coal (Ahmaruzzaman and Sharma, 2005;), fly ash (Wang and Jiang, 2007), red mud (Tor et al., 2006), waste sludge (Jain et al., 2004) and zeolites (Yousef et al., 2011) etc.

LD slag (Linz Donawitz (LD) converter slag), a solid waste of Steel making industries, consists of various components like oxides of Calcium, Magnesium, Iron etc. along with Silica (Das et al., 2007) and may be a good adsorbent for phenol removal due to its unique porous structure, with a sufficient surface area and a wide particle distribution. However, the adsorption capacity of raw LD slag was quite limited (Das et al., 2007) and needs to be enhanced by applying different activation techniques which involves several important parameters. Response surface methodology (RSM) with Box Behnken design can be a very good optimization tool (Montgomery, 1991; Pillai and Gupta, 2016) for knowing the interaction and influence of these significant

parameters on the preparation of modified LD slag for better adsorption. The focus of the present work is therefore to utilize LD slag as an economical low cost adsorbent for phenol removal with detailed study on a) Box Behnken design for optimization of parameters involved in activation or modification technique of LD slag b) phenol adsorption equilibrium and kinetic characteristics on modified LD slag.

2. Experimental Method and Optimization of Parameters

The LD slag used in this study, was collected from the TATA Steel, Jamshedpur, India. The slag, ground and sieved to 0.2 mm particle size, was treated with hydrochloric acid (HCl) at different concentrations (0.2-1N) and then washed and dried at room temperature for 24 hr. Microwave oven (Model 20PG3S, IFB) having a frequency of 2.45 GHz, was used for heating the acid treated LD slag uniformly at different power levels and variable duration for the activation of the adsorbent (Foo and Hameed, 2011). The physical and chemical and characteristics of both raw and modified LD slags were carried out by standard techniques. The specific surface area, pore volume and pore size of the adsorbents were determined by BET apparatus (Quantachrome, AUTOSORB-1, USA). The composition was determined using X-ray fluorescence spectroscopy technique (PANalytical, AXIOS) and the surface textures of the modified LD slag samples were analyzed in Zeiss Merlin scanning electron microscope.

Artificial wastewater having initial phenol concentrations (10–80 mg/L) was synthesized by dissolving desired amount of phenol of purity 99.5% in deionized water. Adsorption of phenol with LD slag was measured at an adsorbent dose of 0.5 g in 100 ml of aqueous solution in a set of 250 mL stoppered Erlenmeyer flasks. The pH was kept at 6 and the contact time was about 24 hours. The samples were filtered and the residual concentration of phenol in the solutions were determined using direct photometric method of ASTM Method (ASTM Standard D, 1976) by a double beam UV–vis-spectrophotometer (Perkin-Elmer, Lambda25) at a wavelength of 505 nm.

Optimization of interaction effects of the significant parameters involved in preparation of modified LD slag was performed using 3-factor, 3-level Box Behnken design. In the present investigation, HCl concentration, A (0.2-1 N); microwave time, B (2-10 min) and power, C (240-1200 W) were chosen as the independent variables with three equidistant levels; coded as low (-1), medium (0), and high (+1) and adsorption uptake was chosen as response, Y. Based on Design of experiments, 17 experiments were carried out to correlate the response (Y) with the independent variables (Montgomery, 1991).

3. Result & Discussion

3.1 Surface characterization of modified LD slag

Composition of the raw LD slag by XRF technique is documented in Table 1. The main components of the steel slag were calcium oxides and iron oxides followed by silicon and aluminium compounds. Detail characteristics properties of modified LD slag including external surface area, total pore volume and average pore diameter are also summarized in Table 1. From the present observation, it can be clearly found that the BET surface area of modified LD slag greatly improves compared to raw LD slag due to the development of additional pores because of microwave heating. LD slag prepared in this work showed porous structure as compared to the other reported slag adsorbents (Xue et al., 2009).

Table 1: Compositions and surface area of raw and modified LD slag

Type of slag	CaO (%)	Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	P_2O_5 (%)	MgO (%)	Other oxides(%)	Surface area(m^2/g)	Pore volume(cm^3/g)
Raw LD slag	55.119	27.732	9.999	1.140	1.469	1.774	2.767	81.18	0.124
Modified LD slag	30.006	50.304	13.863	0.011	2.155	2.232	1.429	14.51	0.054

The morphological structure of LD slag can be seen from the SEM photographs, as 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, as a result a high increase in pore volume is seen (Xue et al., 2009). 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 (Foo and Hameed., 2012).
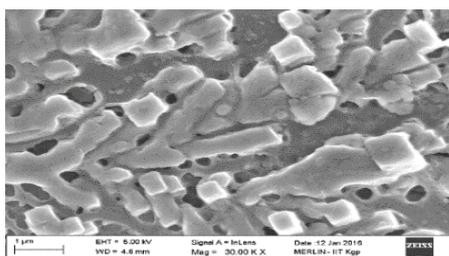
Figure 1: SEM image of the modified LD slag

3.2 Optimization of modification parameters LD slag using Box Behnken design

Box Behnken design for optimizing the response i.e. adsorption uptake (Q_e), using 17 experimental data, has been used to develop the following mathematical relationship between dependent variable (Q_e) and the independent variables i.e. acid concentration (A), microwave time (B) & power (C),

$$Y = 0.327 + 4.167A + 0.408B + 0.001C - 2.74 A^2 - 0.025B^2 - 6x10^{-7}C^2 - 0.029AB - 8.5x10^{-4}AC - 1.3x10^{-4}BC \tag{1}$$

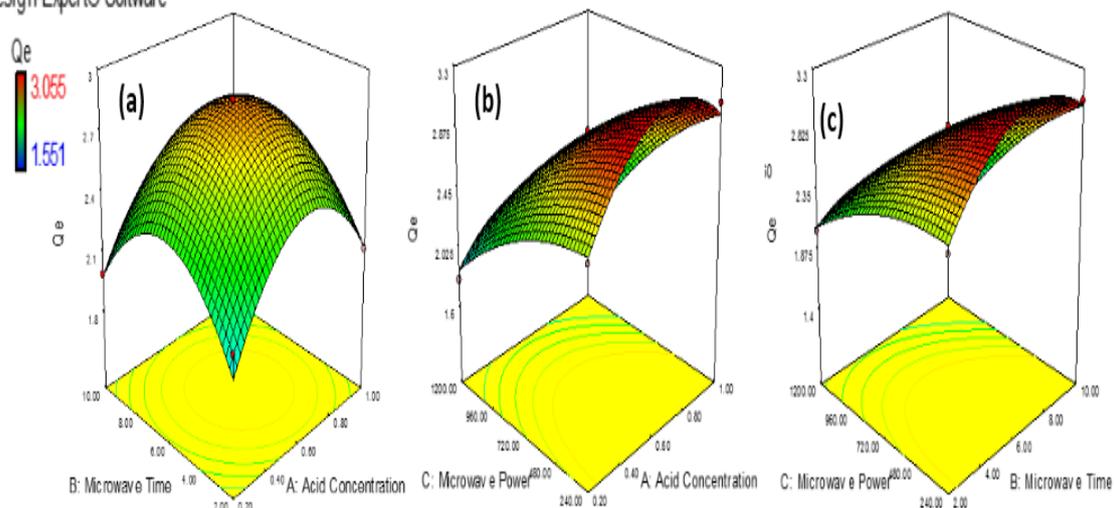*Figure 2: 3D response surface plot of effect of independent variables on adsorption uptake, (a) Qe vs. A and B; (b) Qe vs. A and C; (c) Qe vs. B and C*

The anlysis of variance (ANOVA) suggests that the experimental results fit to the response surface quadratic model quite well with the so called P-value ("Probability> F-value") less than 0.0001. The corelation coefficient (R^2) value for the adsorption uptake Q_e is obtained as 0.9885 confirming the best fit of the model. Adjusted R^2 (Adj R^2) value of 0.9736 further shows the high significance of the model. Coefficient of variance (C.V.) value of 3.55 % is under desirable range indicating that all the experimental results are dispersed within the satisfactory range from mean (Pillai and Gupta, 2016). The effects of two independent variables on the response, Q_e at one time keeping the third variable constant at the central value is presented in Figure 2. It can be noticed from Figure 2(a), medium acid concentration and higher microwave time are favourable for high adsorption uptake of phenol by modified LD slag while the microwave power is kept constant at the 720 W. Figure 2(b) clearly shows that in the lower microwave power and moderately high acid concentration are required for maximum adsorption uptake when microwave time is kept at 6 mins. It is depicted from Figure 2(c) that the adsorption uptake is maximum at lower microwave power and higher microwave time when the acid concentration is constant at 0.6 N. The probable reason for this effect can be understood as it is known that the acid treatment basically increases the porosity of the LD slag by removing surface impurities developing a porous structure on the surface. It provides a high internal surface area for microporous diffusion of phenol on its surface (Xue et al., 2009), resulting more adsorption uptake. A high temperature could be achieved inside the microwave oven in shorter time due to the uniform internal and volumetric heating. So, at a specific power and time, the thermal activation of the adsorbent takes place by releasing moisture and other

impurities from the adsorbent surface with the creation of small cavities, which enhances the adsorption (Foo and Hameed, 2012). But, as the power level increases, the adsorption uptake gradually decreases due to excessive overheating which may cause the destruction of the surface structure of the LD slag resulting less surface area and porosity. The maximum values of adsorption uptake Q_e, is obtained by proper selection of input variables. As per the best formulation, the maximum adsorption uptake of phenol by modified LD slag can be achieved as 3.252 (mg/g) at the optimum acid concentration of 0.64 N, microwave time as 6.99 min and the microwave power is 244.25 W. The desirability for maximizing the response is 1.0. Experimental adsorption uptake of phenol onto modified LD slag is obtained as 3.04 (mg/g) under above optimum process variables.
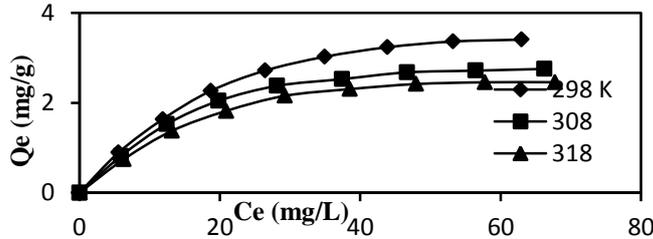

Figure 3: Equilibrium curves of phenol on modified LD slag at different temperatures.

3.3 Adsorption isotherm studies

The adsorption equilibrium studies of phenol over modified LD slag were carried out at 298, 308, 318 K as shown in Figure 3. The phenol adsorption uptake of the LD slag decreases with increasing temperature and the maximum phenol adsorption uptake was obtained as 3.4 mg/g at 298 K. Both Langmuir and Freundlich isotherm models have been fitted for understanding the adsorption performance and equilibrium characteristics. The Langmuir model is based on the assumptions of homogenous adsorption sites and absence of interactions between adsorbed components. Langmuir equation is expressed as (Langmuir, 1916):

$$Q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{2}$$

where Q_0 (mg/g) is the maximum monolayer adsorption capacity and K_L (L/mg) the energy of adsorption. The Freundlich model instead is an empirical model assuming a heterogeneous adsorbent surface and exponentially increasing adsorption capacity of the adsorbate. It is shown as (Freundlich, 1906):

$$Q_e = K_F r C_e^{1/n} \tag{3}$$

where K_F (L/mg) and n are Freundlich isotherm constants. The plots are shown in Figure 4 & Figure 5. The results of the isotherm fittings are presented in Table 2. Based on the correlation coefficient, linearized Langmuir Equations shows better fit than the Freundlich Equation with a correlation coefficient (0.9984). Therefore, it can be opined that the adsorption process of phenol by LD slag is a monolayer adsorption (Liu et al., 2010).
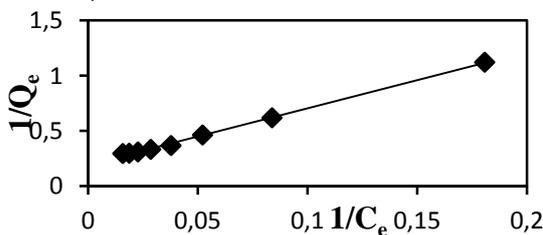

Figure 4: Langmuir Isotherm of phenol adsorption on modified LD slag at 298 K
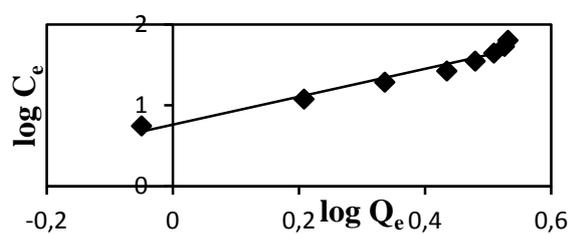
Figure 5: Freundlich Isotherm of phenol adsorption on modified LD slag at 298 K

Table 2: 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
5.163	0.038	0.9984	5.7889	0.580788	0.9576

3.3 Adsorption kinetic study

The adsorption uptake of phenol Q_t (in mg/g) at contact time t, was calculated using,

$$Q_t = \frac{(C_i - C_{t}))V}{W}$$ (4)

where C_i is the initial phenol concentration in the aqueous solution(mg/L), C_t is the phenol concentration in the aqueous solution at time t (mg/L). The transient adsorption data of phenol onto modified LD slag was modelled using both pseudo-first-order model and pseudo-second-order model as expressed in Eq. (5) and Eq. (6) respectively.

$$Q_t = Q_e(1 - e^{-k_1 t})$$ (5)

$$Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t}$$ (6)

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) and k_2 (g/mg min) is the adsorption rate constant of pseudo-first-order and pseudo-2nd-order model. The fitting parameters for both the kinetic models are presented in Table 6 which clearly reveal that pseudo-second-order model fitted the experimental data quite well as the correlation coefficient tends to unity and the experimental and theoretical adsorption uptakes are more consistent with each other concluding the rate-limiting step might be chemisorption (Ho and McKay, 1998).
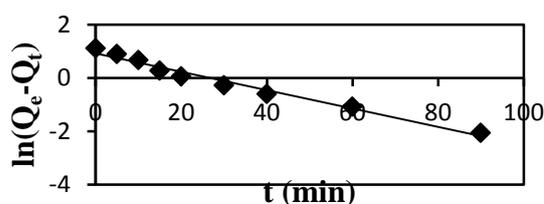

Figure 6: Plot of pseudo-first-order model of phenol adsorption kinetics LD slag at 298 K.
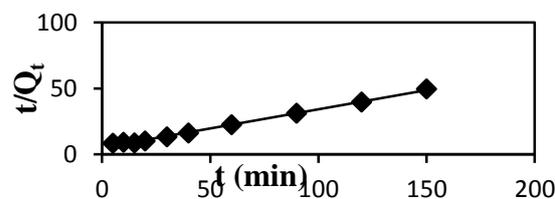
Figure 7: Plot of pseudo-second-order model of phenol adsorption kinetics LD slag at 298 K.

Table 6: Values of parameters of kinetic models for phenol 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	3.02	2.496	0.034	0.9785
Pseudo-second-order model	3.02	3.447	0.0162	0.9959

3.4 Adsorption Thermodynamics

The thermodynamic parameters e.g. change in enthalpy (ΔH_0), change in entropy (ΔS_0), and free energy change (ΔG_0) can be determined by using Eqs. (8) and (9):

$$\Delta G_0 = -RT \ln K_D$$ (8)

$$\ln K_D = -\frac{\Delta G_0}{RT} = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT}$$ (9)

where $K_D = \frac{Q_e}{C_e}$, R (8.314 J/mol K) is the universal gas onstant, and T (K) is the absolute solution temperature. The values of ΔH_0 and ΔS_0 values are obtained from the plot of $\ln K_D$ vs $1/T$ as shown in Table 4.

Table 4: Values of thermodynamic parameters of the adsorption process.

ΔH_0(kJ/mol)	ΔS_0(kJ/mol K)	ΔG_0 (kJ/mol)		
		298 K	308 K	318 K
-15.476	-0.0077	-7.228	-8.144	-8.768

Negative ΔG_0 values at all temperatures; clearly state that the adsorption process is a feasible process and it's spontaneous in nature (Foo and Hameed, 2012). Negative value of ΔH_0 (-15.476 kJ/mol) indicates exothermic nature of the physical adsorption of phenol onto modified LD slag. The negative value of ΔS_0 (−0.0041 kJ/mol K) proposes that the fixation of the phenol molecule at the solid-liquid interface turns less random.. Henceforth, the adsorption of phenol onto modified LD slag is an enthalpy driven process (Yousef et al., 2011).

4. Conclusions

In this work, modified LD slag has been processed successfully as a low cost adsorbent for the removal of phenol. The modification parameters i.e. HCl concentration, microwave heating power and time have been optimized successfully by Box Behnken design. Batch adsorption shows the maximum monolayer phenol adsorption uptake as 3.4 mg/g for phenol at 298 K. Adsorption equilibrium data fits the Langmuir Isotherm model describing it as monolayer adsorption process. The adsorption kinetics follows the pseudo-second order model. Thermodynamic analysis of the adsorption of phenol onto modified LD slag proves that the process is spontaneous in nature and it's an enthalpy driven process.

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