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RESEARCH ARTICLE

DYNAMIC ADSORPTION OF THE TEXTILE DYE ACID GREEN ON A FIXED BED OF ACTIVATED CARBON FROM HENS' EGGSHELLS

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Abstract

The present work constitutes a contribution to the circular economy through the valorization of chicken eggshells, an abundant waste in Côte d'Ivoire, through a alternative to commercial activated carbons. The precursor was chemically activated with 30% phosphoric acid for 24 hours at a rate of 200 g per 100 ml of acid, then calcined at 600°C for 1 hour. In-column adsorption on the CAC30 fixed bed was influenced by bed height, column feed rate and initial dye solution concentration. AG42 removal tests showed that breakthrough and saturation times increased with height and decreased with increasing feed rate and AG42 solution concentration. The amount adsorbed increased with bed height and concentration, and decreased with feed rate. The rate constant increases with flow rate and decreases with bed height and effluent concentration. The adsorption kinetics of AG42 on the CAC30 compact bed can be described by the models of Thomas, Bohart and Adams and Yoon and Nelson.

Introduction:-

The presence of textile dyes in surface waters is a major health concern. Indeed, in the absence of effective systems for removing these substances from the effluents of the many dyeing units, mainly artisanal, installed in the city of Abidjan, they end up in the waters of the Ebrie lagoon [1]. However, these dyes have proved difficult to biodegrade [2], with effects on the aquatic environment, biodiversity and human health [3]. Some dyes are carcinogenic, mutagenic and teratogenic, and are likely to cause several ailments [4]. Their elimination from wastewater is becoming imperative and a major priority for the protection of ecosystems and human health. Several technologies have been developed to reduce or even eliminate these substances from dyehouse effluent before discharge. These include biological, chemical and physical techniques [5]. Among these techniques, adsorption has particularly attracted our attention due to the simplicity of its implementation and the non-selectivity of the adsorbents used [3]. However, due to its cost, commercial activated carbon remains the limiting factor for large-scale implementation,

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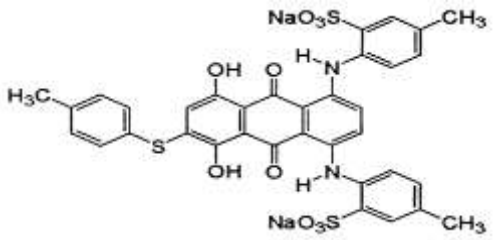
particularly in developing countries such as Côte d'Ivoire. Our study proposes to valorize hens' eggshells as activated carbon for the removal of the dye Acid Green 42 in dynamic mode on a fixed bed of activated carbon in an aqueous medium.

Materials and Methods:-

Preparation of activated carbon (CAC)

Hen eggshells, collected from markets in Abidjan, were washed in hot water and dried to remove oil residues and impurities before being ground in a Romer Labs-type grinder, washed with distilled water and oven-dried at 110°C for 24 hours. The crushed material was sieved using an electric sieve shaker (RETSCH-AS 200). The crushed material was cold-impregnated for 24 hours in a 30% phosphoric acid solution at a ratio of 200 g to 100 mL acid. The impregnate is then dewatered and oven-dried for 24 hours at 110°C before being calcined at 600°C in a muffle furnace (NABERTHERM) for 1 hour. After cooling, the activated carbon is washed several times with distilled water to remove the activating agent, then dried in an oven at 110°C for 24 hours. The fraction between 1 and 2 mm was selected for the AG42 dye removal tests, whose characteristics are summarized in the following **Table I**:

Table I:- Characteristics of the textille colorant Acid Green 42 [6].

Common Name	**Acid Green 42**
Structure and chemical name	Alizarin cyanine green 3GW 
Family	Anthraquinonic dye
Molecular formula	$C_{35}H_{26}N_2Na_2O_8S_3$
Case number	6425-06-5
Molecular mass	744.77 g.mol-1
Solubility	High solubility in water and alcohol
Purity	99,5%

Preparation of AG42 solutions

The AG42 stock solution, with a concentration of 1 g/L, was prepared by dissolving 1 g of powder in 1 liter of distilled water at boiling temperature. Daughter solutions for analysis were obtained by successive dilutions of the stock solution for adsorption tests. The adsorption spectrum of the solution from 400 to 800 nm was used to determine the molecule's maximum adsorption wavelength (578 nm**)**. A dye calibration curve was established to determine residual concentrations in adsorption tests on prepared carbons.

Experimental set-up

The set-up consists of a column topped by a large-capacity separating funnel which acts as a reservoir. It is a standard glass column, 40 cm high and with an internal diameter of 3 cm. The reservoir and column are fitted with valves to regulate the flow of colored effluent onto the carbon bed. Masses of 2 g of glass wool were used to distribute the effluent over the entire surface of the carbon column and to separate the treated effluent from the carbon at the column outlet.

Adsorption tests in dynamic mode

We were interested in the design criteria for fixed-bed systems, in this case, the running time of an adsorbent to remove a pollutant from a given solution before regeneration is required. This period is known as the column operating time. The effect of certain parameters on dynamic adsorption on breakthrough curves has been studied. These parameters are bed height, feed rate and initial solute concentration.

Influence of coal bed height

Tests were carried out with CAC30 at heights of 5, 10 and 15 cm. The fixed carbon bed was kept compact between two layers of glass wool. The column was treated with 3 L of 100 mg/L effluent at a flow rate of 8 mL/min. Samples are taken at regular intervals to monitor the residual dye concentration at the column outlet. Samples are analyzed using a Visible spectrometer.

Influence of flow rate on adsorption

Tests are carried out as before, with a 5 cm height of CAC 30 and a dye concentration of 100 mg/L. These tests are carried out at different flow rates (4, 8, 12 mL/min). Samples are taken at regular intervals to monitor changes in residual dye concentration. Samples are analyzed using a Visible spectrophotometer.

Influence of concentration on adsorption

Tests are carried out as above, with a 5 cm height of CAC 30. Tests are carried out at a flow rate of 8 mL/min at different concentrations (100, 150 and 200 mg/L). Samples are taken at regular intervals to monitor changes in residual dye concentration. Samples are read using a UV-Visible spectrophotometer.

Determination of adsorbed quantities

A relatively simple calculation is used to determine the quantities of fixed dye. For the calculations, each experimental value represents the average of three trials. Adsorbed quantities and adsorption rates are determined from equations 1 and 2**.**

$$\boldsymbol{Taux\ d'adsorption}(\%) = \frac{(\mathbf{Ci-Ct})}{\boldsymbol{Ci}} \times \mathbf{100} \quad (1)$$

$$\boldsymbol{Qt} = (\mathbf{Ci - Ct}) \times \mathbf{V/\ m} \quad (2)$$

Qt: quantity of dye adsorbed per unit mass of carbon (mg/g); Ci: initial dye concentration (mg/L); Ct: residual concentration at equilibrium (mg/L); V: adsorbate volume (L); m : mass of carbon (g).

Modeling kinetics

In this study, three mathematical models developed from equations elaborated by [7], [8], and [9] were used to describe, predict and estimate experimental data obtained from dynamic studies performed on the fixed bed to predict breakthrough curves.

Thomas model

The Thomas model is based on the irreversible isotherm model of Bohart and Adams. It has been used to describe the adsorption of organic, inorganic and heavy metal compounds [10]. This simplified design model ignores both intraparticle mass transfer resistance and direct external resistance. This means that the adsorption rate is controlled by the surface reaction between the adsorbate and the unused capacity. This expression is given as follows:

$$\mathbf{ln}\left(\frac{C_0}{C_t} - \mathbf{1}\right) = \frac{k_{Th}Q_0m}{\mathbf{F}} - \boldsymbol{k_{Th}C_0t} \quad (3)$$

With : C_o : Initial coloant concentration ($mg.L^{-1}$); C_t : Dye concentration at time (t) ($mg.L^{-1}$); m : Bed mass (g); K_{Th} : Thomas constant ($L\ .mg^{-1}\ .min^{-1}$); Qo : Maximum solute adsorption capacity ($mg.g^{-1}$); F : Feed rate $(L.min)^{-1}$

Yoon and Nelson model

Yoon and Nelson developed a relatively simple model to describe the breakthrough of a gaseous compound on an adsorbent. This model is based on the assumption that the variation in the probability of adsorption of the solute is proportional to the probability of adsorbate breakthrough. This equation is expressed as follows

$$\frac{C_t}{C_0} = \frac{\mathbf{1}}{\mathbf{1+exp(k(\tau - t))}} \quad (4)$$

Where: k is the speed constant (s^{-1}) is time required for 50% drilling (s)
The linear form of the Yoon and Nelson model is as follows:

$$\mathbf{ln}\left(\frac{C_t}{C_0 - C_t}\right) = \mathbf{kt - \tau k} \quad (5)$$

Plotting as a function of time can be used to deduce the parameters of this model.

Bohart and Adams model

This model is represented by the equation:

$$ln\left(\frac{C}{C_0}\right) = KC_0t - KN_0\frac{Z}{U} \quad (6)$$

Where, C_o : initial concentration (mg/L); U : velocity in the reactor assumed to be empty (cm/min); N_o : dynamic adsorption capacity (mg/l); Z : packing height (cm); K : Bohart and Adams velocity constant.

By plotting the straight-line Ln(C/Co) versus time (t), we can determine the model parameters.

Results and Discussion:-

Influence of bed height on adsorption of AG42 dye

The study of adsorption of AG42 on CAC30 in a column was carried out by varying the bed height (5 cm, 10 cm and 15 cm) and setting the feed rate and dye concentration at 8 mL/min and 100 mg/L respectively. The results are shown as breakthrough curves in **Figure 1**.

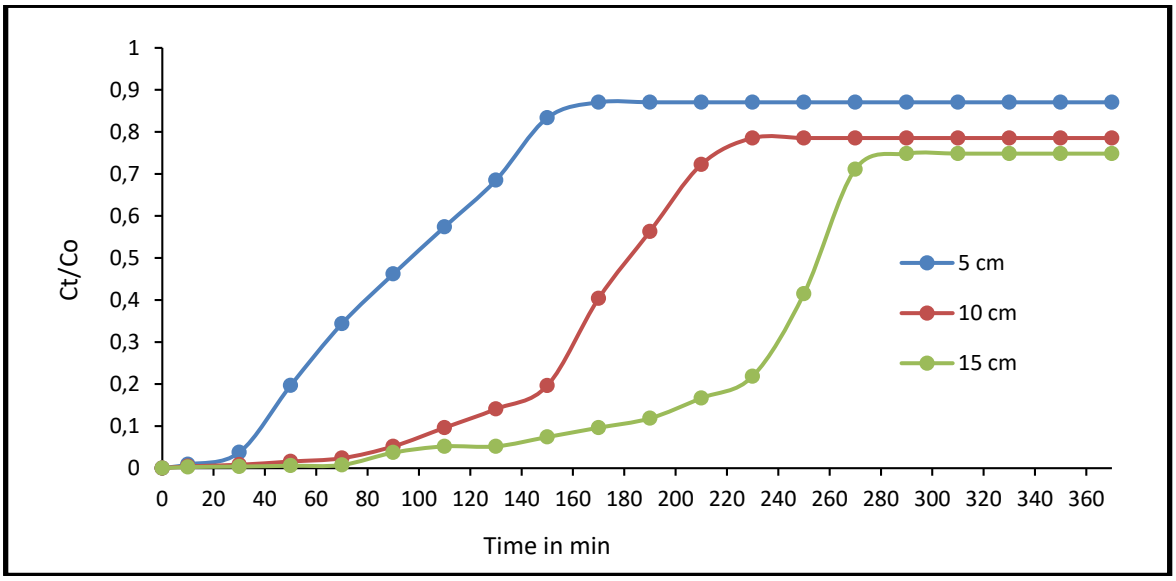


Figure 1:- Influence of CAC30 height on column adsorption.

The curves have three parts. The first part characterizes the bed's maximum efficiency or breakthrough time, when the solute concentration at the column outlet is low (5% of the initial concentration). This break-through time varies from 30 to 110 min for the CAC30 when heights vary from 5 to 15 cm. The greater the height, the longer the residence time and the greater the number of sites. This can be explained by the fact that when the effluent is sent to the column with new adsorbent, the molecules encounter free sites for adsorption. Molecules that have not been adsorbed continue along the carbon bed to find virgin sites on which they can bind. In this way, the bed becomes saturated and the adsorption zone (adsorption front) initially located above the bed gradually moves towards the saturation zone located at the lower end of the bed [11]. The effluent concentration at the outlet then becomes increasingly close to the initial concentration, indicating saturation of the column; this constitutes the second part of the curve. The third part is characterized by a plateau reflecting bed saturation, at which point the concentration at the column outlet is very close to the initial concentration. Bed saturation is reached after 170, 230 and 290 min for CAC30 heights of 5, 10 and 15 cm. The greater the height, the more sites and the longer the breakthrough time. Guendouz and Rezzaz-Yazid [12] studied the biosorption of methylene blue on date pedicels in a column and obtained similar results, concluding that retention is favored by greater heights. Roxanne *et al* [13] also made a similar finding when removing arsenic on a chitosan-based adsorbent in a fixed bed.

Influence of flow rate on column adsorption of AG42 dye

To study the influence of flow rate on the fixation of AG42 on the carbon bed, tests were carried out by setting the bed height at 5 cm and the effluent concentration at 100 mg/L. The tests were carried out at different flow rates of 4, 8 and 12 ml/min. The results are shown in **figure 2**.

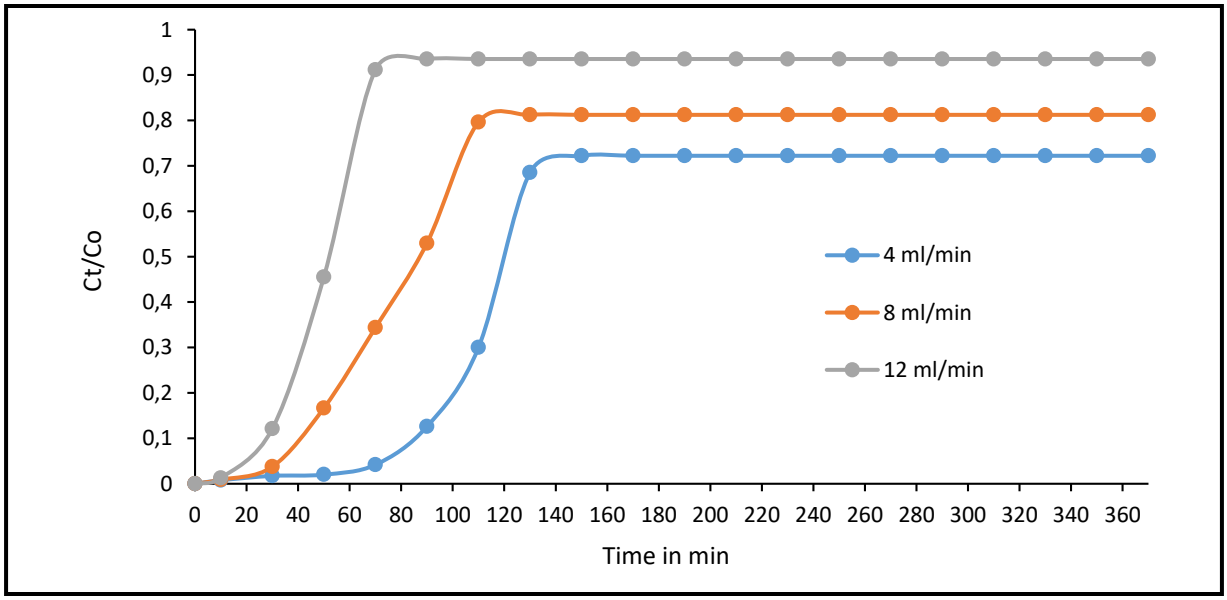


Figure 2: Influence of flow rate on column adsorption of AG 42 on CAC 30

Analysis of the figure reveals a decrease in coal bed fixation capacity with increasing flow rate. This is reflected in lower breakthrough and saturation times. The CAC30 has breakthrough times of 70, 40 and 20 and saturation times of 150, 110 and 70 minutes respectively for flow rates of 4, 8 and 12 mL/min. A similar finding was reported by Guendouz and Rezzaz-Yazid [12] in their study of methylene blue biosorption on date pedicels. They argued that an increase in flow rate limits the diffusion of the solute, which does not have enough time to diffuse into the adsorbent particles. Low flow rates are characterized by low velocities and long contact times. Increasing the contact time between the dye and activated carbon improves the binding of solute molecules, delays column breakthrough and reduces the speed of movement of the adsorption front [14].

Influence of concentration on column adsorption of green 42

To study the influence of concentration on the binding of AG 42 to the carbon bed, tests were carried out with the bed height set at 5 cm CAC 30 and the effluent flow rate at 4 mL/min. Tests were carried out at different concentrations of 100, 150 and 200 mg/l. The results are shown in **figure 3**.

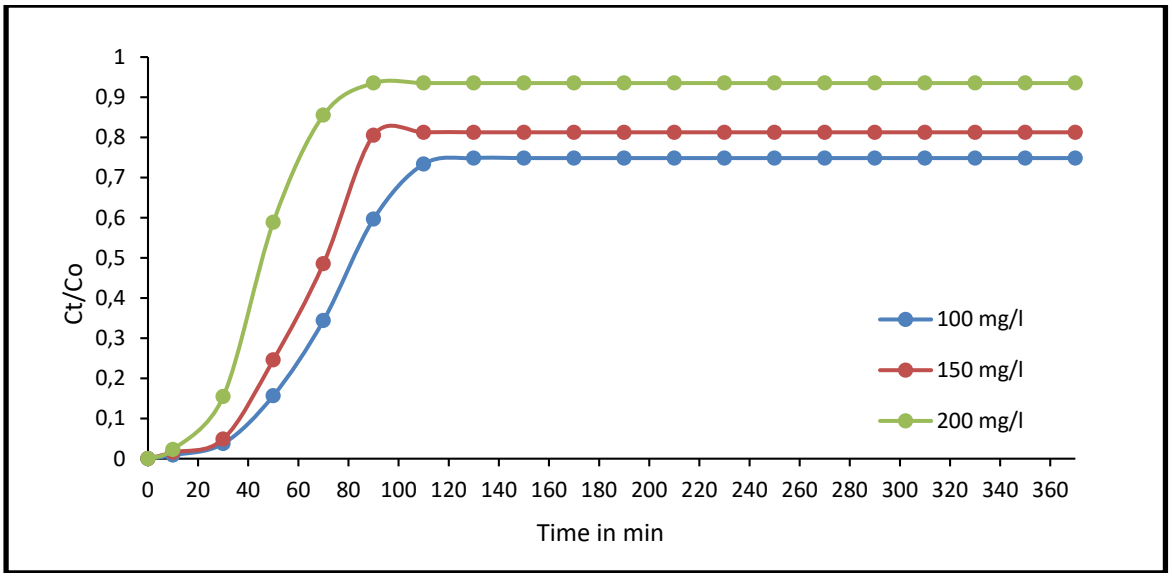


Figure 3: Influence of initial concentration on adsorption of AG 42 on CAC30

Analysis of the figure reveals that an increase in concentration induces a decrease in bed breakthrough and saturation times. Indeed, when the concentration increases from 100 to 200 mg/L, breakthrough time drops from 40 to 20 minutes and saturation time from 170 to 110 minutes. A similar finding was reported by Guendouz and Rezzaz-Yazid, [12] in their study of methylene blue biosorption on date pedicels. The authors observed a decrease in saturation time from 250 to 170 min when the dye concentration was increased from 10 to 40 mg/L. According to the authors, this was due to the presence of a strong concentration gradient between the solution and the adsorbent surface. According to Soro and *al.*, [15], having made a similar observation when removing safranin from a clay-based adsorbent, increasing concentration leads to a decrease in breakthrough time.

Modeling drilling curves

In this study, three mathematical models were used to describe, predict and estimate the large-scale use of this remediation method, based on experimental data obtained from fixed-bed studies. The following table summarizes the results obtained.

Table 2:- Parameters calculated from kinetic models.

Thomas' model					
Z (Cm)	Co (mg/L)	F (mL/min)	Qo (mg/g)	K_T (L/min.mg) $\times 10^{-4}$	R^2
5	100	8	2,01	7,01	0,97
10	100	8	2,60	2,9	0,99
15	100	8	3,05	1,77	0,99
5	100	4	2,52	2,66	0,96
5	100	8	2,05	6,91	0,99
5	100	12	1,98	10,95	0,97
5	100	8	2,06	6,88	0,99
5	150	8	2,77	4,68	0,98
5	200	8	2,92	4,17	0,99
Bohart and Adams model					
Z (Cm)	Co (mg/L)	F (mL/min)	No (mg/mL)	K_{BA} (L/min.mg)$\times 10^{-4}$	R^2
5	100	8	1,86	6,31	0,96
10	100	8	2,24	2,86	0,98
15	100	8	2,60	1,76	0,99
5	100	4	2,19	2,19	0,96
5	100	8	1,89	1,89	0,99
5	100	12	1,76	1,76	0,99

5	100	8	1,90	6,19	0,98
5	150	8	2,68	3,96	0,98
5	200	8	2,98	3,06	0,99
Yoon and Nelson model					
Z (Cm)	Co (mg/L)	F (mL/min)	τ (min)	K_{YN} (min^{-1}) $\times 10^{-2}$	R^2
5	100	8	75,73	7,01	0,97
10	100	8	195,66	2,90	0,99
15	100	8	343,51	1,77	0,99
5	100	4	189,42	2,66	0,96
5	100	8	76,97	6,91	0,99
5	100	12	49,56	10,95	0,97
5	100	8	91,82	6,88	0,99
5	150	8	55,85	7,03	0,98
5	200	8	21,06	8,34	0,99

Analysis of the Thomas model results reveals that increasing the bed height increases the adsorption capacity and decreases the adsorption constant (K_{TH}). Increasing the feed rate decreases the adsorption capacity and increases the adsorption constant (K_{TH}**).** Christophe [16], has shown in his studies that adsorption capacity increases with adsorption bed height. He explains this by the increase in residence time with increasing adsorption bed height. Thomas' model reveals an increase in adsorption capacity and a decrease in the adsorption constant (K_{TH}) with increasing initial concentration. Similar trends were reported by Benzekri [3] when removing three dyes (methylene blue, malachite green and G orange) on two activated carbons one based on olive pits and a commercial activated carbon (Organosorb 10). This author noted an increase in the amount of Methylene Blue adsorbed from 27.3 to 60 mg/g and 28.9 to 57.3 mg/g when the Methylene Blue concentration was increased from 100 to 200 mg/l on Organosorb 10 and the olive kernel-based AC respectively.

The results of Bohart and Adams show that as the height increases, the adsorption capacity of AG42 on the CAC30 fixed bed increases and the adsorption rate constant decreases. The best adsorption capacity (N_0) is 2.98 mg/mL for an adsorption rate constant (K_{BA}) of 1.76 $\times 10^{-4}$ L/min.mg. The adsorption capacity decreases and the adsorption rate constant increases with increasing feed rate. It should be noted that for this model, increasing the initial concentration increases the adsorption capacity of the bed and decreases the adsorption rate constant. Other authors have obtained similar results [17-18].

The values of the Yoon-Nelson parameters (K_{YN} and τ) were determined from this model in relation to time (t) under various operating conditions (**Table II)**. Values of the adsorption rate constant (K_{YN}) increased with flow rate, while values of τ (time to 50% breakthrough) decreased as flow rate increased. These results are in agreement with those of Seghier [19]**.** He obtained a decrease from 542.12 to 304.73 min when the feed rate increased from 2 to 6 mL/min**.** Increasing the initial concentration decreases the time (τ) and increases the adsorption rate constant (K_{YN}). However, when the fixed bed height is increased, (τ) increases while (K_{YN}) decreases. Benzekri [3]**,** observed the same trends in his study. Indeed, in this study, he observed an increase in time τ from 219 to 404 min and 166 to 366 min respectively for Organosorb 10 commercial carbon and that based on olive pits, when the height varies from 5 to 7 cm. R^2 values ranged from 0.96 to 0.99 for all three models. This indicates that all three models can be used to describe the adsorption of AG42 on CAC30.

Conclusion:-

The study of adsorption in dynamic mode revealed that increasing activated carbon bed height and concentration induces an increase in adsorption capacity and saturation time. However, an increase in feed rate leads to a decrease in column efficiency, through a reduction in adsorption capacity and bed saturation time. The adsorption capacity of the activated carbon bed increases with the initial concentration of GA 42. However, this increase is accompanied by a decrease in bed saturation time. All three models (Thomas, Bohart and Adams and Yoon and Nelson) are able to describe the adsorption of AG42 on activated carbon from hens' eggshells.

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