ADSORPTION BEHAVIOUR OF DEXTRIN ONTO ACTIVATED OYSTER SHELL

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Abstract

The effect of initial dextrin concentration, contact time, pH, temperature and added calcium ion on the adsorption behaviour of dextrin onto oyster shell is investigated. The results obtained show that increase in concentration and temperature below the boiling point of dextrin enhances the adsorption process. It was found in this study that adsorption density varies with pH and is maximum within the range of 2 to 7. The plot of amount of dextrin adsorbed against the concentration of the adsorbate was hyperbolic which conforms to Legmir isotherm. The free energy of dextrin oyster shell adsorption system was found to be 13.23kg/mol and the specific area of the oyster shell for this work was 70.8m ^{2}/g.

Keywords: *Adsorption, dextrin, oyster shell, behaviour, crushing, drying*

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1. INTRODUCTION

Many adsorbents such as silica get, activated alumina, carbons, and zeolites have been found useful for different adsorbates in different separation technique (Wei, 1994). When molecules moved from a bulk fluid to an adsorbed phase, they lose degrees of freedom and the free energy is reduced. Adsorption in always accompanies by the liberation heat and for physical adsorption, the amount of heat is similar in magnitude normally associated with a chemical reaction (Charles, 1991)

A number of investigators (Subramanian et al, 1988: Caesar, 1968, Weber, 2002) have studied the depression behaviour of starch and its derivatives in the flot6ation of hematite and quarts. Electrostatic interaction and hydrogen bonding have been suggested as a mechanism for the adsorption of polyelectrolytes by Miller et al 1983. according to clap et al, 1998 starch adsorption occurs via hydrogen bonding between the solid surface and the hydroxyl groups on the polymer. Their result showed that common starch in negatively charged in aqueous solution in the pH range of 3 to 11. The amount of dextrin adsorbed on quartz, however is clearly considerably than that on molybddenite. It was suggested that the adsorption process may be due to hydrophobic bonding with the polymer molecule displacing water molecules at the interface (Liu et al, 1989; Onuoha, 1995). Experimental evidence has shown that the external addition of metal ion enhances adsorption of starch. In the case of dextrin adsorption, the hydrophobic theory lies heavily on the fact that the minerals that adsorbs dextrin are hydrophobic which could be either anisotropic (tale and molybdenite) or heterogeneous (Hals, 1974).

Dextrin dissolves in water to form a sticky solution. It is chiefly used in mixing glues, adhesives on postage stamps ad sticky paper for Steffen textiles to produce a “head” on beer and other carbonated beverages (Hals, 1974). Oyster is on edible bivalve mollusk (one with a two pieced shell). The two parts of an oyster shell are different in size and shape for example Pearl and Bermuda oysters (Gregg el al, 1982) Oysters live attached to occen bottom in hard-surface areas called oysters beds and are found in all temperature and tropical oceans. The three genera of oyster shells (pyenodonta, crassotrea, ostrea) are returned to the beds to provide places on which larvae may set. Cultivated oyster shell beds helps in avoiding depletion in the river beds. Crushed oyster shells are fed to chickens. The shells are also burned and slaked to make lime for fertilizer. Crushed oyster shells can be used as adsorbent (Peterson et al, 1991). Oyster shells are composed of carbonaceous materials, when of carbonaceous materials, when heated in absence of air, mush of the substance devolatilizes, leaving behind a prorous structure of carbon that usually, also, contains some hydrogen (Frish et al 1999). This may then be activated by controlled oxidation with steam or carbon dioxide to further open up the pores and increase total surface area. During the heating process, the oyster shell surface is exposed more by the expansion, which occurs. Also, heating reduces the layers together (Subramanian et al 1988; Caesar 1998). There are four ranges of temperatures at which characteristic transformation or changes are produced in a carbonaceous materials (such as oyster shell) when thermally heated (Healy et al 2002; Khasla et al, 2004). The aim of this study is to establish he adsorption mechanism of dextrin using

oyster shell. also, in investigate the role played by the nature of oyster shell surface on the mechanism of dextrin adsorption as a function of pH, temperature, dextrin concentration, agitation time and presence and absence of calcium ion.

2. EXPERIMENTAL

The oyster shell sample used for this study was obtained from Bonny water side in River State. The dextrin is a pharmaceutical grade, and other materials used are cone. Sulphuric acid, P-nitro phenol, phenol, dil hydrochloric acid, dil sodium hydroxide, calcium sulphate and distilled water. The equipment made use of include pH meter, mechanical sieve, a shaker, glass electrode, thermometer, spectrophometer, hot place, weighing balance and electric furnace etc.

2.1 Preparation of thermally Activated Oyster Shell and Determination of its specific surface Area.

The oyster shell sample was size-reduced by crushing, grinding and screening. A weighed sample of 250g of the screened by Hall 1974 for 2 hours. The activated oyster shell was cooled in a desicator and stored in a dried and air-tight container to avoid the absorption of moisture. A stock solution of 100mol/L of P-nitro phenol was prepared from eight samples of different concentrations ranging from 10-80mol/L. the absorbance of each solution was measured with a 20uv/ visible spectrophotometer at 400nm. To one gram of oyster shell contain in eight different test tube was added 10mls of each of the prepared eight concentrations of P-nitro phenol. The test tubes were shaken manually at room temperature and adsorption equilibrium was attached at 25min. after 20mins, the test tubes containing the samples were centrifuged to ensure complete setting of activated oyster shell. The supernatant liquors were decanted and the absorbance of each decanted liquor of P-nitro phenol was then measured on the spectrophotometer at 400nm. A plot of equilibrium concentration of P-nitro phenol oyster shell versus equilibrium concentration of P-nitro phenol was obtained. The specific surface area is given by the formula

$$S.S.A = X_m NA \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

Where X_m = The monolayer capacity in mol/g
N = The Avogado's number
A = The area of the surface occupied by each solute molecules in m^2

2.2 Preparation of Dextrin Stock solution and Determination of concentration of Dextrin Solution.

Dextrin stock solution was prepared by causticizing since it is a starch derivative, instead of boiling in water or autoclaving. Two grams of dextrin was weighted into a volumetric flask and a 2000mg/l stock solution was prepared with distilled water. The suspension was form which was causticized with 2% potassium hydroxide solution and the mixture was stirred to obtain a homogeneous solution. Dextrin samples of concentrations ranging from 0 to 80mg/l were prepared from the stock solution. Two ml of each of these solution was pipetted into a phenol solution. Then 5ml of cone. Sulphuric acid was added rapidly making sure that the acid drained directly into the solution without touching the side of the test tubes. An instant brown colour was formed. The tubes were than allowed to stand of 10mins, and was shaken and place in water bath at room temperature for 15min before their absorbance were read using a Bauseh and Lomb spectrophotometer at 490nm.

2.3 Adsorption Experiments

2.3.1 Concentration on Adsorption

One gram activated oyster shall sample crushed to 75μm was pulped using 10ml of distilled water. The pH of the pulp was adjusted to 4,7 and 11 respectively. This was followed by the addition of 40ml of different dextrin solution concentrations to the six-labeled test tubes containing one gram of pulped activated oyster shell. Then the labeled tubes were agitated mechanically at room temperature for 30mins. The mixtures were allowed to stand for 12hours to ensure complete equilibrium. The oyster shells were then removed by filtration using filter paper. Then, 10ml of the filtrates were collected and analyzed spectrophotometrically at 490nm. The amount of dextrin absorbed as dextrin concentration before and after the adsorption reaction was calculated, followed by adsorption density, that is, dextrin adsorbed at equilibrium divided by specific surface area of the oyster shell.

2.3.2 Contact Time on Adsorption

One gram of crushed oyster shell of pH 7 was pulped using 10ml of distilled water in six different test tubes. Then 40ml of dextrin solution of initial concentration 3000mg/L was added into the text tubes. The test tubes were shaken at 10, 220, 30,40,50 and 60 minutes respectively at room temperature. The samples in the test tubes were filtered and analyzed spectrophotometrically at 490nm.

2.3.3 pH on Adsorption

One gram of prepared oyster shell sample crushed to 75pm was pulped with 10ml of distilled water. The pH of the pulp was adjusted to 2,4,6,8,10 and 11 dextrin solution of concentrations 400mg/L and 2000mg/L respectively was added into six test tubes. The tubes were agitated for one hour at room temperature and allowed to stand for 12 hours for complete equilibrium. The oyster shell was removed by filtration and 10ml of the filtrates were collected and analyzed spectrophotometrically at 490nm. The amount of dextrin absorbed as dextrin concentration before and after the adsorption reaction were calculated.

2.3.4 Temperature on Adsorption

Forty ml of dextrin solution of pH 7 and initial concentration 100mg/L was equilibrated to the required temperature of 27, 30, 50 and 70^{o}C. One gram of activated

oyster shell samples crushed to 75μm were added to the solution in six test tubes and shaken for 30mins. Then the tubes were allowed to stand overnight to ensure equilibrium adsorption. The oyster shell was filtered and 10ml of the filtrate from each tube was analyzed spectrophotometrically at 490nm.

2.3.5 Added ion (Ca^{2+}) on Adsorption

One gram of pulped oyster shell was mixed with $CaSO_4$ of initial concentration 100mg/L and followed by the addition of 40ml of different dextrin solution concentration to six different test tubes. The tubes were agitated at room temperature for 30mins. The mixtures were allowed to stand for 12hours for complete equilibrium. The oyster shell was filtered and 10ml of the filtrate were collected and analyzed with a spectrophotometer at 190nm.

2.3.6 Different Concentration of Added ion (Ca^{2+}) on Adsorption

One gram of pulped oyster shell wan mixed with different concentration of added ion of the range 0, 50, 100, 200, 250 and 300mg/L and to each was added 40ml of 100mg/L of dextrin solution in a test tube. The different test tubes were shaken for 30mins at room temperature. The mixtures were allowed to stand for 12hours for complete equilibrium. The oyster shell was removed by filtration and 10ml of the filtrates were collected to be analyzed with the spectrophotometer at 490nm.

3. RESULTS

Below are the results of the various experiments carried out in this work.

Table 1: absorbance for Various Concentration of Para-nitrophenol (PNP) solution at 400nm

Concentration of PNP (mol/litre)	Absorbance at 400nm
10	0.268
20	0.406
30	0.545
40	0.683
50	0.820
60	0.58
70	1.097
80	1.234

Table 2: Concentration of Dextrin and Absorbance of 490nm

Concentration of PNP (mol/litre)	Absorbance at 400nm
0	0.00
10	0.13
20	0.26
30	0.38
40	0.50
50	0.65
60	0.76
70	0.90
80	1.02

Table 3a: effect of Concentration on Dextrin Adsorption into Oyster Shell (pH7.0)

Initial Cone. Of Dextrin (mg/L)	Absorbance Equilibrium at 490nm	Equilibrium Concentration (mg/L)	Dextrin Adsorbed at Equilibrium Cone. (mg/L)	Absorption Density (mg/m^3)
500	1.4	110	390	5.51
1000	3.7	290	710	10.03
2000	6.2	490	1510	21.33
3000	8.9	700	2300	32.49
4000	14.3	1125	2875	40.61
5000	24.3	1911.2	3088	43.60

Table 3b: Effect of Concentration on Dextrin Adsorption onto Oyster Shell (pH ±11)

Initial Cone. Of Dextrin (mg/L)	Absorbance Equilibrium at 490nm	Equilibrium Concentration (mg/L)	Dextrin Adsorbed at Equilibrium Cone. (mg/L)	Absorption Density (mg/m^3)
500	0.7	50	450	6.36
1000	1.9	150	850	12.00
2000	3.7	290	1710	24.15
3000	5.2	410	2590	36.58
4000	8.4	660	3340	47.18
5000	11.5	904	4096	57.85

Table 3c: effect of Concentration on Dextrin Adsorption onto Oyster shell (pH 4)

Initial Cone. Of Dextrin (mg/L)	Absorbance Equilibrium at 490nm	Equilibrium Concentration (mg/L)	Dextrin Adsorbed at Equilibrium Cone. (mg/L)	Absorption Density (mg/m^3)
500	1.3	100	400	5.65
1000	3.0	240	760	10.73
2000	6.3	500	1500	21.18
3000	10.6	840	2160	30.51
4000	14.6	1150	2850	40.25
5000	18.6	1470	3530	49.90

Table 4: Effect of Agitation Time of Dextrin adsorption onto Oyster Shell (pH 7) Initial concentration 3000mg/l)

Time (min.)	Absorbance equilibrium at (490nm)	Equilibrium concentration (mg/l)	Dextrin Adsorbed at Equilibrium (mg/l)	Adsorption Density (mg/m^3)
10	9.1	720	2280	32.20
20	6.9	540	2460	34.75
30	5.4	430	2570	36.30
40	4.0	310	2690	37.99
50	4.3	340	2660	37.57
60	4.4	350	2650	37.42

Table 5a: Effect of pH on Adsorption of Dextrin onto Oyster Shell (Initial concentration 4000mg/l)

Time (min.)	Absorbance equilibrium at (490nm)	Equilibrium concentration (mg/l)	Dextrin Adsorbed at Equilibrium (mg/l)	Adsorption Density (mg/m^3)
2	6.4	500	2500	49.44
4	4.2	330	3670	51.84
6	2.0	160	3840	54.24
8	2.5	200	3800	53.67
10	3.0	240	3760	53.11
11	5.8	460	3540	50.00

Table 5b: Effect of pH on Adsorption of Dextrin onto Oyster Shell (Initial concentration = 2000mg/l)

Time (min.)	Absorbance equilibrium at (490nm)	Equilibrium concentration (mg/l)	Dextrin Adsorbed at Equilibrium (mg/l)	Adsorption Density (mg/m^3)
2	10.7	850	1150	16.24
4	8.1	640	1360	19.21
6	4.4	350	1650	23.31
8	3.9	310	1690	23.87
10	6.0	470	1530	21.61
11	9.3	730	1270	17.94

Table 6: Effect of Temperature on Adsorption Behaviour of Dextrin onto Oyster Shell Sample (pH = 7.0. Initial dextrin concentration 1000mg/l)

Temperature "C	Absorbance Equilibrium at 490nm	Equilibrium concentration (gm/l)	Dextrin Adsorbed at Equilibrium (mg/l)	Adsorption Density (mg/m)
10	1.2	90	910	12.85
30	0.9	70	930	13.13
50	0.7	50	950	13.42
70	0.3	20	980	13.84

Table 7a: Effect of Added ion (Ca^{2+}) on adsorption of Dextrin onto Oyster shell (pH-7.0. Initial concentration 1000mg/l)

Initial Cone Dextrin	Absorbance Equilibrium at 490nm	Equilibrium concentration (gm/l)	Dextrin Adsorbed at Equilibrium (mg/l)	Adsorption Density (mg/m)
500	1.0	80	420	5.93
1000	2.0	160	840	11.86
2000	40	300	1700	24.01
3000	7.0	520	2480	35.03
4000	9.0	680	3320	46.89
5000	12.0	900	4100	57.91

Table 7b: Effect of Different concentration of Added ion (CO2+) on Dextrin Adsorption onto Oyster Shell (Initial Concentration of Dextrin 1000mg/l)

Initial Cone of Ca2+ ion (mg/l)	Absorbance Equilibrium at 490nm	Equilibrium Concentration (gm/l)	Dextrin Adsorbed at Equilibrium (mg/l)	Adsorption Density (mg/m)
0	3.8	290	710	10.03
50	0.3	220	780	11.02
100	0.2	160	840	11.86
200	0.4	300	700	9.88
250	0.4	450	550	7.76
300	0.8	600	400	5.65

4. DISCUSSION

The adsorption mechanism of organic polymers such as dextrin are considerably more complex than that of simple ions or molecules (Gregg et al, 1982). The actual adsorption of dextrin onto activated oyster shell is thought to be by multiple point attachment, arising from the interaction between the hydroxyl (OH) functional group of dextrin with sites on the shells. The conformation of dextrin on the activated oyster shell is complicated, because it is extremely unlikely that each segment of the dextrin is attached to surface. The polymer chain adsorbs at several points along its length and unabsorbed trains of segment between these points, form loops or bridges extending into the solution. The higher the flexibility of a polymer, the more complicated will be its conformation on the activated oyster shell or into their pores, this is almost the stage that determines the adsorption rate. From Table 1 and 2 shows an increase in absorbance at various concentration of paranitrophenol and dextrin at 400 and 490nm. The calibration curve of table I gave a linear plot. (figure 1), which obeys the Bear Lanberts law.

The study of various concentrations of dextrin at different pH (tables 3a-3c) showed that an increase in the concentration of the dextrin (adsorbate), enhances the adsorption density which increase the affinity of adsorbate to be adsorbed at the surface of the oyster shell. The effect of agitation/contact time on adsorption onto oyster shell as shown in Table 4 revealed that an increase in the agitation time of contact, increases the adsorption rate for a time range of 10-40mins and then, an instantancous decrease in adsorption density for a time range of 40-60mins.

The effect of pH on the adsorption behaviour of dextrin onto oyster shell at initial concentration of 2000 and 400mg/l was investigated, and the results in Tables 5a and 5b showed that the adsorption process of dextrin does not depend strongly on pH. However, from the result, it was observed that, an increase in adsorption density occurs from a pH range of 2-6 and a decrease for pH range of 6-11. Adsorption of dextrin was favoured by the increase in temperature below the boiling pint of dextrin as shown in Table 6.

The addition of calcium ion (Ca^{2+}) to the dextrin concentration increases the adsorption rate linearly and increases adsorption density for Ca^{2+} concentration of 0 to 100mg/l as well as decreases the adsorption rate for Ca^{2+} concentration of 100 to 300mg/l as displayed in Table 7a and 7b respectively.

A plot of dextrin adsorbed versus initial concentration of dextrin (Table 3) conforms to langmuir isotherm (figure 2). The free energy of dextrin oyster adsorption system was calculated to be 13.23KJ/mole by applying Anchnius equation at 28^oC, the operating temperature for this study and the kc value of 5.05×10^{-03} obtained by least square analysis of the equation

$$C=\frac{Kc\ CmC}{1+KcC}$$ (Charles, 1991).

The specific surface area of the oyster shell used for this study was calculated to be
70 m^2/g.

5. CONCLUSION

This study shows that the adsorption of dextrin onto oyster shell is characterized by physical adsorption resulting from hydrophobic bonding. The adsorption process was followed by the Langmuir isotherm. It was observed that increase in temperature facilitate adsorption of dextrin its boiling point. Also, the slight dependence of adsorption process on pH, indicates that electrostatic interaction in not a contributing factor on the adsorption energy.

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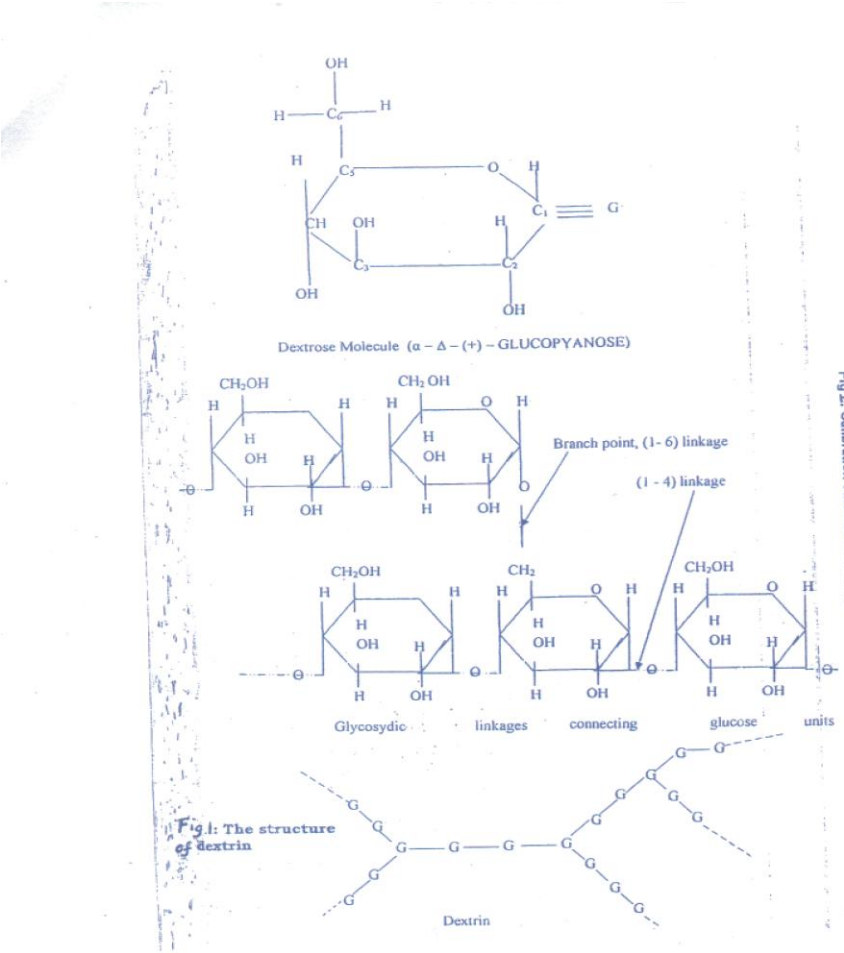

Fig 1: The structure of dextrin

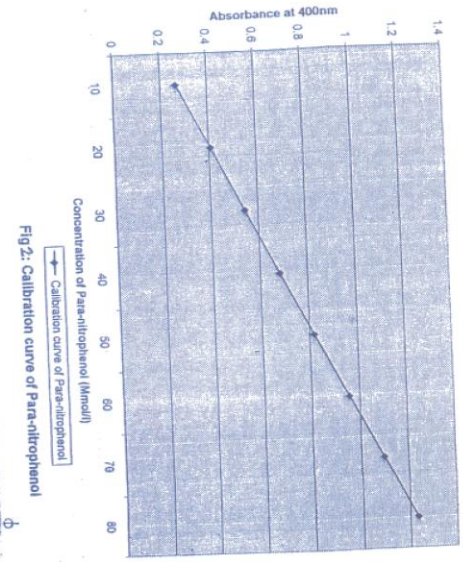

Fig2: Calibration curve of Para-nitrophenol

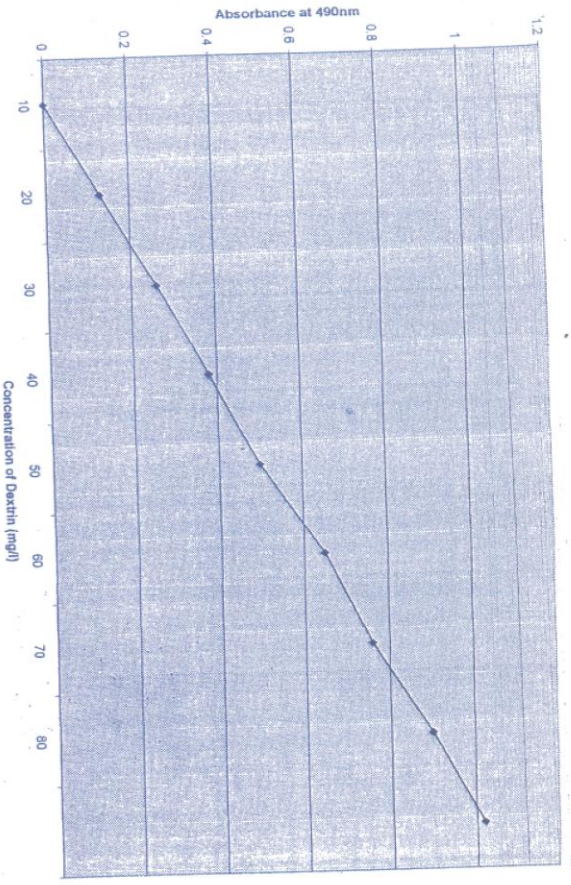

Fig3: Calibration curve of the Dextrin

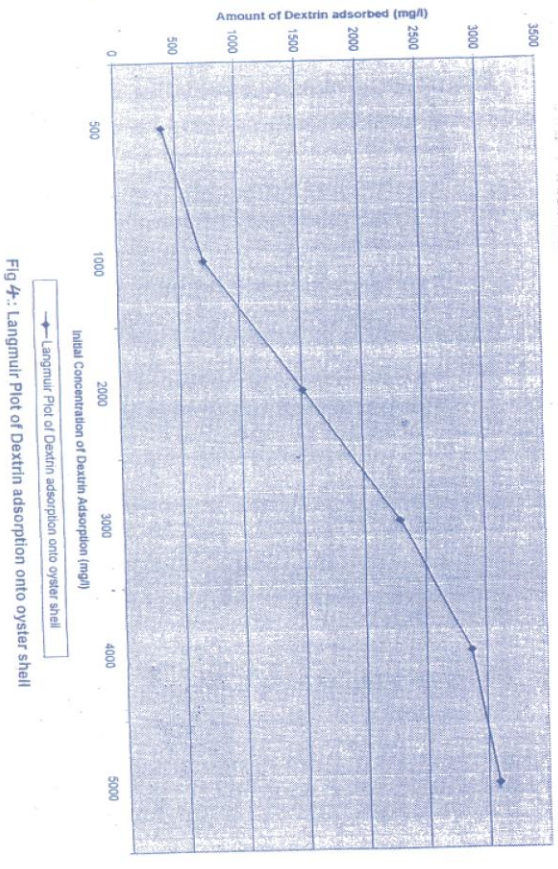

Fig 4: Langmuir Plot of Dextrin adsorption onto oyster shell