Removal of Reactive Red 120 on Fe-Hydrotalcite: Isotherms Study.

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ABSTRACT: *HDL-MgFe is a Hydrotalcite that represent a compound lamellar double hydroxide. It was prepared through the continuous co-preparation method. The solid was characterized by surface area measurements, X-ray diffraction and temperature-programmed desorption of CO_2. The adsorbent was used for the adsorption of Reactive Red 120 dye, and the factors affecting the adsorption were discussed, including concentration of adsorbent solid and contact time. The adsorption isotherms data were fitted to the Langmuir, Freundlich, Redlich-Peterson, Sips and BET models. The most suitable adsorption conditionswere found at a contact time of 60 min and solidconcentrarion of $2g.L^{-1}$. The results for MgFe hydrotalcite showed a high adsorption with percentage about 90% of dye removal. Langmuir and Redlich-Peterson models were the isotherms that best described the removal process.*
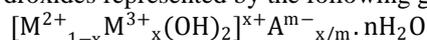***KEYWORDS:*** *Isotherms adsorption, Reactive Red 120, Fe-Hydrotalcite.*

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I.   INTRODUCTION

Hydrotalcites are lamellar double hydroxides represented by the following general formula:

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{m-}_{x/m} \cdot nH_2O$$

Where M^{2+} is a divalent metal cation, M^{3+} is a trivalent cation, A^{m-} is an intercalated anion with charge m, x is the ratio of divalent and trivalent cations and n is the number of mols of water. These compounds eliminate negatively charged species by surface adsorption and also by anion exchange, because they have a very large surface with spaces between layers(Cavani et al., 1991). Hydrotalcites can present a wide variety of applications depending on their properties (composition, crystallinity, thermal stability and acid-base adjustable properties). Among the mostly applications can be mentioned the use as heterogeneous catalysts, anionic exchangers, in the pharmaceutical industry and as adsorbents of pollutants in effluents(Vaccari, 1998; Xu et al., 2011; Rives et al., 2013; Fan et al., 2014; Zubair et al., 2017; Bharali and Deka, 2017).

Shan et al.,(2015)reported the obtaining of magnesium and aluminum hydrotalcite and its evaluation for the removal of three red dyes by the adsorption method. The results obtained show that the dyes were adsorbed with efficiency by the hydrotalcite and the kinetic models found were of second order and the isotherms corresponded to the Langmuir model.Lazaridis, Karapantsios, and Georgantas.,(2003)studied the removal of a reactive dye, Cibacron Yellow LS-R, from aqueous solutions by adsorption onto hydrotalcite particles and the model that described the process was Langmuir isotherm.Y.-J. Li et al.,(2006)reported the study of the preparation of Mg-Al hydrotalcite and the evaluation of its adsorbent properties for the removal of thiocyanate using the calcined and natural solid and the adsorption isotherms showed correspondencefor the Langmuir.

The studies cited have a common characteristic in the adsorption process, the study of isotherms models.Thisisveryimportantbecausetheexperimentallymeasuredadsorptionisotherms and breakthrough curves are conventionally used to design new ads orption based separation processes. Adsorption is other ms are the out come of static ads orption experiments where the ads or bate and adsorbent are kept in contactfor a long time untilequilibriumisreached(Poursaeidesfahani et al. 2019).

In this context, the objective of this work was to evaluate the effect of the Fe hidrotalcite for the removal of Reactive Red 120 dye and find the models that can describe with precision the experimental results of adsorption isotherms, specify the parameters that determined the process behavior.

II. EXPERIMENTAL

The adsorbate used was Reactive Red 120 was obtained from Sigma-Aldrich.

The adsorbent solid was prepared by the continuous co-preparation method previously reported (Perez-Lopez et al. 2006). Two aqueous solutions were prepared: solution "1", with the nitrates of the metals; $Mg(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$. Solution "2" of the mixture of NaOH and Na_2CO_3. The solutions 1 and 2 were mixed simultaneously in a reactor (CSTR), with a constant temperature and pH. The precipitate was maintained under agitation for 1 h at 50 °C and then vacuum filtered, washed with deionized water and dried in an oven at 80 °C overnight.

2.1. Characterization

The solid were characterized by X-ray diffraction (XRD) where the patterns were collected through the powder method with a Bruker D2-Phaser diffractometer;N_2adsorption/desorption (BET)were performed on a NOVA 1000e equipment (Quantachrome Instruments); and temperature-programmed desorption (TPD-CO_2) where the profiles were performed in a multipurpose system.

2.2. Adsorption experiments

The adsorption tests were performed in a batch mode using volumes of 100mL at 25 °Cof Reactive Red 120at 30mg.L^{-1}. The equipment used to determine the adsorption parameters (contact time and solid concentration) was the Wagner Agitator model MA160BP from Marconi and the concentration of dye was analyzed in the Thermo Scientific spectrophotometer model Genesis 10S UV-VS at wavelength of 535 nm. All experiments were performed in duplicate. Considering that the prepared adsorbent has alkaline properties, the experiments were carried out at the natural pH of the solution containing the solids, which were approximately 8.

2.3 Adsorption isotherms

For these experiments, 2 g.L^{-1} of HDL-MgFe was used and the adsorption time was 60 min and natural pH. The experiments were carried out in bench refrigerated incubator Shaker (CIENTEC - model CT-71RN) at temperatures of 25 ºC. The experimental results was adjusted to Langmuir(Langmuir 1918), Freundlich(Rad, Haririan, and Divsar 2015), Sips(Debord et al. 2016), BET (eq. 7) (Pajarre and Koukkari 2018)and Redlich-Paterson models(Wu et al. 2010).

$$q_e = q_m K_L \frac{C_e}{1+K_L C_e} \text{ (eq. 4)}$$

$$q_e = K_F C_e^{1/n} \text{ (eq.5)}$$

$$q_e = \frac{q_{max} b C_e^\gamma}{1+b C_e^\gamma} \text{ (eq. 6)}$$

$$\frac{p}{v(p_0-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_0} \text{ (eq.7)}$$

$$q_e = \frac{K_R C_e}{1+\propto C_e^\beta} \text{ (eq. 8)}$$

where q_e (mg·g^{-1}) is the equilibrium adsorption amount at equilibrium concentration of C_e (mg·L^{-1}); q_m is the maximum capacity of the adsorbent (mg·g^{-1}); v is the total volume of the adsorbed gas, v_m the volume of the adsorbed gas in a unimolecular layer covering the surface, p is the pressure, p_0 the saturation pressure, c is a constant and K_L is the Langmuir adsorption constant (L·mg^{-1}), K_F (mg^{1-n}·L^n·g^{-1}) and n are the Freundlich affinity coefficient and linearity, respectively.

III. RESULTS AND DISCUSSION

3.1 Characterization

The XRD profile of the adsorbent solid can be observed in the Figure 2. The diffractogram of HDL-MgFepresent peaks characteristics to the general structure of the hydrotalcites, which show three main peaks at approximately 11, 23 and 34°. These reflections correspond to diffraction bycristal planes (003), (006) and (009) and represent the separations between layers. The plane is spaced one-third per unit cell distance apart and corresponds to the interlayer.The intense peak (003) that corresponding to 11° signal, indicates the formation of highly crystalline solid(Shekoohi et al. 2017). Thus, the hydrotalcite synthesized presented a good crystallization and a structure between layers similar to those reported in the literature (Nguyen, Nguyen, and Nguyen 2018; López et al. 2019; Yang et al. 2016).
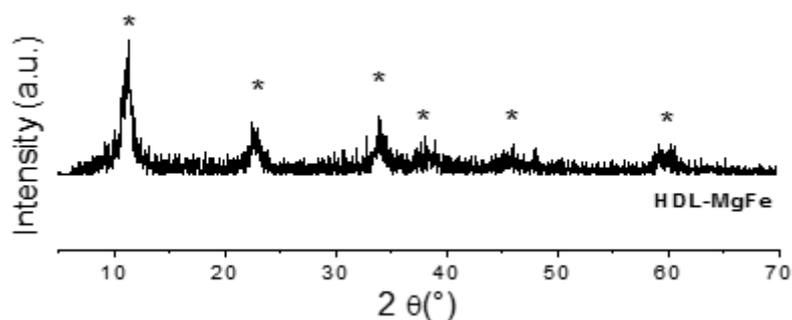
Figure 1. X-ray diffractogram of the HDL-MgFe hydrotalcite.

The specific surface for the solid was 118.9 $m^2.g^{-1}$. The HDL-MgFe has a larger surface which is in accordance with the lower crystallinity of HDL-MgFerevealed in XRD profile (Figure1). This fact is important because the rate of adsorption of adsorbent solids depends inversely on particle size and the adsorption properties depend on their shape, internal surface area and pore size distribution.

The total number of basic sites on the surface can be determined by the temperature at which the desorption peak occurs, the value found was 0.23 $mmol.gcat^{-1}$. As that samples reveal maximum desorption temperatures (Tmax) above 280ºC, which corresponds to medium (240-303°C) and strong (326-396°C) sites (Pavel et al., 2012); and in this case, the maximum of temperature found was 385°C, showing that HDL-MgFe provides strong basic sites, important characteristic for the acid dye removal.

3.2. Effect of solid concentration

Adsorption experiments of studied the behavior of HDL-MgFe concentration for Reactive Red 120 removal, are show in Figure 2.
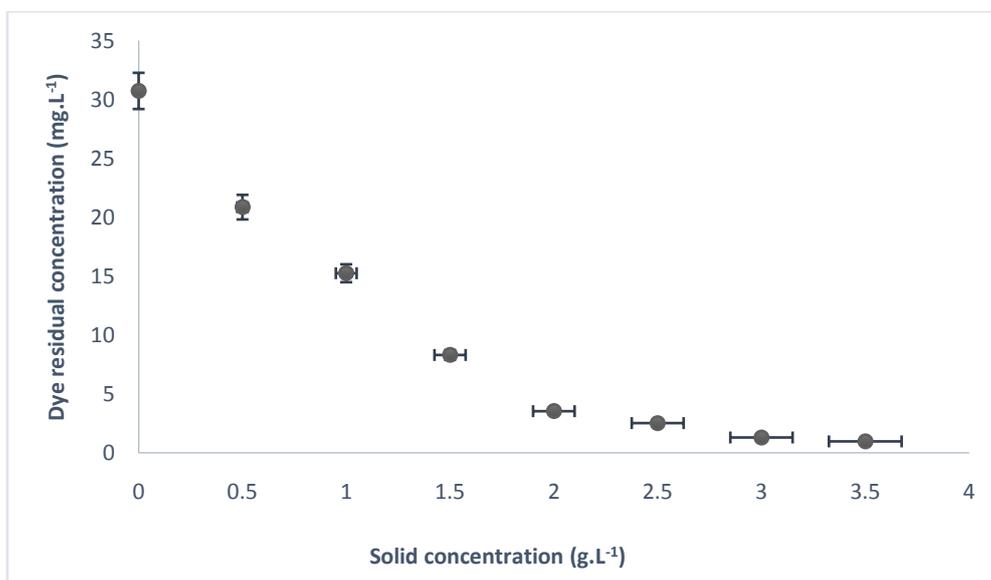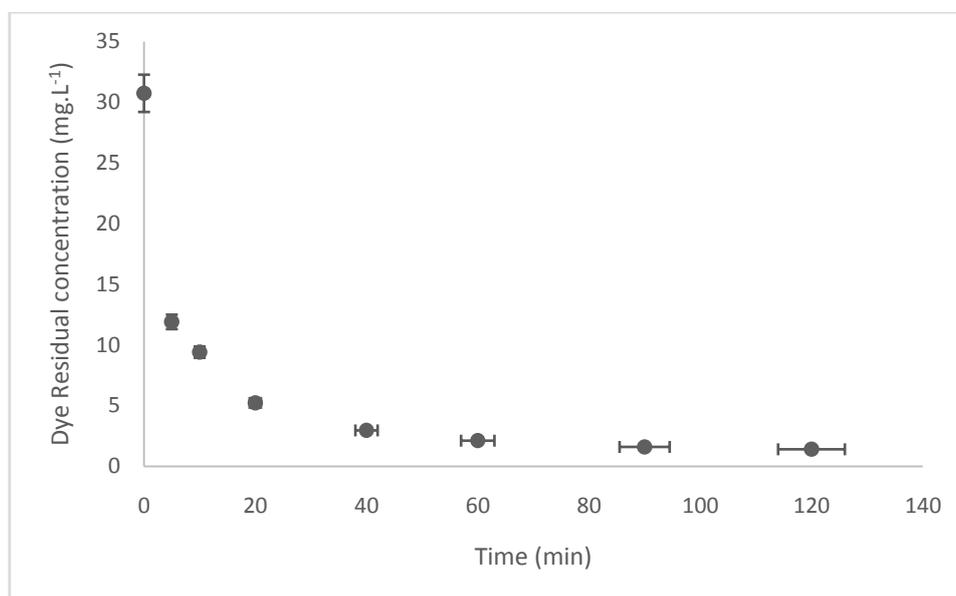

Figure 2. Effect of the solid concentration in the removal of Reactive Red120 dye. Conditions: adsorption time 30 min, initial concentration 30 $mg.L^{-1}$ of the dye, natural pH.

Figure 2 shows that the concentration of the adsorbed dye increases with increasing the adsorbent dosage until arriving to equilibrium, while continuing to increase the solid concentration, after equilibrium, the dye removal is not significative. The results obtained can be explained by evaluation of the behavior of the total adsorption area, where the adsorption in the surface cause an increase in adsorbent concentration and an increase in the number of available and active sites for dye molecules.After of 2 $g.L^{-1}$of HDL-MgFe, the equilibrium was attained, which indicates thesaturation of the solid surface with the about 90% of the dye removalwhich corresponds to residual concentration of 2,5 $mg.L^{-1}$(dye initial concentration was 30 $mg.L^{-1}$). This fact may be related to the HDL-MgFe hydrotalcite present a larger surface area, resulting in a greater total dye removal capacity. Therefore, this date was used for the follow tests.

3.3. Effect of contact time

Figure 3shows theremovalofReactive Red 120 dye at differentadsorptiontimes.The adsorbent dosage for the solid was2.0 g.L^{-1} for HDL-MgFe.

Figure 3. Effect of contact time in the removal of Reactive Red 120 dye. Conditions: solid concentration 2g.L^{-1}, initial concentration 30 mg.L^{-1} of the dye, natural pH.

It can be seen in the figure 3 that HDL-MgFe solid present a fast kinetics for the Reactive Red 120 removal which after about 5 min, more than 60% of the dye was removed. This result is important since a rapid removal of pollutant and arrive of equilibrium in a short period of time shows that the adsorbent used was efficient.

Also, it can be seen that kinetics of dye removal was faster up to about 20 min and after a period of 60 minutes the removal occurred slowly and the concentration variation was not relevant over time. Initially all the active sites were free in the solid surface which results in a fast adsorption. When occupied by the sorbate, these free sites decrease, leading to the saturation of the solids. Therefore, it was determined that the best condition for the removal of Reactive Red 120 on HDL-MgFe was in a time of 60 min.

3.4. Adsorption isotherms

Adsorption isotherm is an invaluable curve describing the phenomenon governing the retention of a substance from the aqueous porous media or aquatic environments to a solid-phase(Foo and Hameed 2010).

Therefore, to establish the most appropriate correlation for the equilibrium curves and to estimate the parameters of the isotherms, the Langmuir, Freundlich, Redlich-Peterson, Sips and BET models were adjustedto experimental data. In order to predict whether the adsorption of the Reactive Red120 in aqueous solution was efficient or not, the shape of the isotherm, the statistical parameters and the values of the constants for each non-linearized model were taken into consideration. The experimental values of qe and Ce are initially treated with the linearized equations in order to determine the models parameters and the isotherms are reconstituted using the determined values (Hamdaoui and Naffrechoux 2007).

Figure 4 shows the experimental adsorption isotherms and compared with models of Langmuir, Freundlich, sips, BET and Redlich-Peterson for removal of Reactive Red 120 using HDL-MgFe.
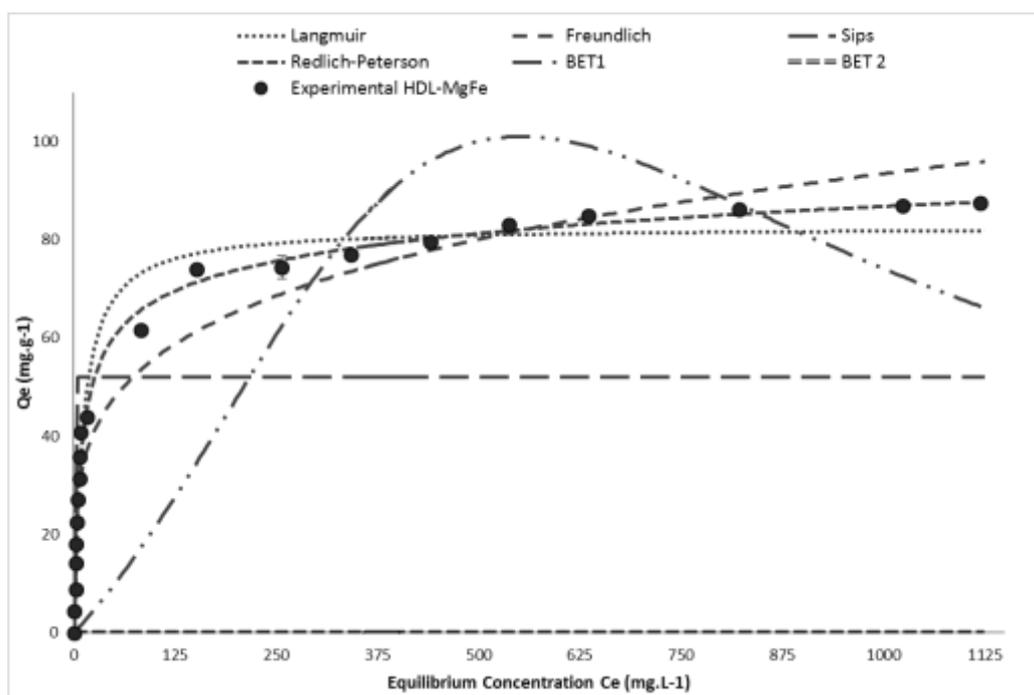
F**igure4**. Comparison between values predicted by the Langmuir, Freundlich, Sips, BET and Redlich-Paterson models and the experimental data isotherm of Reactive Red 120adsorption in HDL-MgFe. Conditions: Natural pH, adsorption time 60 min, adsorbent dose 2 g.L^{-1}.

In Table 1 it can be seen that the models that best described the equilibrium data of the Reactive Red 120 with HDL-MgFe were Redlich-Peterson model as it had an R^2 value closer to 1 with a value of 0.9943 and exhibited a minor error of 0,108.

Table1. Parameters of the Langmuir, Freundlich, Redlich-Peterson, Sips, BET 1 and BET 2 isotherms for the adsorption of Reactive Red 120 dye in HDL-MgFe.

Freundlich		Langmuir	Redlich-Peterson	Sips	BET 1	BET2
k_f 20.025		qmax 82.594	qm 48.872	qm 52.085	9.29E-06	qs 179.820
N	4.484	KL 0.0945	Kr 0.2243	b 940.596	K_2 0.0018102	C_{BET} 6.295E-06
			N 0.9156	g 10.844	qbet 19682.133	Cs 3.728
		R^2 0.9822	R^2 0.9943	R^2 0.1305	R^2 0.3815	R^2 -2.5833
$R^2$0.9451				Error 16.531	Error 11.758	Error 68.124
Error1.043		Error0.339	Error0.108			

Figure 4and table 1 show the adsorption isotherm models consideredfor Reactive Red 120 removal onHDL-MgFe and its parameters.

Freundlichisothermis a modelthat can be expressedthe no limit for the ads or ption capacity because adsorption quantity tends to infinity when the solution concentration increases. It can be seen in the table 1 that in this model, the empirical term N obtained was 4,484 and according with Giles, Smith, and Huitson.,(1974), when n>1 the curve qe vs. Ce will present concave shape in relation to the axial plane, therefore the adsorption isotherm is satisfactory. However, considering the R^2 (0.9451) and error (1.043), Freundlich was not model that more approximated to experimental data.

The R^2 for the models of Langmuir (0.9822) and Redlich Peterson (0.9943) shows that did not present a significant difference between them. The Langmuir model consider the adsorption in monolayer and represents the chemical adsorption in different adsorption sites. Redlich–Peterson model is a hybrid isotherm featuring both Langmuir and Freundlich isotherm that represent adsorption equilibriumona concentration, can be applied either in homogeneous or heterogeneous systems due to its versatility.

Sips model is an isotherm that relates the Langmuir and Freundlich model and predicts the systems of heterogenous adsorption and work around the limitation of the adsorbate concentration associated with Freundlich isotherm (Debord et al. 2016). BET 1 and 2 models were developed to derive multilayer adsorption systems with relative pressure ranges that is most widely applied in the gas–solid equilibrium systems (Foo and Hameed 2010).

Sips, BET 1 and BET 2 cannot described the experimental data. The models not adjusted to experimental results as can be seen in the Figure 4. Table 1 shows that que R^2 are 0.305, 0.3815 and -2.58, respectively, that are values that not represent a good behavior. The models that have a better correlation with the experimental data are Langmuir (qmax 82.594) andRedlich Peterson (qm 48.872) sincetheyadjust the experimental date in a satisfactory way unlike the other models studied that besides not adjusting the data, they do not describe the thermodynamic behavior of the adsorption process. These models indicate that the processes occurred at homogeneous and specific sites.

The HDL-MgFe solid showed a good behavior of the basic sites indicating a realtion between strength and number of basic sites that involves the dye chemistry and the acid-base properties of the solids. The retention of the dyes by the materials involves several attractive forces, such as ionic interactions, Van de Waals forces, hydrogen bonds and covalent bonds. Depending on the type of the dye, one or more forces act in the adsorption process.

Theresultsofthemodelswerecomparedwiththoseobtainedbyotherauthorsusingthesamedye   and differentsorbentsolids.

Srikantan, Suraishkumar, and Srivastava., (2018)studied the influences the ads orption equilibrium of Reactive Red 120 onhairyrootsof H. annuus. The ads orption equilibrium parameters were adjusting to experimental data and the best estimated was for Langmuir is other mw it h them aximumdye ads orption capacity of the roots increasing from0.26 mg g^{-1} to 1.51 mg g^{-1}.

Jawad et al., (2019)investigated a biofilm ofcross-linkedChitosan- Ethylene GlycolDiglycidyl Ether (Chi-EGDE) as a biosorbent for Reactive Red 120. The adsorption data of dye on the biofilm were in agreement with Langmuir isotherm with a maximum adsorption capacities of 165.3 mg.g^{-1}.

Li et al., (2014)studied Reactive Red 120 removalmodifyingonlysozyme. The ads orption behaviour of lysozyme by the Reactive Red 120 modified magnetic chitos an micro spheres fitted the Langmuir modelwitha maximum adsorption capacities of 116.9 mg.g^{-1}.

Demarchi, Campos, and Rodrigues., (2013) that presents a study of the use of chitosan–iron(III) crosslinked with glutaraldehyde (Ch-Fe) as an adsorbent for the Reactive Red 120 in batch and fixed-bed systems. The maximum adsorption capacity was calculated from the adsorption isotherms, and well fitted by the Langumir–Freudlich isotherm model with the maximum capacity of 433 mg.g^{-1}.

As can be seen in the different studs all models evaluated for the removal of reactive red with different sorbent solids describe a Langmuir equilibrium. The results obtained by the present study with a value of qmax=82.594 mg.g-1 and qm=48.872 mg.g-1 for HDL-MgFe, which is a good value comparing with others adsorbents . The values of qm and qmax obtained in the present work exhibit good results and showing that the basic solids tested in the present study are a good alternative for acid dyes removal as Reactive Red 120.

IV.   CONCLUSIONS

The results of the XRD analysis show that the obtained solid had high crystallinity with hydrotalcite-type structure.The effect of the trivalent ion on the properties of the magnesium-based hydrotalcite was significant, since iron favors the formation of a solid with a good specific area HDL-MgFe of 118.9 m^2.g^{-1}. Alkaline characteristics reveal to be more important than the specific surface area of these hydrotalcites for the removal of Reactive Red120 dye.The effect of solid concentration on Reactive Red 120 removalshowed that was reached close to 90% of the dye removal with adsorbent dosage of 2 g.L^{-1} for HDL-MgFe,and the most suitable condition for the removal of the Reactive Red 120 is given in a time of 60 min.The adsorption isotherms showed that the Langmuir and Redlich-Peterson models described best the equilibrium data of the Reactive Red 120 dye on HDL-MgFe indicate that the processes occurred at homogeneous and specific sites.

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