

Synthesis of hydroxyapatite-alginate composite: Methylene blue adsorption

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1. Introduction – Many investigations have been conducted on physico-chemical methods of removing colorful effluents, which include the use of coagulants, oxidizing agents, ultra-filtration, electro-chemistry and adsorption. Most of these methods have limitations such as high capital and operational cost, low efficiency, sensitive operating conditions and production of secondary sludge [1]. Adsorption by a low-cost adsorbent attracts attention as an economic and efficient method for dye removal from the aqueous solutions. Thus various researchers have focused on the preparation of new efficient and low-cost adsorbents from natural or biological materials or industrial wastes. In recent times, the preparation of biopolymer supported inorganic composites has attracted much attention due to their unique structure and properties. The synergistic effect of biopolymer and inorganic material will improve the mechanical properties of the composite [2]. Sodium alginate (SA) is a natural linear polysaccharide, non-toxic and biodegradable biopolymer which was commonly used as a binder for preparing various composite materials. It has tendency to swell in water and other mechanical weakness, its application in wastewater treatment is limited [3]. In this respect, it can be blended with hydroxyapatite (HAp), inorganic material, to overcome the drawbacks of alginate and to combine the good characteristics of both materials. In this study, both sphere and film forms of alginate- hydroxyapatite composite materials were synthesized and these composite adsorbents were used for the methylene blue (MB) removal. The effects of different environmental conditions were investigated. Also, at the optimum conditions; the MB adsorption capacities of HAp-SA spheres, HAp-SA films, alginate spheres and HAp were compared to interpret the effectiveness of composite materials. Equilibrium and mass transfer modeling, thermodynamic and adsorbent characterization studies were also carried out.

2. Experimental – Preparation of HAp-SA composite materials and adsorption studies

0.6 g of HAp was stirred in 60 mL distilled water for 60 min, and then it was sonicated for 10 min because the particles extremely tended to agglomerate in water. This cycle was repeated once more to obtain a homogeneous and fine dispersion. 0.6 g of SA was added to the prepared HAp solution. The resulting HAp-SA solution was stirred magnetically at 1400 rpm for 6.0 h to have a homogeneous mixture. The final mixture was dropped by needle injection syringe into 0.1 mol L⁻¹ of CaCl₂ and the solution was stirred slowly for 2.0 h. The prepared spheres were washed with distilled water and were dried overnight in an oven at 60 °C. For preparing composite films, filter papers were cut and immersed into the HAp-SA mixture. By this mean the solution was adsorbed on the filter paper surface. Next, the saturated filter papers were put into 0.1 mol L⁻¹ CaCl₂ solution and stirred slowly for 2 h. The treated filter papers were washed with distilled water and were dried overnight in an oven at 60 °C. The resulting composite films were recovered from filter papers [4].

0.1 g of adsorbent, except for adsorbent concentration experiments, was mixed with 100 ml of the desired initial dye concentration and initial pH in Erlenmeyer flasks. The flasks were agitated on a shaker at constant temperature for 5 h. Samples were taken at pre-determined time intervals (0, 0.5, 2.0, 5.0, 10, 20, 30, 60, 120, 180, 240 and 300 min). Experiments were repeated for different parameters. The unadsorbed MB dye concentration in supernatant was analyzed at 665 nm wavelength with spectrophotometer.

3. Results and Discussion

3.1. Effect of environmental conditions

Initial pH: Initial pH is the most important parameter affecting the adsorption processes. The variation of MB adsorption on HAp-SA spheres with initial pH was shown in Fig. 1a. As shown in Fig. 1a; the maximum adsorbed MB amount at equilibrium was obtained at initial pH 9.0, and high adsorption capacities were also obtained in the wide pH range. The surface charges of HAp-SA spheres in the pH range become negative that can easily interact with the positive ions of MB and finally result to high MB adsorption.

Initial MB concentration: Variation of the adsorption data of MB on HAp-SA for the initial dye concentrations with time is given in Fig. 1b. As seen from Fig. 1b; generally, the adsorption of MB was rapid initially and then the adsorption was gradual and finally attained saturation at equilibrium [5]. Also, the adsorbent effectively removes at low initial concentrations; at higher concentrations the adsorbed

amounts reach a maximum capacity as indicated by the plateau of the data. This may be due to the saturation of the adsorption sites at higher MB concentrations.

Adsorbent concentration: The adsorption of MB onto HAp-SA spheres was studied by varying the adsorbent concentration 0.1- 4.0 g/L. Fig. 1c shows the plot of equilibrium adsorbed amounts (mg/g), and dye removal efficiencies (%) against adsorbent concentrations (g/L) of HAp-SA spheres. As can be seen from Fig. 1c; the adsorbed amounts decreased with increasing adsorbent concentration, but the adsorption percentages increased up to 1.0 g L⁻¹ of the adsorbent concentration, and then didn't change with further increase in adsorbent concentrations; so the optimum adsorbent concentration was obtained as 1.0 g L⁻¹. The increase in adsorption percentages is due to that increasing adsorbent concentration serves to increase the surface area and the number of active sites for adsorption. The decrease in adsorbed amounts may be due to that all active sites are entirely exposed and utilized at lower adsorbent concentration and only part of active sites are exposed and occupied by MB at higher adsorbent concentration.

Temperature: The batch adsorption study was performed at 293, 298, 313 and 333 K to ascertain the effect of temperature on the MB removal, and the results are presented in Fig. 1d. According to Fig. 1d; the adsorption capacity of adsorbent decreased with increasing temperature and the optimum temperature was determined as 25°C due to its exothermic in nature. Also, the thermodynamic parameters such as Gibbs free energy ($\Delta G = -RT \ln K_c$), enthalpy (ΔH) and entropy (ΔS) were calculated by using Van't Hoff equation ($\ln K_c = [\Delta S/R] - [\Delta H/RT]$) in order to evaluate the effect of temperature on adsorption process of MB onto HAp-SA spheres. Thermodynamic studies indicated that the adsorption was exothermic ($\Delta H = -19.316 \text{ kJ mole}^{-1}$), decreasing in randomness of adsorbed species ($\Delta S = -50.46 \text{ J mole}^{-1}$) and spontaneous ($\Delta G < 0$).

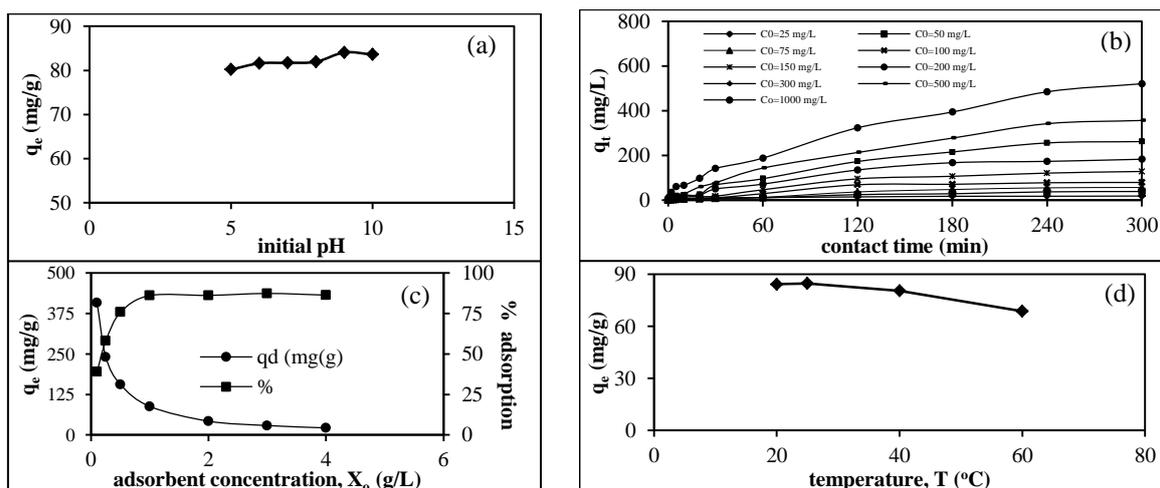


Figure 1: The effects of different environmental conditions

3.2. Equilibrium studies

Adsorption isotherm models are usually used to describe the interaction between the adsorbent and the adsorbate when the adsorption process reaches equilibrium, affording the most important parameter for designing a desired adsorption system. In this study, the linear forms of the Langmuir [$1/q_e = 1/Q^0 b(1/C_e) + 1/Q^0$], Freundlich [$\ln q_e = \ln K_f + (1/n) \ln C_e$] and Dubinin-Radushkevich [$\ln q_e = \ln q_m - \beta \cdot \epsilon^2$] isotherms were adopted to describe the adsorption behaviors of MB onto HAp-SA spheres. The isotherm constants with regression coefficients (R^2) and error values [$ARE = (100/P) \sum (q_{e,cal} - q_{e,exp}) / q_{e,exp}$] are presented in Table 1. As can be seen from Table 1; the higher R^2 and lower ARE values for Langmuir isotherm model indicated that the Langmuir model fitted the experimental data better than the other models. This case showed that the adsorption of MB onto HAp-SA spheres took place in a homogeneous manner. Many researchers reported the maximum MB adsorption capacities for various adsorbents such as 88.89 mg g⁻¹ for polydopamine microspheres[6], 94.34 mg g⁻¹ for NaAlg-g-poly (AA-co-AAm)/clino hydrogel nanocomposite [7], and 193.16 mg g⁻¹ for crosslinked chitosan/bentonite composite [8].

Accordingly; HAp-SA spheres used in this work exhibited significant potential for the MB removal. The Dubinin-Radushkevich (D-R) isotherm model makes it possible to determine the order process adsorption, chemical or physical thanks to the adsorption mean free energy value $[E=1/(2\beta)^{0.5}]$ while Langmuir and Freundlich models do not give information on the adsorption mechanism. If the energy value lies between 8 and 16 kJ mole^{-1} , the adsorption process is controlled by a chemical mechanism, while for $E < 8 \text{ kJ mole}^{-1}$, the adsorption process proceeds through a physical mechanism [9]. According to Table 1, the calculated energy values for all temperatures were lower than 8 kJ mol^{-1} , which was indicating that the adsorption of MB onto HAp-SA spheres proceeded through physisorption.

Table 1: Isotherm model constants with regression coefficients and error values

T (°C)	Langmuir				Freundlich				Dubinin-Radushkevich		
	Q°	b	R ²	ARE	K _f	1/n	R ²	ARE	q _m	E	R ²
20	632.11	0.0030	0.999	8.9412	2.3203	0.8974	0.9655	10.8924	154.74	133.82	0.9763
25	656.59	0.0048	0.9944	7.4559	3.0307	0.9482	0.9831	10.3237	194.47	129.16	0.9894
40	566.25	0.0017	0.9983	4.4528	1.5261	0.8541	0.9782	9.5451	205.02	94.51	0.9849
60	463.82	0.0037	0.9985	14.3455	1.9772	0.8920	0.9236	15.4413	355.20	51.15	0.9921

(Q° (mg g^{-1}), b (L mg^{-1}), K_f ($\text{mg/g(L/mg)}^{1/n}$), q_m (mg/g), E (kJ/mole))

3.3. Weber-Morris intraparticle diffusion model

For adsorption process, the solute transfer is usually characterized by either external mass transfer or intraparticle diffusion or both. Weber-Morris intraparticle diffusion model ($q_t = K_i t^{0.5} + I$) is the most commonly used model for identifying the mechanism involved in the adsorption process. Table 2 shows the Weber-Morris model parameters with regression coefficients for MB adsorption onto HAp-SA spheres. According to Table 2; the internal (K_i) and external (I) diffusion effects gradually increased with increasing initial dye concentrations. Moreover, it was observed by intraparticle diffusion model that both intraparticle and film diffusion were effective in the removal. Fig. 3 represents the comparison of external diffusion effects of HAp-SA spheres and films. Apparently, plots in Fig. 2 show multilinearity characterization for the studied adsorption process. The first sharp portion relates to the diffusion of MB through the solution to the external surface of HAp-SA spheres, the second subdued portion is the slow adsorption stage, where intraparticle diffusion is rate-controlled, and the last portion represents the equilibrium [10]. Theoretically, values of intercept, I, give an idea about the thickness of boundary layer, i.e., larger the intercept, greater is the boundary layer effect or external diffusion resistance [11]. Fig. 2 also shows that I value of HAp-SA film is smaller than the sphere one, indicating lower external diffusion resistance, which results in early reaching to the equilibrium. The time to reach equilibrium is 60 min for films while it is 240 min for spheres.

Table 2: Weber-Morris model parameters

Co, mg/L	K _i ($\text{mg g}^{-1} \text{min}^{-1/2}$)	I	R ²
25	3.244	13.54	0.994
50	4.782	16.26	0.980
75	7.484	27.30	0.993
100	10.84	33.40	0.990
200	15.48	39.60	0.996
300	19.42	44.66	0.998
500	24.49	51.98	0.998

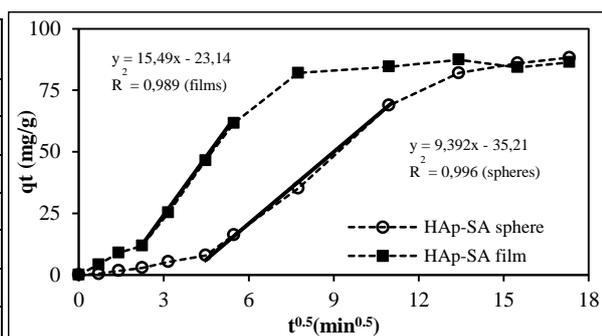


Figure 2: The comparison of HAp-SA spheres and films

3.4. Adsorbent characterization

HAp-SA spheres, HAp-SA films, SA spheres and HAp were characterized with FT-IR analysis pre- and post- adsorption, the spectrums are presented in Fig. 3. The HAp spectrum shows absorption bands at 562, 602, 629, 962 and 1026 cm^{-1} corresponding to the PO_4^{3-} ions of the apatite whereas in the HAp-SA spheres and films, the PO_4^{3-} ions appeared at 563, 600, 960, and 1028 cm^{-1} , and at 561, 607, 632, 960, and 1024 cm^{-1} , respectively [12]. In FT-IR spectra of SA, the characteristic peaks of SA can be seen at around 1600 and 1414 cm^{-1} (carboxylate stretching vibrations), the broad band at around 3300 cm^{-1} (hydroxyl

groups stretching absorption), the bands between 900 and 1200 cm^{-1} (O–C–O stretching of ether groups and –C–O stretching of alcoholic groups), and also the weak peak at 816 cm^{-1} (–Na–O) [13, 14]. The observed bands at 1589 and 1418 cm^{-1} for HAp-SA spheres, 1598 and 1394 cm^{-1} for HAp-SA films suggest that the formation of a chemical bond between the inorganic phase and the organic polymeric matrix; i.e., the interaction between the positive charge of calcium and the negative charge of the carboxyl group in SA [15]. Besides, FT-IR spectra of MB-loaded adsorbents did not display any significant changes, such as bond breaking or formation, which was indicating that the adsorption processes occurred physically, as determined by D-R isotherm model.

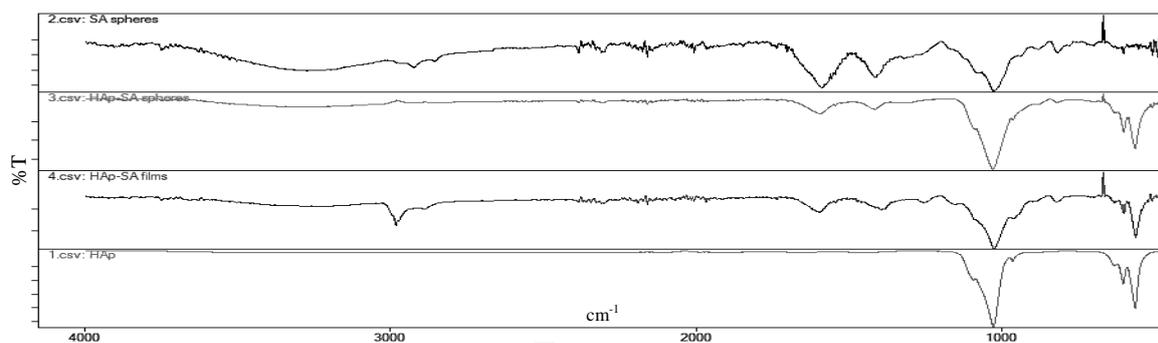


Figure 3: FT-IR spectrums of HAp-SA spheres, HAp-SA films, SA spheres and HAp

4. Conclusions – The experiments of MB adsorption onto HAp-SA spheres were conducted in a batch mode and the results were compared with HAp-SA films, SA spheres and HAp. For HAp-SA spheres; optimum initial pH, initial dye concentration, temperature and adsorbent concentration were determined to be 9.0, 300 mg L^{-1} , 25 $^{\circ}\text{C}$ and 1.0 g L^{-1} , respectively. At the optimum conditions; the MB adsorption capacities of HAp-SA spheres, HAp-SA films, alginate spheres and HAp were determined as 87.89, 83.86, 70.09 and 10.09 mg g^{-1} , respectively. These results show that the envisioned synergistic effect of HAp-SA composite materials could be obtained successfully. The maximum monolayer coverage capacity of HAp-SA spheres calculated from Langmuir isotherm model was found as 656.59 mg g^{-1} ; besides; the adsorption occurred physically according to the adsorption energies lower than 8 kJ mol^{-1} calculated from D-R isotherm model that also indicating exothermic nature of the adsorption. Weber-Morris model analysis showed that both intraparticle and film diffusion were effective in the removal; and also, HAp-SA films exhibited lower resistance to the external diffusion, which caused to fast equilibrium. Thermodynamic studies showed that the adsorption process was exothermic and spontaneous. The adsorbents were characterized with FT-IR analysis, and it was concluded that the process was physical adsorption. Consequently, the advanced adsorption properties were obtained by synthesizing HAp-SA composite materials, which could be used effectively for MB removal from aqueous solutions.

5. References

- [1] Rao K. S., Mohapatra M., Anand S., and Venkateswarlu P., *Int J Eng Sci Technol.* 2.7 (2010): 81-103.
- [2] Ecaterina Stela D., *Advanced Separations by Specialized Sorbents*, CRC Press, (2014): 92.
- [3] Ngah W.W., and Fatinathan S., *Chem Eng J.* 143.1 (2008): 62-72.
- [4] Googerdchian F., Moheb A., and Emadi, R., *Chem Eng J.* 200 (2012): 471-479.
- [5] Mahmoud D.K., Salleh M.A.M., Karim W.A., Idris A., and Abidin Z.Z., *Chem Eng J.* 181 (2012): 449-457.
- [6] Fu J., Chen Z., Wang M., Liu S., Zhang J., Zhang J., and Xu, Q., *Chem Eng J.* 259 (2015): 53-61.
- [7] Rashidzadeh A., Olad A., and Salari D., *Fiber Polym.* 16.2 (2015): 354-362.
- [8] Bulut, Y., and Karaer, H., *J Disper Sci Technol.* 36.1 (2015): 61-67.
- [9] Chowdhury S., Mishra R., Saha P., and Kushwaha P., *Desalination* 265.1 (2011): 159-168.
- [10] Wang H., Yuan X., Wu Y., Huang H., Zeng G., Liu Y., and Qi Y., *Appl Surf Sci.* 279 (2013): 432-440.
- [11] Tan I.A.W., Ahmad, A.L., and Hameed, B.H., *J Hazard Mater.* 154.1 (2008): 337-346.
- [12] Sivakumar M., and Rao K. P., *J Biomed Mater Res A.* 65.2 (2003): 222-228.
- [13] Rashidzadeh A., and Olad A., *Carbohydr Polym.* 114 (2014): 269-278.
- [14] Dhanapal V., and Subramanian, K., *Carbohydr Polym.* 108 (2014): 65-74.
- [15] Pandi K., and Viswanathan N., *Carbohydr Polym.* 112 (2014): 662-667.