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Fabrication of Nanoporous Functionalized Hydroxyapatite as High Performance Adsorbent for Acid Blue 25 Dye Removal

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ABSTRACT

In this study, nanoporous hydroxyapatite was synthesized and functionalized via tetraethylenepentamine in order to obtain a novel adsorbent for efficient removal of Acid Blue 25 dye from aqueous solution. Functionalized hydroxyapatite was characterized by Fourier transform infrared spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and N_2 adsorption-desorption. Batch adsorption studies were performed to investigate the effect of various parameters such as pH, initial dye concentration, adsorbent dosage, contact time and temperature. The results illustrated that dye removal percentage was reduced with incrementing pH of the solution and dye concentration. Maximum removal of Acid Blue 25 in the solution having an initial dye concentration of 40 mg/L using 10 mg of adsorbent at 25 °C was 88%. Experimental kinetic data obeyed the pseudo second order model was appointed in 180 min. The Freundlich isotherm model also represented a suitable fit with adsorption data. The thermodynamic study was indicated that the adsorption process was spontaneous and exothermic. Results confirmed that FHAp adsorbent possesses the potential to be used as a suitable candidate for Acid Blue 25 Dye removal from aqueous solutions.

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1. INTRODUCTION

Dye contaminated effluents are accounted as one of the contaminants that enter the environment through wastewater discharges of industries such as textile, dyeing, color production, food, papermaking and plastics; that may lead to serious harms to agriculture and agricultural regions [1]. So, to avoid any harm, removal of these dyes from wastewaters, before discharging them, is an essential environmental point, which needs careful attention [2]. Since synthetic dyes are highly resistant to biological degradation and are highly stable in the environment; biological methods are not efficient for the removal of most of these synthetic dyes [3].

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There are many physical and chemical proccesses such as coagulation, filtration, dispersion, precipitation, oxidation, adsorption and membrane separation to remove dyes from wastewaters [4]. Among the above mentioned methods, adsorption technique has attracted the attention of many researchers due to being the easy operation, cost-effective, high efficiency and regeneration [5].

Acid Blue 25 (AB25) is one of the anionic dyes that is commonly used dyes for dyeing wool, silk, leather, paper and cellulose, which is discharged to the environment by industrial wastewaters [6].

Hanafiah et al. [7] investigated the acid blue 25 adsorption on base treated *Shorea dasyphylla* sawdust in a batch adsorption process. The result showed that the maximum adsorption capacity of BTSD was 24.39 mg/g. Yang et al. [8] studied the biosorption of modified and unmodified biomass of *Penicillium* YW 01 for Acid Blue 25. The result indicated that maximum

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biosorption capacity of acid blue 25 dye onto modified biosorbent was 118.48 mg/g under phosphoric–phosphate buffer with initial dye concentration of 200 mg/L at 30°C [8].

Many adsorbents like modified activated carbon [9], Shrimp shell [10] and modified banana peel [11] were proposed to AB25 removal from aqueous solutions. Hydroxyapatite (HAp)[$Ca_{10}(PO_4)(OH)_2$] is the inorganic fraction that forms bones with many applications in bone replacement, biomedical ceramic implants' production, drug delivery systems and wastewater treatment [12]. The HAp has also become very important for the removal of heavy metals from aqueous solutions [13]. Investigations on the contaminants elimination using adsorption have shown that surface modification *via* functional groups can develop adsorbent efficiency [12]. Amine functional groups are appropriate choices for functionalizing adsorbents due to extraordinary bonding strength and high selectivity [14]. In this study, functionalized hydroxyapatite (FHAp) by tetraethylenepentamine (TEPA) was used to remove AB25 from aqueous solution. Hydroxyapatite was synthesized by precipitation method and was fictionalized by the amine functional group. Effect of parameters like pH, adsorbent dosage, the initial concentration of dye, contact time and temperature on adsorption efficiency was investigated. Inaddition, adsorption isotherms, kinetic and thermodynamic were studied.

2. MATERIALS AND METHODS

2. 1. Reagents Dipotassium hydrogen phosphate, ethanol and tetraethylenepentamine (TEPA) all in analytical grade, were purchased from Merck and used without further purification. The Acid Blue 25 (AB25) dye was +used as absorbate and its chemical structure and properties are shown in Table 1. To prepare the solution, distilled water was used during the experiment.

2. 2. Preparation of Adsorbent

2. 2. 1. Synthesis of Hydroxyapatite Particle In this research, hydroxyapatite was synthesized using the co-precipitation method. In order to synthesis of hydroxyapatite, Calcium acetate and dipotassium hydrogen phosphate solutions were prepared with concentrations of 0.06 mol/L and 0.1 mol/L, respectively. Equal volumes (150 mL) were removed from each solution and both were added dropwise to 200 mL of water in the reaction flask over a period of 30 minutes. The reaction flask was immersed in a water bath heated to 100°C. The reaction mixture was then stirred and boiled under constant temperature for one hour. The precipitate was rinsed with distilled water and dried in an oven at 80 °C [15].

TABLE 1. Strouhal number for different geometric cases

Chemical formula	$C_{20}H_{13}N_2NaO_5S$
Molar mass (g/mol)	416.38
λ_{max} (nm)	602
Appearance form	Blue powder

2. 2. 2. Hydroxyapatite Functionalization To functionalize hydroxyapatite, the wet impregnation method with tetraethylenepantaminewas used. 2.81 g of tetraethylenepentamine was dissolved in 20mL ethanol for 30 min under stirring. Then, 0.2g hydroxyapatite was added to the ethanol-TEPA solution and temperature of the solvent was maintained at 80°C. After 2 hours of stirring, the sample was centrifuged and dried in an oven at 80°C for 10 hours [14].

2. 3. Adsorbent Characterization Fourier-Transform Infrared (FTIR)spectroscopy of HAp and FHAp samples was performed on the Bruker-Tensor 27 IR spectrometer in the wavelength range of 400-4000 cm^{-1}. The crystallinity of the samples was determined by X-Ray Diffraction (XRD) using a X'PERT PRO device (Phillips Company, Netherlands) in the range of 2θ from 10 to 80°. The morphology of the samples was determined by Field Emission Scanning Electron Microscopy (FESEM), TESCAN MIRA3 model, which is equipped with an Energy Dispersive Spectroscopy (EDS) analyzer to determine the elements present in the samples. Specific surface area, pore volume and mean pore diameter of samples were calculated using nitrogen adsorption-desorption analysis at 77 K (BELSORP model, BEL company, Japan).

2. 4. Batch Adsorption Experiments In order to carry out the adsorption experiments, the AB25 stock solution was prepared at a concentration of 500 mg/L by dissolving a specific amount of AB25 powder in distilled water. Other concentrations required during the experiment were obtained by dilution of the stock solution. In all stages of the batch absorption experiments, a given amount of the absorbent FHAp was added to the flasks containing 10 mL AB25 solution in the concentrations needed. The samples were then transferred to a shaker at 250 rpm. After the desired time elapsed, the samples were removed from the shaker and centrifuged at 6000 RPM for 15 minutes. At the end, to the final assay of concentration of AB25, the absorbance of the supernatant was measured using a UV/VIS.SU-6100 spectrophotometer at a maximum wavelength of 602 nm. To control pH in all steps, 0.1 mol/L HCl or NaOHwere used.

3. RESULT AND DISCUSSION

3. 1. Characterization of Adsorbent

3. 1. 1. FTIR Spectroscopy To study the chemical structure and functional groups of HAp and FHAp adsorbent, FTIR analysis (Bruker-Tensor 27 IR spectroscopy) was used. FTIR spectra for samples are shown in Figure 1. In both spectra, some peaks are observed at approximate wavelengths of 566 cm^{-1} and 1603 cm^{-1}, which are related to the bending modes of the O-P-O bond in phosphate (PO_4^{3-}) groups of the hydroxyapatite structure. Also, the peaks resulting from the P-O stretching bonds of the phosphate groups in HAp and FHAp networks can be observed in the approximate regions of 962 cm^{-1}, 1034 cm^{-1} and 1115 cm^{-1} [13].The spectralpeak in 3571 cm^{-1} represents the stretching modes of the O-H bond of the hydroxyl group present in the hydroxyapatite structure, which cannot be observed after functionalization. The vibrational modesin the approximate region of 871 cm^{-1} and 11435 cm^{-1}belong to the adsorption bands of carbonate (CO_3^{2-}). The presence of these peaks may be a result of the solubility of CO_2 of the environment within the samples during synthesis. The observed peaks in 1633 cm^{-1} and 3444 cm^{-1} represent the hydroxyl group of the water adsorbed to the surface of samples [16]. A slight decrease in the intensity of the FHAp peak in this region and the transfer of the peak from 1633 cm^{-1} to 1650 cm^{-1} can also point to the formation of a bond between the hydroxyl group on the surface of HAp and the amine group of TEPA. In addition, new peaks appear at 2850 cm^{-1} and 2924 cm^{-1} in the FHAp, indicating the CH_2 stretching modes in the TEPA network. Also, poor peaks appearing at 1461 cm^{-1} and 1564 cm^{-1} express symmetric and asymmetric NH_2 bends, respectively [14]. According to the results, it can be said that the synthesis of HAp and its functionalization with TEPA was successful.

3. 1. 2. X-Ray Diffraction Analysis (XRD) Figure 2 illustrates the XRD patterns of HAp and FHAp samples. According to the JCPDS Standard of HAp, it can be confirmed that the crystalin phase belongs to hydroxyapatite which is formed in the synthesized samples. Moreover, the disappearance of fairly mild peaks caused by the plates (301), (131) and (113) in the XRD pattern can be due to the presence of amine functional groups in the functionalized FHAp. Furthermore, it is seen that the intensity of the peaks of the FHAp sample has increased compared to that of HAp, implying the increasing size of crystals after the functionalization. Calculation of the crystalline grain size of the samples by the Scherrer equation also confirms such increases. From the same angular position in both samples, we can propose that the same structure of HAp has retained after the functionalization [17].

3. 1. 3. FESEM and EDS Analyses FESEM analysis was used to investigate the morphology and structure of the synthesized adsorbent. Figure 3 shows FESEM images with the results of the EDS analysis of HAp and FHAp samples. As illustrated, the samples have plate-shape like morphology and HAp particles were in a more scattered state before being functionalized while there is a tendency for particles of FHAp to flocculate [18].

This may be due to increased particle contact in the presence of functional groups in TEPA. The presence of C and N elements in the results of the EDS analysis of the FHAp sample confirms the presence of amine functional groups on the surface of Hap [14]. In addition, according to the results, the Ca/P molar ratio was very close to the stoichiometric ratio of 1.67.

3. 1. 4. N_2 Adsorption-desorption Analysis N_2 adsorption-desorption isotherms for HAp and FHAp samples are presented in Figure 4. As can be seen, both samples are of the V-type isotherm, which is a characteristic of the porous material containing the mesoporous [19]. The results of the BET analysis are provided in Table 2.

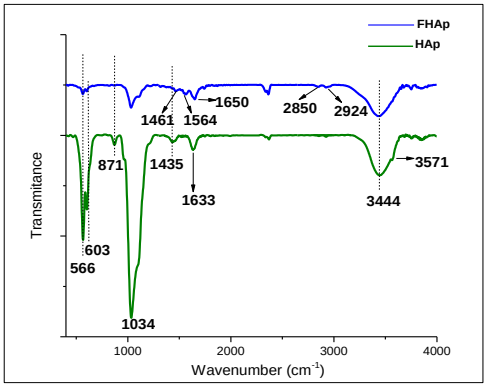

Figure 1. FTIR pattern of samples

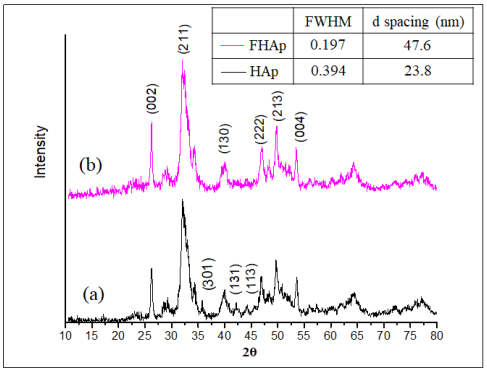

Figure 2. XRD patterns of (a) HAp, (b) FHAp

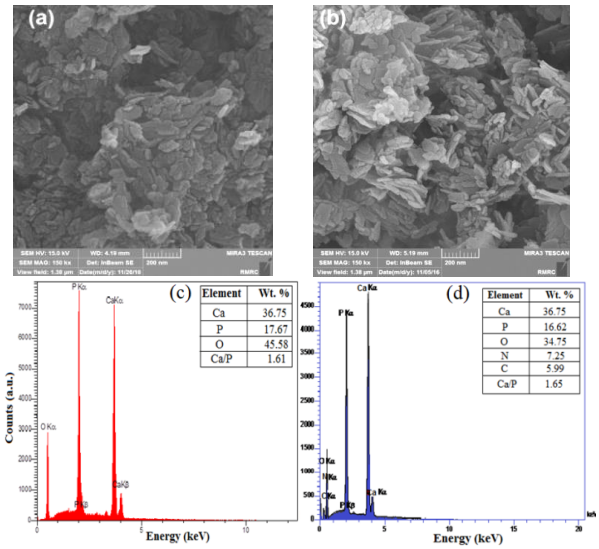

Figure 3. FESEM images and EDS spectra of HAp (a, c) and FHAp (b, d)

TABLE 2. BET characteristics of samples

Sample	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Mean Pore Diameter (nm)
HAp	126.26	0.1278	4.81
FHAp	90.722	0.097	4.165

As the BET results show, the specific surface area of HAp has decreased after the functionalization, which can cause the blockage of some pores by TEPA [20]. In addition, the pore volume and mean pore diameter have decreased after being functionalized. Also, BJH diagrams of the samples in Figure 4 shows that the pore size distribution of both samples is in the range of 1.5-40 nm, indicating that most of the porosity of the surface of both samples is mesoporous [21]. This result is also consistent with the nitrogen absorption-desorption isotherm graph.

3. 2. Batch Adsorption Study

3. 2. 1. pH Effect Initial pH of the solution is one of the most important parameters in adsorption process, since pH changes lead to alteration of adsorbate molecule ionization and variation of adsorbent surface charges [22]. Figure 5 shows the initial pH effect on adsorption of AB25 dye via FHAp. The pH range of 2 to 9 with an adsorbent dosage of 10 mg and initial AB25 concentration of 40 mg/L at 25 ˚C was investigated.

As can be seen, adsorption of AB25 dye via functionalized nanoporous Hydroxyapatite decreases as the solution pH increases from 2 to 9. Different performances of adsorbent in different pH can be related to adsorbent surface charge.

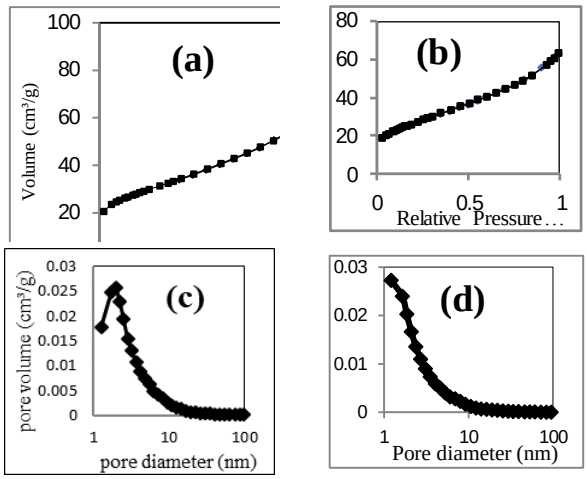

Figure 4. N_2 adsorption-desorption isotherms and BJH diagrams of HAp (a, c) and FHAp (b, d)

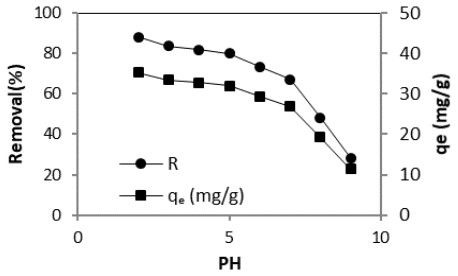

Figure 5. Effect of pH on adsorption of AB25 onto FHAp

The highest adsorption of AB25 dye via FHAp was seen in an acidic condition of pH 2, which can be due to the generation of positive charge on adsorbent surface in the acidic pH that results in a better adsorption of anionic dye via electrostatic attraction. In addition, the weaker AB25 adsorption under higher pH may be explained by a significant competition between anionic groups of AB25 and OH^- ions toward adsorption sites [23].

3. 2. 2. Dye's Initial Concentration Effect Figure 6 shows the results of AB25 dye's initial concentration effect in the range of 40 to 100 mg/L, pH value of 2 and contact time of 180 min at 25 ˚C. As it can be seen, dye's initial concentration increment from 40 to 100 mg/L results an increase in AB25 adsorption, since the mass transfer driving force increased which was higher in compare to dye's initial concentration. As the dye's initial concentration increases, AB25 dye removal percentage decreases. It can be related to saturation of adsorption sites on adsorbent surface, which means a reduction in adsorption potential [24]. Since the highest dye removal percentage was observed in dye's initial concentration of 40 mg/L, it is considered as the optimum concentration for the next experiments.

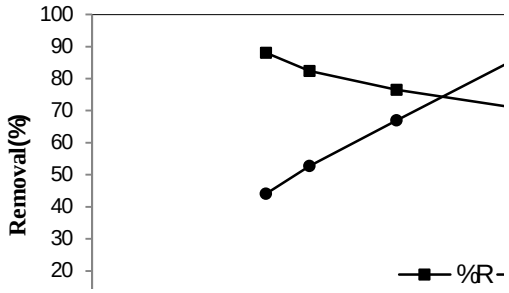

Figure 6. Effect of initial concentration of AB25 dye on adsorption onto FHAp

3. 2. 3. Adsorbent Dosage Effect The results of FHAp amounts' effect on AB25 adsorption are shown in Figure 7, which was studied in the dosage range of 1 to 15 mg/L as an initial concentration and pH value of 2 at 25˚C. Based on the results, dye removal percentage was increased with the increment of adsorbent dosage and reaches its maximum value in 10 mg of adsorbent amount. With the decrement of adsorbent amount, available contact surface of adsorbent can be decreased. Therefore dye molecules compete with each other and most of the molecules remain in the solution which leads to a reduction in the dye removal percentage.

Since dye's initial concentration is kept constant in 40 mg/L, an adsorbent amount increase results in an increment of adsorption sites with respect to dye molecules and only a few adsorption sites are filled with dye molecules, so adsorption capacity decreases [25]. A 10 mg of adsorbent was chosen as the optimum adsorbent dosage for the next steps with the aim of having the highest removal percentage and adsorption capacity.

3. 2.4. Adsorption Isotherms In this research, Langmuir, Freundlich and Temkin isotherm models were used for analysis of experimental equilibrium data of AB25 dye adsorption using FHAp.

In Langmuir theory, it is assumed that adsorption is carried out on limited numbers of adsorption sites.

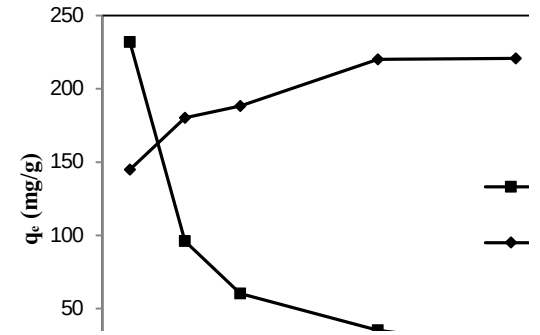

Figure 7. Effect of adsorbent dosage on adsorption of AB25 onto FHAp

In this model, adsorption is also considered to be monolayer and the adsorbent surface has homogeneous energy.

Freundlich isotherm is an experimental equation which assumes a multi-layer adsorption on nonhomogeneous surfaces and a nonhomogeneous distribution of energy on the active sites of adsorbent based on linear.

Temkin isotherm is based on this theory that adsorption heat of all molecules in one layer reduces linearly by covering the layer via molecules, which can be related to interactions of adsorbent and adsorbate [9].

According to the results based on the correlation coefficient (R^2), Freundlich isotherm model was better fitted to the experimental data which can be due to a nonhomogeneous distribution of FHAp surface. Also, according to the $R_L$and 1/n values obtained, adsorption process is favorable for Langmuir and Freundlich models.

3. 2. 5. Contact Time Effect and Adsorption Kinetic Contact time plays a major role in the adsorption process modeling. The effect of contact time in the range of 15 to 270 min with 10 mg of adsorbent dosage, 40 mg/L of AB25 concentration and value of pH 2 at 25 ˚C is illustrated in Figure 8. It is observed that both the dye removal percentage and adsorption capacity were increased with the time enhancement due to the more opportunity for occupying of the adsorbent sites by adsorbate molecules.

TABLE 3. Parameters of adsorption isotherms

Isotherm Model	Parameter	Calculated Value
Langmuir	q_m (mg/g)	76.62
	K_L (L/mg)	0.174
	R_L	0.0543-0.125
	R^2	0.9182
Freundlich	K_F (L/mg)	18.7
	1/n	0.3831
	R^2	0.9843
Temkin	B	19.245
	K_T (L/mg)	1.27
	R^2	0.9553

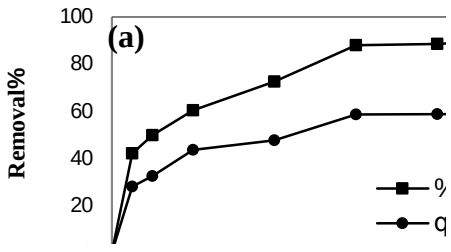

Figure 8. Effect of contact time on AB25 adsorption

Adsorption kinetic predicts the adsorption capacity with time and is essential for the determination of adsorption mechanism and the reaction approach in a system. Pseudo first order and pseudo second order kinetic models are the most used ones among models given for the determination of kinetic.

Table 4 shows the kinetic parameters of AB25 dye adsorption via FHAp. Based on the results, pseudo second order kinetic model is a proper model for the description of adsorption kinetic of AB25 on FHAp.

3. 2. 6. Temperature Effect and Adsorption Thermodynamic Thermodynamic parameters provide useful information on the adsorption process such as spontaneity and feasibility, endothermicity or exothermicity and energy variations. These parameters are enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) variations that are calculated.

Figure 9 depicts the variety of adsorbed dye amount with respect to temperature and Table 5 shows the thermodynamic parameters of adsorption process of AB25 dye on FHAp.

TABLE 4. Adsorption kinetic rate constants

Kinetic Model	Parameter	Calculated Value
Pseudo first-order	q_e (mg/g)	20.34
	K_1 (min^{-1})	0.0076
	R^2	0.917
Pseudo second-order	q_e (mg/g)	39.84
	K_2 (g/mg min)	0.0007
	R^2	0.984

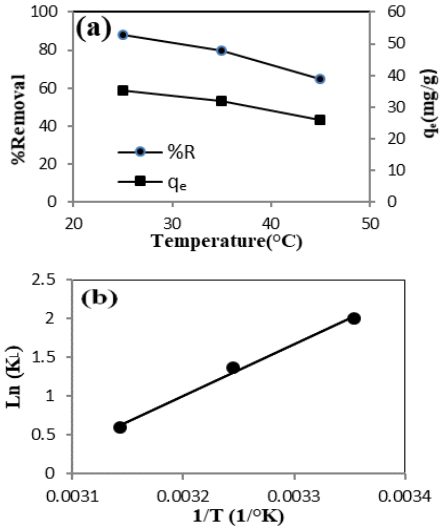

Figure 9. Effect of temperature (a) and Vant'Hoff plot of AB25 adsorption on FHAp

TABLE 5. Thermodynamic parameters for adsorption of AB25 on FHAp

Temperature (°C)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol.K)
25	-4.956		
35	-3.518	-55.167	-0.168
45	-1.582		

According to Figure 9, both the adsorption capacity and removal percentage was reduced with the increment of temperature. So the adsorption process of AB25 dye via FHAp is an exothermic process. The negative value of ΔH° also confirms the exothermicity of the adsorption process. Negativity of ΔG° values reveals the process spontanously occurs . In addition, the values of ΔG° were in the range -20 to 0 kJ/mol that indicating the physical adsorption.The negative value of ΔS° is a sign of chaos reduction, which can be due to adsorbate molecules' placement on adsorbent sites that makes them more orderly.

4. CONCLUSION

In this study, hydroxyapatite (HAp) was synthesized by a simple co-precipitation method and was functionalized by tetraethylenepentamine (TEPA). The samples prepared were characterized by FTIR, XRD, FESEM, and N_2 adsorption-desorption analyses. The specific level, cavity volume and mean cavity diameter of hydroxyapatite decreased after functionalization. Functionalized hydroxyapatite was used as an adsorbent to remove the dye Acid Blue 25 in an aqueous solution. The influence of different factors such as pH, initial concentration of Acid Blue 25, contact time, adsorbent dosage and solution temperature were investigated by batch experiments. Results of the studies showed that Acid Blue 25 removal percentage has increased with the increase in pH and absorbent dosage. The maximum dye removal percentage in the optimal conditions (pH=2, dye initial concentration=40 mg /L, 10 mg absorbent, contact time=180 min and T=25°C) was 88%. The result of the studies was shown that the Freundlich isotherm model is a more appropriate model for describing the adsorption process. Also, the adsorption kinetics follows a pseudo-second-order model. Moreover, thermodynamic studies were shown that the process of adsorption of AB25 dye on the functionalized hydroxyapatite is a spontaneous and exothermic. According to the results, the functionalized hydroxyapatite can be used as an efficient adsorbent to remove the dye from the aqueous solution.

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Fabrication of Nanoporous Functionalized Hydroxyapatite as High Performance Adsorbent for Acid Blue 25 Dye Removal

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چکیده

هدف از این تحقیق، سنتز یک نانوجاذب کارآمد برای حذف رنگ از محلول آبی می‌باشد. برای این منظور، هیدروکسی-آپاتیت سنتز و با استفاده از تترا اتیلن پنتامین عامل‌دار گردید. شکل‌شناسی، اندازه ذرات و مشخصات ساختاری نانوجاذب به وسیله آنالیز اسپکتروسکوپی مادون قرمز فوریه، پراش اشعه ایکس، میکروسکوب الکترونی روبشی، پراش انرژی پرتو ایکس و جذب-واجذب گاز نیتروژن مورد بررسی قرار گرفت. در مرحله بعد عوامل مؤثر بر حذف رنگ اسید بلو ۲۵، از قبیل pH محلول، غلظت اولیه رنگ در محلول، میزان جاذب، دما و زمان تماس ارزیابی شد. نتایج نشان داد که درصد حذف رنگ با افزایش pH و غلظت رنگ محلول کاهش می‌یابد. حداکثر حذف رنگ اسید آبی ۲۵ در محلول حاوی غلظت اولیه رنگ ٤٠ میلی گرم در لیتر با استفاده از ۱۰ میلی‌گرم جاذب در دمای ۲۵ درجه سانتیگراد ۸۸ درصد بود. مطالعه تعادلی و سینتیکی جذب نشان داد که جذب رنگ اسید بلو ۲۵ توسط نانو جاذب هیدروکسی‌آپاتیت عامل‌دار شده از مدل ایزوترم فروندلیچ و مدل سینتیکی شبه درجه دوم پیروی می‌کند. مطالعات ترمودینامیکی نیز نشان‌دهنده گرمازا و خودبخودی بودن فرآیند جذب بوده است. نتایج بیان می‌نماید جاذب FHAp به عنوان یک کاندید مناسب برای حذف اسید آبی ۲۵ از محلول های آبی مورد استفاده قرار گیرد.

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