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Journal of Nanostructure in Chemistry 2 (1) (2011)43-52 Contents list available at JNSC Journal of Nanostructure in Chemistry (JNSC) I.A.U. journal homepage: www.jnsc.ir Adsorption

Study the of Lysozyme **from aqueous solution** onto **Hydroxyapatite Nanopowders**

4

1 2 3 3 V. Haddadi , E. Taghdir P. Ahanghari and R. Abjame

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Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, IRAN

3. Department of Chemistry, Islamic Azad University,

shaher-e- Qods- Branch, Tehran, IRAN ARTICLE INFO Article history: Received 1 February 2011 Accepted 10 May 2011 Keywords: Hydroxyapatite, Nanopowders, Lysozyme, Adsorption, Thermodynamics Parameters A B S T R A C T In this study, a series of laboratory tests were

conducted to investigate the efficiency of hydroxyapatite (HAP) nanopowders towards
adsorption of lysozyme from aqueous solution. In the present research, HAP nanopowders
synthesized from egg-shell characterized using SEM and FT-IR. The adsorption of lysozyme
was

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1 mg/mL using 0.1 g

adsorbent in 100 mL of lysozyme solution.

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Adsorption data were fitted to a linearly Langmuir isotherm.

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Thermodynamics

parameters were also calculated to study the effect of temperature on adsorption process.

21

An adsorption kinetic study revealed that the adsorption process followed first order kinetics.

1

1. Introduction Calcium hydroxyapatite $[\text{Ca}(\text{PO})_2(\text{OH})_2]$ is in the

space group P63/m; its unit cell parameters are $a = b = 0.943 \text{ nm}$ and $c = 0.688 \text{ nm}$, and it
possesses two different binding sites (C and P sites) on the particle surface. Thus, it contains a
multiple site binding character for proteins [1–3]. The crystal structure of

2

HAP is depicted in Fig. 1. After dispersing HAP particles in the aqueous media,

2

calcium atoms (C sites) are exposed on the Hap – surface by dissolution of OH ions at the particle surface.

15

Hence, HAP is widely applied for to separating various proteins in a high-performance liquid chromatograph (HPLC) system

2

[4, 5]. In the past decade, some authors have conducted fundamental studies of the adsorptions of bovine serum albumin (BSA:

2

isoelectric point (Pi) = 4.7, molecular mass = 67200 Da), lysozyme (Pi = 11.1, molecular mass= 14600 Da, lysozyme

onto various kinds of synthetic HAP particles [6–12]. These studies clarified that the saturated amount of adsorbed

2

BSA 44 V. Haddadi et al. / Journal of Nanostructure in Chemistry 2 (1) (2011)

depends on the molar ratio of Ca to phosphate (Ca/P) of the materials used. The adsorption of BSA is increased with an increase in the Ca/P ratio, due to the electrostatic attractive forces between negatively charged BSA and the less negatively charged HAP having high Ca/P ratios at pH 6. On the contrary, the saturated amounts of adsorbed lysozyme on HAP particles is decreased with an increase in the Ca/P ratio, but no remarkable relationship with the Ca/P ratio was detected for the neutral proteins [11,

2

12]. Other groups have

also disclosed that the $2+$ adsorption of BSA onto HAP is governed by Ca ions

2

complexing to BSA molecules (binding effect) together with the operation of C sites [13]. However, this binding effect of Ca^{2+} ions is minor because the fraction of dissolution of surface Ca ions of HAP is low (1.2–3.2%) in a neutral aqueous solution. of all the

proteins were decreased with an increase in the improvement of HAP crystallinity whereas desorption enthalpies (ΔH_{des}) were increased. This opposite results on ΔH_{ads} and ΔH_{des} revealed that HAP possesses a high adsorption affinity to proteins [14].

HAP nanopowders possess high biocompatibility and adsorption properties. They have been widely used as carriers for drugs and genes, adsorbents for chromatography to separate proteins, and removal of heavy metal ions to recover the contaminated soils, wastewater and fly ashes, etc.

[15-21].

The objective of this study HAP was to characterize the

n nanopowders obtained from egg shell using SEM and FT-IR. As well as investigating the

potential candidate of HAP nanopowders as a new biocompatible adsorbent for the adsorption of lysozyme from aqueous solution. The effects of contact time, initial lysozyme concentration, pH, temperature

on the lysozyme adsorption,

kinetic, equilibrium and thermodynamic parameters at various temperatures and concentration were investigated. . 2. Materials and Methods

Crystal structure of HAP from perpendicular to c-axis.

2

Furthermore, since the number of functional groups is small, the binding effect of the counter ions was only slightly detected on the adsorption of lysozyme, even though the systems could dissolve divalent and trivalent ions. Some authors investigated adsorption behavior of proteins onto HAP particles using a flow microcalorimeter. It has been found that the heat of adsorption of all proteins exhibits endothermic heat [14], i.e., the adsorption enthalpies (ΔH_{ads}) exhibited positive values. The ΔH_{ads} values

2

2.1. Reagents and chemicals Different chemicals used in the present study were of analytical grade and obtained from Merck. 10 mg/mL stock lysozyme solution was prepared by dissolving 10 mg of

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lysozyme (From Roche Bio- molecular Company, Germany) in 25 mL freshly

deionized water. The required concentration of lysozyme solution was obtained by serial dilution of 10 mg/

20

mL lysozyme

solution. 2.2. Sample preparation HAP samples were prepared from egg shells. The shells were first washed and dried. The pretreated

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(washed and dried) egg shell wastes were ground and sieved to powder (mesh size 30).Then,

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the egg shells were added to aqueous (1:1) H_3PO_4 , kept at

343-313 K for 2-3 h,

under pH:1-3. The following reaction took place: $\text{CaCO}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{CaHPO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ 1
Insoluble matter was separated and removed by filtration. Subsequently, $\text{Ca}(\text{OH})_2$ was added to the solution and was kept at 323-333 K for 24 h, The pH were adjusted 5-9 by 0.

1 M HCl or NaOH. The following reaction represents the type of process that took place: $\text{CaHPO}_4 [(\text{PO}_4)^{6-x}, (\text{CO}_3, \text{OH})^x]$ 1

$(2\text{H}_2\text{O} + \text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}_{10}(\text{OH})_{16}(\text{PO}_4)_6 \cdot x\text{H}_2\text{O})$

At last, the suspension was dried and ground to powder (mesh size 30) to get the sample. 2.3. 1

FT-IR studies Study FT-IR of the

sample was obtained using Perkin Elmer FT-IR spectrophotometer SPECTRU-MRX -I. 1
FT-IR spectrum of the sample was obtained by KBr pellet method. The ratio of the sample to KBr was 1:50.

2.4.

Scanning Electron Microscopy Scanning electron micrograph of the sample was obtained by JEOL JSM - 6480 LV scanning electron microscope. The sample was coated with platinum for 30 s at current of 50 mA before the SEM micrograph was obtained. 2. 1

5.

Batch experiments The lysozyme adsorption experiments from its aqueous solution by HAP were carried out using standard

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1, 2, 3 and 4 mg/mL lysozyme

solution. The adsorption experiments were carried out in 250 mL glass conical flask provided with stopper, by adding 0.1 g of HAP in 100 mL of synthetic lysozyme solution. Stoppers were used to avoid change in concentration due to evaporation. All the experiments were carried out at ambient temperature ($25 \pm 1^\circ\text{C}$). After continuous stirring over magnetic stirrer at about 400 rpm for a pre determined time interval, lysozyme concentration was determined by

1

UV-Vis spectrometer ($\lambda_{\text{max}}=280 \text{ nm}$). One

standards were prepared bracket, the expected sample range and which differing concentration by a factor often. Measurements were done by taking 10 mL of standard and sample into separate 50 mL beaker and 25 mL of lysozyme interference suppressor. All the sample and standards were maintained at same temperature to avoid interference due to difference in temperature. 3. Result and

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Discussion 3.1. Characterization of hydroxyapatite In Fig. 2 shows the FT-IR spectra of HAP

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prepared from egg shells. The spectra record dill

defined and 3- low intensity absorption bands of P-O due to PO_4^{3-} groups in the 1052 cm^{-1} region, which are characteristic of the HAP, as well as of the H-O bands of

1

adsorbed water

[22]. A well distinguished peak at 3467 cm^{-1} indicates the O-H vibration of water. Band at 3467 cm^{-1} so shoulders at 3467 cm^{-1} is due

O-H stretching of 3467 cm^{-1} water of crystallization.

1

The band at 2923 cm^{-1} is apparently due to C-H background of the measurement system [23]. The

SEM micrograph of the sample obtained is shown in Fig. 3. Clusters of HAP particles have a homogenous size. The average size of the clusters

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46 V. Haddadi et al. / Journal of Nanostructure in Chemistry 2 (1) (2011) was 300 nm . Fig. 2. FT-IR pattern of HAP

for increase in pH 5 to 9, for initial lysozyme concentration of

1

1 mg/mL .

It is evident from the above data that there was increase in percentage removal for increase in pH from 5 to 9 but for further increase in pH beyond 7, there wasn't any increase in removal. It may be due to the fact that HAP is not stable under acidic condition and hence exhibited poor removal efficiency. And the percentage removal stood almost constant for pH 8-9.

According to the results the pH does not affect the percentage removal for pH 7 and above. However in the pH below 7 it has significant effect. Therefore care must be taken with acidic solutions.

1

85 80 75 %Removal 70 65 60 HAP 55 50 4 5 6 7 8 9 10 pH Fig. 4. pH versus percentage removal of lysozyme onto HAP

Fig. 3. SEM micrographs of HAP (Magnification $\times 20,000$, 20 kV).

1

3.2. Effect of pH on removal of

30

lysozyme

pH of the aqueous solution is one of the main variable parameters in the adsorption process. The pH may affect the ionization degree of the sorbet and the surface property of the

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adsorbent [24]. Several

different pH tests were carried out and the results are shown in Fig. 4. The percentage removal of lysozyme by HAP increased from 67% to

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83% 3

.3. Effect of contact time and adsorption kinetics Adsorption of lysozyme at different contact time was studied for initial lysozyme concentration of

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1, 2, 3 and 4 mg/mL

keeping all other parameters constant. The result is presented in Fig. 5. The percentage removal was found to increase from 38% to 77%, 42% to 79%, 45% to 81% and 49% to 85% for a contact time of 5 min to 60 min and initial lysozyme concentration of

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1, 2, 3 and 4 mg/mL,

respectively. It is clear from the figure that about 50% removal took place within first 5 min and equilibrium was established after 60 min. The change in the rate of removal might

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be due to the fact that initially all adsorbents site contained replaceable

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hydroxide ion and resolute concentration gradient was also high.

1

%Removal 90 80 70 60 50 40 30

29

20 10 1 mg/mL 2 mg/mL 3 mg/mL 4 mg/

23

mL 0 0 10 20 30 40 50 60 70 80 90 100 Time (min) Fig.

19

5.

Time versus percentage removal of lysozyme onto HAP with initial concentration of

1

1 mg/mL Later, the lysozyme up take

rate by adsorbent was decreased significantly, due to the decrease in number of replaceable hydroxide ions in adsorption sites as well as decrease in lysozyme concentration. Decreased removal rate, particularly, toward the end of experiments, indicates the possible monolayer formation of lysozyme ion on the outer surface. The rate

1

constant K for

adsorption of lysozyme ad was studied by Lagergren rate equation for initial lysozyme concentration of

14

1, 2, 3 and 4 mg/mL [25-26]:

$$\ln(q - q_e) = \ln q_e - K t \quad (1)$$

26

1

Also a linear form of pseudo-second order model (Eq. (2)), Ho and McKay's pseudo-second order model [27], for the adsorption of

12

lysozyme onto HAP was illustrated in Table 1.

$$t/q = 1/q_e + (1/q_e^2) K t \quad (2)$$

24

q

(both in mg/g) are the amounts of lysozyme adsorbed at equilibrium and at time 't', respectively. The plots of $\ln(q - q_e)$ versus 't' at different time interval was almost linear, indicating the validity of Lagergren rate equation of first order kinetics. The

1

linear fit between the t/q and contact time (t) for pH can be approximated as pseudosecond order kinetics.

8

The

adsorption rate constant (K), 1 calculated from the slope of the above plot is presented in Table 1. It was observed from the data that the adsorption rate constant values were almost similar for initial lysozyme concentrations of

1

1, 2, 3 and 4 mg/mL.

It was concluded that the adsorption rate constant was independent of initial lysozyme concentration.

1

Also the amount of 21r was more than 22r, it's concluded adsorption of lysozyme on HAP following

pseudo first order reaction. Table 1-. Rate constants (Pseudo first and second order)

33

obtained from the graph for HAP with different initial concentrations of

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lysozyme.

Pseudo first Pseudo second a q_e b q_e

31

2 r 1 T (K) K 1 K 2 298 2.33 0.05 2.51 0.9871 1.89 0.12 2.12 0.97024 a: Calculated, b: Experimental 3.4.

Effect of temperature The effect of temperature on the adsorption of lysozyme with initial concentration 1, 2, 3 and 4 mg/ mL onto HAP was studied using optimum

5

contact time (60 min)

and the results are presented as percent age removal of lysozyme versus temperature (Fig. 6). The percent age removal of lysozyme with initial concentration 1 mg/mL, increased from 71% to 82%, the percentage removal of lysozyme with initial concentration 2 mg/mL, increased from 74% to 85%, the percentage removal of lysozyme with initial concentration 3 mg/mL, increased from 78% to

88%,

and the percentage removal of lysozyme with initial concentration 4 mg/mL, increased from 80% to 91% for 15°C to 45 °C temperature.

a q e b q e 2 r 2 48 V. Haddadi et al. / Journal of Nanostructure in Chemistry 2 (1) (2011) 100 1.4 90 80 1.2 70 1 %Removal 60 50 40 30

1 mg/mL 2 mg/mL 3 mg/mL 4 mg/mL

lnKc 0.8 0.6 0.4 y = 1181.8x - 2.8959 R² = 0.9895 20 10 0.2 0 285 290 295 300 305 310 315 320 Temperature (K) 0 0.0031 0.00315 0.0032 0.00325 0.0033 0.00335 0.0034 0.00345 0.0035 1/T (1/K)

Fig. 6. Temperature versus percentage removal of lysozyme with hydroxyapatite, initial lysozyme concentration

Fig. 7. Van't Hoff plots, lnK

versus 1/T for HAP, initial c lysozyme concentration of 1, 2, 3 and 4 mg/

mL of 1, 2, 3 and 4 mg/mL (pH=7 and optimum time= 60 min)

It is evident from the figure that, at the temperature of 15 °C the removal was more than 65% and with increase in temperature, the percent age removal increased slowly and reached almost 91%, which indicates the endothermic nature of the process. This was further supported by calculating thermo- dynamic parameters. The change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of adsorption were calculated using the following equations

1

[28]: $\ln K_c = -\Delta H / RT + \Delta S / R$ $\Delta G = \Delta H - T\Delta S$ where ΔS and ΔH

are the changes in entropy and enthalpy of adsorption, respectively. A plot of $\ln K_c$ versus $1/T$ for initial lysozyme concentration of 1, 2, 3 and 4 mg/ mL were linear and

5

is represented graphically in Fig. 7. The K

value was calculated c using the following equation

11

[28]. (3) (4)

Values of ΔH and ΔS were

35

evaluated from the slope and intercept of Van't Hoff plot and represented in Table 2. The positive values of ΔS indicate some structural changes in the adsorbent and also reflect the affinity of the adsorbent for lysozyme species. The positive value of entropy (ΔS) indicates the increase in randomness so the on going. Negative value of ΔG at each temperature indicates the spontaneity of on going adsorption. A decrease in values of ΔG with the increase in temperature suggests more spontaneity of lysozyme adsorption at higher temperature. The endothermic nature of the process was once again confirmed by the positive value of enthalpy (ΔH). Positive value of enthalpy (ΔH) suggests that entropy is responsible for making the ΔG value negative. So, the adsorption process was spontaneous, since the entropy contribution was much higher than that of enthalpy.

1

Table 2. Thermodynamic parameters using HAP $K = C_1 / C_2$ (5) ΔH (kJ/mol) ΔS (kJ/Kmol) 288K ΔG (kJ/mol) 298K ΔG (kJ/mol) 308K ΔG (kJ/mol) 318K ΔG (kJ/mol) 2 R 11.5 0.063 -5.58 -7.12 -7.65 -8.12 0.9895 where C

is the amount of lysozyme ion adsorbed 1 per unit mass of HAP and C is the concentration 2 of lysozyme in aqueous

11

solution. 3.5.

Adsorption isotherms Analysis of adsorption isotherms are important for developing a model that can be used for adsorption

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process design and the isotherms obtained under different temperatures can provide basic data for thermodynamics study to deduce adsorption mechanism. In the present work, the results obtained from the equilibrium adsorption experiments, at the temperatures of 288, 298, 3018 and 318K and at the lysozyme solution initial pH, were analyzed according to the most frequently employed models Freundlich and Langmuir isotherms

3

[29-31]: $Q = K C_e^{1/n}$ $Q_0 / (1 + K C_e)$

And the linear forms of these isotherms are as follows, respectively

3

.

1 ln Qe = ln K F + ln Ce (8) n

27

1 Qe Le (6) (7) 1 1 1 = + () (9) Q Q KC 0 0 where C

is the adsorbate equilibrium concentration e in the liquid (mg/L); Q_0 is the adsorbate equilibrium amount in solid phases (mg/g); Q_0 is the maximum adsorption capacity according to Langmuir mono-layer adsorption (mg/g); K_L is constant according to the Langmuir isotherm (L/mg);

3

K

$(\text{mg/g})(\text{L/mg})^{-1/n}$ and n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The values of K_F and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\ln Q$ versus $\ln C_e$.

6

$1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) and unfavorable ($1/n > 1$) [32].

8

And the

values of Q_0 and K_L can be calculated from the slope and intercept of the linear plot of $1/Q_e$ versus $1/C_e$. The adsorption isotherm

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for lysozyme onto HAP surface is calculated

parameters are listed in Table 3.

34

Table 3. Parameters obtained from Langmuir and Freundlich isotherms. HAP Langmuir Freundlich

28

2 Temperature Q 0 K L R1 K F 1/n 288 38.35 1.71 0.942 16.12 0.233 0.912 298 33.12 1.50 0.949 15.88 0.220 0.922 308 30.12 1.32 0.968 15.39 0.212 0.931 318 27.16 1.12 0.968 14.89 0.201 0.940

Based on the correlation coefficient as shown in Table

32

3, isotherm Langmuir

represents a better fit of experimental data than Freundlich and isotherms in all temperature. It indicates that the surfaces of

3

adsorbents are

mainly made up of heterogeneous adsorption patches [52] in addition to less homogeneous patches [34]. Freundlich constant, n , is a measure of adsorption intensity. As seen from Table 3, the values of $1/n$ for both adsorbents were below 1 at all the experimental temperatures, which indicate high adsorption intensity [35]. The Freundlich constant, K , which is related to the adsorption capacity, also shows that the adsorption capacity increased with temperature increase, indicating that the adsorption processes are exothermic in nature. But the increase of the values of $1/n$ with the temperature decrease suggests the increasing trend of the adsorption intensity. As temperature increased, the more lysozyme molecules were adsorbed, the keener the competitions for the limited adsorption sites and the stronger the attraction among the molecules, which resulted in increase of adsorption intensity. To compare the adsorption capacity of different surfaces adsorbent towards the lysozyme with that of

3

adsorbents were selected. 2 R 2 50 V. Haddadi et al. / Journal of Nanostructure in Chemistry 2 (1) (2011) For lysozyme the adsorption capacity of HAP surface was 38.35 mg/g at 288 K, concentration of lysozyme 1mg/mL and pH 7. The favorability of the lysozyme

adsorption process onto adsorbents surfaces evaluated using a dimensionless parameter (R) derived from the Langmuir expression. It is L defined as follows:

16

$R_L = \frac{C_0}{C_0 + C_e}$ The adsorption process can be defined as

irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) in terms of R_L 13

[36]. Table 4. The amount of R for adsorption of L T (K) 288 298 308 318 lysozyme onto HAP Lysozyme concentration (mg

/ml) 1 2 3 4 1 2 3 4 1 2 3 4 1 2 3 4 18

R_L 0. 369 0. 226 0. 163 0. 128 0. 400 0. 250 0. 182 0. 143 0. 431 0. 275 0. 202 0. 159 0. 472 0. 309 0. 229 0. 17

182 The calculated values of R for adsorption of L lysozyme onto HAP

fall between 0 and 1, thus the adsorption of lysozyme onto adsorbents is favorable. 25

4. Conclusion

revealed that the average size of the HAP clusters were 300 nm. Optimum dose of HAP was found to be 0.3 g /100mL of synthetic solution. It is evident from the pH study that there was increase in per-centage removal for increase in pH from 2 to 6 but for further increase in pH beyond 6, there wasn't any increase in removal. It was found from the study that the equilibrium was established after 40 min. Adsorption of lysozyme was found to follow first order kinetics. The effect of temperature on the adsorption of lysozyme onto HAP was studied using optimum adsorbent dose. It was observed that there was increase in percentage removal of lysozyme with increase in temperature. The effect of initial concentration was studied and was found that the percentage removal of lysozyme decreased from 96% to 80% for initial lysozyme concentration of 100 mg /L to 200 mg /L. The 1

percentage removal was found to remain constant with increase in pH and the optimum pH was found to be 6. The removal of lysozyme by HAP was very efficient and can bring down the lysozyme concentration to its permissible limit. The process can be employed as a primary step for the removal of lysozyme to meet permissible limit of lysozyme in surface and ground water. Acknowledgement The authors are grateful to

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acknowledges Islamic Azad University, Islamshahr Branch for financial support.

HAP was synthesized from egg shell by sole gel method. Synthesis was ascertained by adopting various characterizing methods. HAP exhibited much greater specific surface area. SEM micrograph

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