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Barbara PIECZYKOLAN[1] and Izabela PŁONKA[1]

SORPTION PROCESS OF ACID YELLOW 36 ON SLUDGE-BASED ACTIVATED CARBON

SORPCJA BARWNIKA ACID YELLOW 36 ZA POMOCĄ WĘGLA AKTYWNEGO WYTWORZONEGO Z OSADU CZYNNEGO

Abstract: The study of sorption of dye Acid Yellow 36 on SAC (sludge-based activated carbon) was conducted. For this purpose, anaerobically digested and dewatered sewage sludge was dried at 105ºC to constant weight. Next this sludge was milled to a particle with a diameter of 0.5-1.0 mm and subjected to chemical activation by hydrogen peroxide. After oxidation process the sludge was subjected to thermal transformation in a muffle furnace at 600ºC. In this way obtained a powder activated carbon based on activated sludge (so-called SAC). Based on the results of the study the most favorable parameters of sorption process was achieved as follows: pH value equaled to 2.5 and reaction time equaled to 30 minutes. The linearized forms of Freundlich and Langmuir isotherms showed that the highest value of correlation factor was obtained in the case of Langmuir model. However, in this case, the negative value of constant isotherm was achieved. Therefore, it can be assumed that more accurately in this case is the Freundlich model or other model which was not examined during that studies.

Keywords: sewage sludge, activated carbon, dyes, sorption isotherm, sorption kinetic, Freundlich isotherm, Langmuir isotherm

Introduction

The synthetic dyes are widely used in different kind of industry such as textile, leather, paint, etc. therefore during production a colored wastewater are generated. That wastewater has to be purified and uncolored. Some dyes used in industry are toxic to the water environment. The can also be carcinogenic. The process of photosynthesis may be disturbed as a result of the discharge the untreated colored wastewater into the receiver.

The Acid Yellow 36 is one of that kind of dye which has negative impact on water environment. It has the very toxic and carcinogenic properties. Moreover the dye involves negatively on fishes. The mortality, the loss of weight, changes in body colours and restlessness of fishes during the toxicity tests were observed. Moreover, it has an adverse effect on the nervous system of fishes causing involuntary movements of their body. The Acid Yellow 36 is widely used in paper, soap, tannery, cosmetics, wax, polishes and many others industries [1, 2].

There are many different methods used for treatment of colored wastewater. These methods include: membrane techniques [3, 4], sorption [5] and advanced oxidation processes [6, 7]. The sorption has high efficiency, low-cost, availability, and is easy to design. The most often applied sorbent is the activated carbon. It has a very high efficiency however this sorbent is also very expensive. Therefore, the adsorbents produced from wastes are more and more often examined. That kind of sorbents are much cheaper. The wastes such as waste paper [8], kernel plum [9], rice hull [10], olive cake [11], corncob

[1] Faculty of Energy and Environmental Engineering, Silesian University of Technology, ul. S. Konarskiego 18, 44-100 Gliwice, Poland, phone +48 32 237 16 98, fax +48 32 237 10 47, email: barbara.pieczykolan@polsl.pl, rie4@polsl.pl

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[12], apricot stone [13], date stone [14] and coconut husk [15] may be used as sorbents. During the last few years the studies of application of sewage sludge as a sorbent are carrying out. The digested sewage sludge (both anaerobically and aerobically) can be used to produce so called "sludge-based activated carbon". The kind of application of the sewage sludge is also the new way of utilization of that waste. Nowadays the sewage sludge is mainly used as a fertilizer for soil amendment. However, the amount of the sites at which the sewage sludge can be applied is limited. Thus, the use of sewage sludge for production of activated carbon can be an alternative method of final management of that waste.

The isotherm of sorption is used in order to examine that process. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms. The ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium describes the sorption isotherm [16, 17].

There are several isotherm models available for analyzing experimental data and for describing the equilibrium of adsorption. The most commonly models used for examination of dye adsorption process are the Freundlich isotherm and Langmuir isotherm [18-21]. The Freundlich isotherm is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption. The theoretical Langmuir isotherm is often used to describe sorption of a solute from a liquid solution. The development of the Langmuir isotherm assumes monolayer adsorption on a homogenous surface.

The results of the studies of sorption process of dye Acid Yellow 36 are presented in that publication. During the tests the most favorable pH value and reaction time were established. Moreover as a result of the studies the isotherm of sorption was examined according two models: Freundlich and Langmuir.

Experimental

Material of sorbent

During the sorption process an anaerobically digested and dewatered sewage sludge (mixture of excess and raw sludge) was used. It was transformed into sludge-based activated carbon by chemical activation and next combustion in muffle furnace. The sludge was dried into constant mass in 105ºC and milled in laboratory grinder to a particle with a diameter of 0.5-1.0 mm. A hydrogen peroxide was used for chemical activation. Next the sludge was combusted in two stages in muffle furnace. First step was carried out in temperature of 300ºC and next a temperature was risen up to 600ºC. The combustion in both temperatures was carried out by 45 minutes.

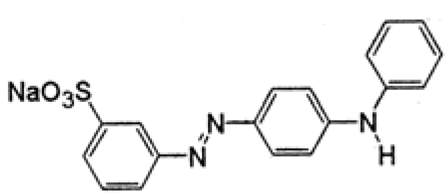

Fig. 1. The chemical structure of Acid Yellow 36 [22]

During the studies an anionic dye Acid Yellow 36 was used (Fig. 1). The working solution of the dye had a concentration equaled to 5 g/dm^3.

Sorption process

The tests of sorption of the dye Acid Yellow 36 was carried out in a static system. The sample of activated carbon (based on the sewage sludge) in a weight of 0.1 g was placed in a closed Erlenmeyer flasks with a capacity of 50 cm^3. During the study a working solution of Acid Yellow 36 witch concentration was equaled to 5 g/dm^3 was used. A suitable amount of working solution of the dye was added into distilled water to obtain required concentration of the Acid Yellow 36. The flasks were placed on a laboratory shaker to ensure constant stirring the contents. The concentration of the dye after sorption process was determined by photometric measurement on the basis of the calibration curve.

Impact of pH value

During the first stage of study the most favorable pH value of the process was chosen. The tests were conducted by using six different value of pH of the dye solutions: 2.5; 4.0; 5.5; 8.5. During that tests the solution of the dye was the same for each sample and was equaled to 70 mg/dm^3. The sorption process was conducted by one hour and after that time the concentration of Acid Yellow 36 was measured in each sample.

Contact time

In order to choose the most favorable sorption time the tests were carried out in different contact times. During that phase of study the concentration of the dye and the pH value of each samples were the same and were equaled to 70 mg/dm^3 and 2.5 respectively. The value of pH was chosen during the first stage of the study.

Sorption isotherm

In the last phase of the tests the isotherm of sorption of the dye on SAC (sludge-based activated carbon) was conducted. In order to obtain that goal, sorption process was carried out for different concentration of Acid Yellow 36. However the sorption time and value of pH were the same for each sample (chose during earlier steps of study).

Based on the results of sorption isotherm, two models of sorption process were analyzed. The Freundlich isotherm is expressed by the following empirical equation (1):

$$q_e = K_F \cdot C_e^n \tag{1}$$

where K_F is the Freundlich adsorption constant [dm^3/g] and n is a measure of the adsorption intensity. This equation is usually linearized in order to determine K_F and n constants. As a result of taking the logarithm of both sides of equation a linear form is obtained (Eq. (2)):

$$\log q_e = \log K_F + n \cdot \log C_e \tag{2}$$

The Langmuir isotherm is expressed by the following equation (3):

$$q_e = \frac{q_m \cdot C_e \cdot K_a}{1 + K_a \cdot C_e} \tag{3}$$

where C_e is the equilibrium concentration [mg/dm^3], q_e the amount adsorbed [mg/g], q_m is q_e for complete monolayer adsorption capacity [mg/g], and K_a is the equilibrium adsorption constant [dm^3/mg]. The linear forms of that equation are expressed as equations (4), (5) and (6):

$$\frac{C_e}{q_e} = \frac{1}{q_m} \cdot C_e + \frac{1}{K_a \cdot q_m} \tag{4}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_a \cdot q_m}\right) \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

$$q_e = q_m - \left(\frac{1}{K_a}\right) \cdot \frac{q_e}{C_e} \tag{6}$$

Results and discussion

Impact of pH value

The tests has shown, that the value of pH of solution during sorption process is very important. It can be observed that as the value of pH increased the effectiveness of sorption process decreased. The smallest concentration of the dye was obtained when the pH value was equaled to 2.5 (Fig. 2). An increase of pH value to 4.0 caused an increase of content of Acid Yellow 36 up to 69.8 mg/dm^3. In the case of other pH value the concentration of Acid Yellow 36 did not significantly change and were in the range of 69.6-69.9 mg/dm^3. This phenomenon could prove that the SAC (used during that research) has negative electric charge of its surface. The Acid Yellow is also an anionic dye. Therefore the use of such a low pH value (what is connected with large amount of hydrogen ions) caused the change of electric charge of SAC surface. The sorption of the dye was thus possible by obtaining a positive surface charge of the SAC.

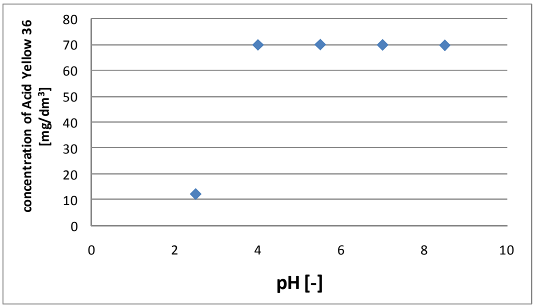

Fig. 2. The impact of pH value on efficiency of dye adsorption

Impact of contact time

Based on the results obtained during the first stage of the study, the impact of contact time of the dye solution with SAC on sorption efficiency was examined.

It could be observed (Fig. 3) that after 30 minutes of contact the SAC with the dye solution the effectiveness of dye sorption obtained the very high level and was equaled to 83.4%. Further increasing the contact time did not significantly improve the efficiency.

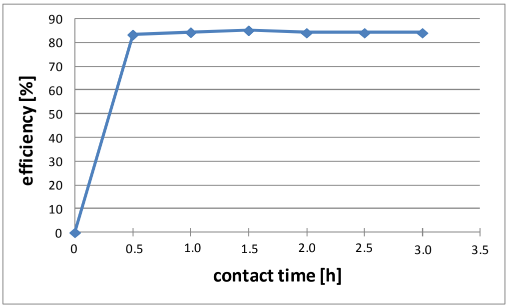

Fig. 3. The impact of contact time on color removal efficiency

Sorption isotherm

During the third stage of the study the isotherm of sorption was examined. Following process parameters were used at that tests: 2 g_{SAC}/dm^3, pH 2.5 and contact time equaled to 30 minutes. The concentration of the dye was in the range of 10-160 mg/dm^3.

Table 1

Parameters of sorption isotherms

Freundlich		Langmuir	
K_F [dm^3/g]	1.1071	K_a [dm^3/g]	–0.019
n [-]	1.4622	q_m [mg/g]	–133.3
R^2[-]	0.9314	R^2 [-]	0.9677

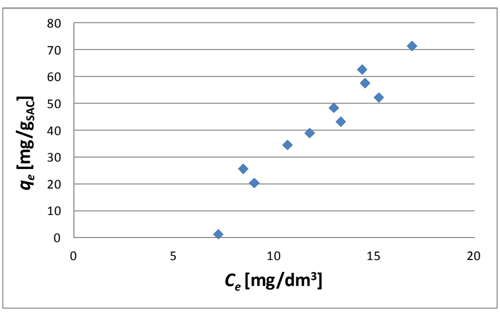

Fig. 4. Sorption isotherm

As a result of that tests the graph of isotherm was plotted (Fig. 4). Moreover, the models of Freundlich and Langmuir were examined. The graph of linearized forms of that models were plotted (Figs. 5a-d). In the case of all prepared graph, the correlation factors were calculated. In the case of Langmuir model the q_m (complete monolayer adsorption capacity [mg/g]), and K_a (the equilibrium adsorption [dm^3/g]) were established for that linearized form which graph obtained the highest correlation factor R^2. The correlation factors and other parameters for Freundlich and Langmuir isotherm are presented in Table 1.

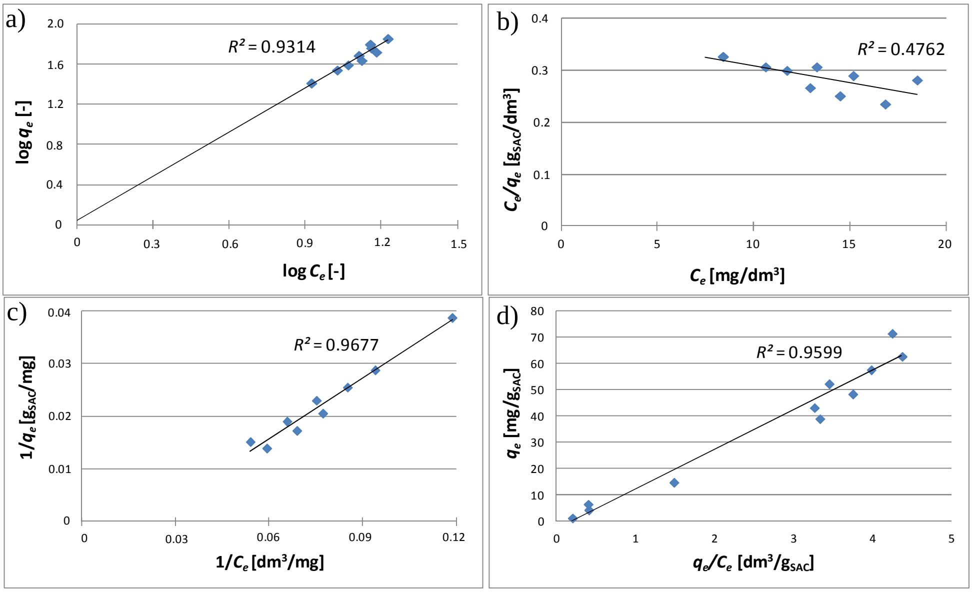

Fig. 5. The linearized forms of isotherm models: a) Freundlich, b) Langmuir according eq. (4), c) Langmuir according eq. (5), d) Langmuir according eq. (6)

Conclusions

1. The study showed that the sewage sludge may be a material from which an activated carbon can be produced. It was also proved that this kind of activated carbon may be used for removal the dye Acid Yellow 36 from its aqueous solution.
2. The most favorable pH value was equaled to 2.5. It can be concluded that the electric charge of SAC is negative. Therefore it was necessary to change the surface charge of the SAC by decreasing pH value.
3. Based on the results of the study it is observed that the adsorption of the dye on the SAC occurred in the first 30 minutes of the process.
4. The study showed that the highest value of correlation factor of linearized forms was obtained in the case of Langmuir model. However in that case the value of q_m was negative. Therefore, it can be assumed that more accurately in this case is the Freundlich model or other model which was not examined during that studies.

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SORPCJA BARWNIKA ACID YELLOW 36 ZA POMOCĄ WĘGLA AKTYWNEGO WYTWORZONEGO Z OSADU CZYNNEGO

Instytut Inżynierii Wody i Ścieków, Wydział Inżynierii Środowiska i Energetyki, Politechnika Śląska, Gliwice

Abstrakt: Przeprowadzono badania sorpcji barwnika Acid Yellow 36 z użyciem węgla aktywnego bazującego na osadzie ściekowym. W tym celu ustabilizowany beztlenowo i odwodniony osad czynny wysuszono w 105ºC do stałej masy. Następnie osad ten zmielono do ziaren o średnicy 0,5-1,0 mm i poddano chemicznej aktywacji za pomocą nadtlenku wodoru. Po tym procesie osad spalono w piecu muflowym w 600ºC, uzyskując w ten sposób pylisty węgiel aktywny bazujący na osadzie czynnym (tzw. SAC - czyli „sludge-based activated carbon”). Dla tak spreparowanego węgla aktywnego przeprowadzono badania procesu sorpcji statycznej względem barwnika Acid Yellow 36. Na podstawie przeprowadzonych eksperymentów stwierdzono, że najkorzystniejsza wartość pH wynosi 2,5, a czas kontaktu jest równy 30 minut. Natomiast bazując na graficznych formach zlinearyzowanych modelów sorpcji według Langmuira i Freundlicha, stwierdzono, że największą wartość współczynnika korelacji odnotowano w przypadku zlinearyzowanej formy równania Langmuira. Jednakże w tym przypadku uzyskano ujemne wartości stałych izotermy, dlatego można przypuszczać, że jednak bardziej prawidłowy jest model Freundlicha lub inny rodzaj izotermy, który nie był analizowany w toku tych badań.

Słowa kluczowe: osad czynny, węgiel aktywny, barwniki, izoterma sorpcji, kinetyka sorpcji, izoterma Fruendlicha, izoterma Langmuira