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Metheylene Blue Adsorption and Preparation Silver Bound to Activated Carbon with Sol-Gel Methods

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Abstract

This study examines the characterization and adsorption features of silver that was added to oxygen containing activated carbons using the sol-gel method. The surface area of the silver coated activated carbon (AC/Ag) Nano-composites, which were prepared using the sol-gel method, was measured with the Braunauer-Emmett-Teller surface area calculation method according to N_2 adsorption at 77 K. The microstructure and surface morphologies of the AC/Ag Nano-composite samples were examined with the use of Scanning Electron Microscope. Methylene Blue removal was performed with AC/Ag-1 with a highest surface area of 658.488 m^2/g, and the Qmax value was calculated as 416. 66 mg/g.
Keywords: Wild chestnut, silver, sol-gel, activated carbon, adsorption, desorption

1. INTRODUCTION

Environmental deterioriation has recently been undergone with the advent of technology-oriented advancements. The soil and water pollutants may appear on the ground and deeper layers of earth due to the contributing factors such as rapid industrial expansion in association with growing population worldwide and even in domestic lands, and unawareness of chemicals used in agricultural and healthcare sectors. It should be remembered that the water pollution in particular has much catastrophic effects on our biologies especially when waste waters become non-clean or even uncleanable drinking waters. Keeping the vital elements secured from these beasts means lots of money and labor to have to be withdrawn from the productive economic actions and transferred into the protecting and cleaning issues of secondary importance. The adsorption method is one out of myriad ways of recovering from this natural disease, which is effective in cleaning air and water from detrimental substances [1]. The material that has been for a long time used as adsorbent is the activated carbon (AC) preferable in this technique. This is currently produced from a substance mostly constituted by carbon atoms active in the soil pollutants. Production of clean water is made through distillation and purification of waste water using ACs. A carbon atom has an interior part and too much porous structure and however cannot be formulated or analyzed chemically [2]. Interestingly, there are three potential ways to get AC: (1) the chemical way, (2) the physical way, and (3) both in combination. Raw materials are carbonized and coal produced and heat-treated. The processing way is how the carbons in coal are physically activated at an optimum temperature through oxidization by gas [3]. Chemical operation can be performed using chemicals such as NaOH, $ZnCl_2$, H_3PO_4, and KOH together with carbonization [4]. The activated carbons produced in these ways are very popular in cleaning water by filtrating or distillating [5].

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Having both chemical and biochemical potentials, for example, silver-coated ACs are appropriate substances to have pure water [6]. Lately, various studies on silve nano materials (AgNPs) have been conducted in the fields of medicine, paint, textile etc. because of their special characteristics [7-9]. Photochemical synthesis [10], laser melting [11], wet chemical synthesis [12], sol gel [13] or any other methods are used for synthesis of AgNPs. This reaction is performed through Ag0 reduction and ligand usage along with both reduction and reservation of character solutions following decomposition (Ag^{+1}) in a proper solution by chemical synthesis.
The activated carbons that were produced through the sol-gel method in the previous study and in this study were coated with silver substances which were then characterized to analyze the features of the adsorption process.

2. MATERIALS AND METHODS

Materials

$AgNO_3$ (Merck), HNO_3 (Merck) (Trisodium citrate) Na_3Ct (Merck), Dimethylaminoethanol (DMAE) was used during the silver while binding the silver. Methylene Blue (MB). The obtained activated carbon samples were washed with ethanol (Merck). A Precisa XB 220A precision scale was used to measure the amounts in the experiments, while the mixing processes were handled with Wisestir MSH-20A and IKA RCT Classic magnetic mixers. All chemicals used are of analytical grade. Ultra-pure water produced by the Millipore Milli Q-system was used in these experiments.

Methods

Activated carbon which was produced and characteristics were determined previously was used in the study [14]. The activated carbons were first oxidized with 69% HNO_3. The obtained AC (1g) was impregnated in a 50 mL $AgNO_3$ solution and stirred for 1 hour at room temperature. The activated carbons coated with Ag^+ ions were then filtered. A 50 mL trisodium citrate (Na_3Ct) solution was added into the AC/Ag^{+1} composite. Then, a 1mL dimethyl ethanolamine (DMEA) solution was added drop wise into the mixture, and the reaction system was stirred for 3 hours at 90 °C. After the solid material was filtered and washed with distilled water, it was dried in the oven for 12 hours at 70° C [8]. As a result, AC/Ag Nano-composite products were obtained. The preparation conditions of the AC/Ag Nano-composites are identified in Table 1.

Table 1. Preparation parameters of AC/Ag nano-composites

Sample	$AgNO_{3(g)}$	Na_3Ct (g)	DMEA (g)
AC/Ag-1	0.5	0.75	0.03
AC/Ag-2	1	1.5	0.06
AC/Ag-3	2	3	0.12
AC/Ag-4	4	4.5	0.18

Devices

Scanning Electron Microscope (SEM) images of the materials were taken with a Scanning Electron Microscope Jeol JSM-6060L. Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed with SHIMADZU IR Prestige 21, and MB amounts were conducted with a UV HITACHI U-2900 Spectrophotometer. The Braunauer-Emmett-Teller (BET) surface area of the obtained products was handled in Bilecik Seyh Edebali University with a MICROMERITIC ASAP 2020. The BET surface area, and pore size were identified by using N2 adsorption data with an analyzer (Gemini Model 2380).

The qualitative structure analysis of the samples was investigated between the positions with 2θ angles of 10-90o by using Rigaku model XRD instrument. An ICP-OES Spectro Arcos spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) was used for determination of silver concentration. The operating parameters of the ICP-OES were set as recommended by the manufacturer.

Adsorption Work

Methylene Blue (MB) was chosen in this study due to its wide application and known strong adsorption onto solids This value is mostly used for the determination of the surface area of pores over 15 A. This shows the value of the adsorbed MB molecules in mg and identifies the adsorption capacity of bigger molecular structures of activated carbon [14]. MB stock solution was prepared by dissolving an accurat amount of MB

in distilled water to achieve a concentration of 1000 mg L−1, and subsequently diluted to the required concentrations. The methylene blue adsorption was made using the mixture of 0.1g AC and 100 mL MB solution blended at the concentration of 100 mg/L for one hour. For the measurement, the MB adsorption UV spectrometry of 664 nm was used. The below equation was used to calculate the MB quantity adsorped from the water solution.

$$qe = \frac{(Co - Ce)}{m} xV$$

Where Co and Ce are the initial and equilibrium MB concentration in mg/L respectively, m is the mass of adsorbent (g) and V is the volume of solution (L).

The removal (%) of MB was calculated using the following equation:

Dye removal (%) $= \frac{(Co-Ce)}{Co} x100$

All adsorption results were reported as the average values for three times experiments.

Desorption Work

AC/Ag covered samples were incinerated at 550 ºC for 16 hours. The samples were then dissolved in 50 mL 10% HNO3. After the samples were dissolved, the solution was washed and filtered with the blue filter paper. ICP-OES (Inductively coupled plasma - optical emission spectrometry) was the method to specify the silver ions (Ag quantities) present in each of the filtrated but dried sample solutions. Results were given in the table 2 and table 3.

3. SONUÇLAR VE TARTIŞMA (CONCLUSIONS AND DISCUSSION)

Properties of AC/Ag1-AC/Ag-4 nano composites

Characterization

The AC/Ag-1-AC/Ag-4 structures were characterized by their silver particle size. The dispersion and accidence of the nanoparticles have been characterized using FT-IR.

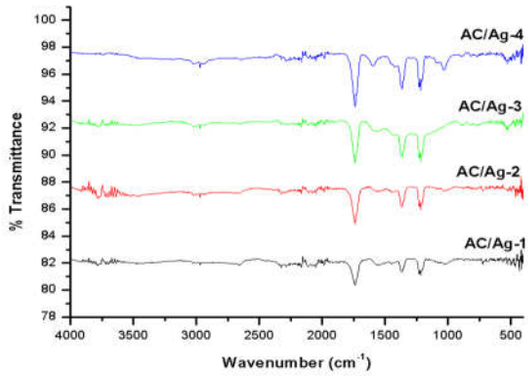

Figure 1. FTIR spectrums of AC/Ag-1-AC/Ag-4 nano composites

On FTIR spectrum the maximum level displayed vibration tension of C=O around 1739 cm^{-1} and C-H at 2971 cm^{-1} in AC/Ag-1 to AC/Ag-4 composites as presented in Fig. 1. The peak around 1739 cm^{-1} showed C=O vibration tension. The adsorbent differences between 1366 and 1217 cm^{-1} frequency were caused by C-H bond bendings and C-O bond tensions. The peak in 1029 cm^{-1} refers to alcohol groups. Similar results are seen in the literature [14, 16].

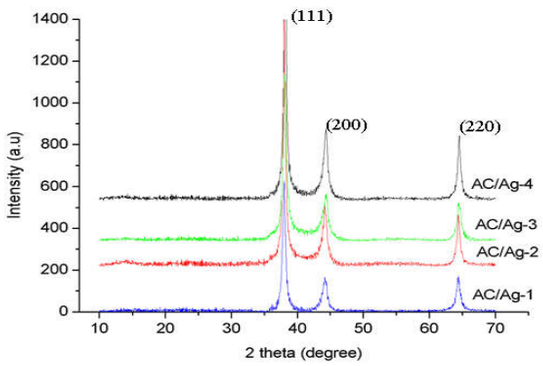

Figure 2. XRD patterns of AC/Ag-1-AC/Ag-4 nano composites

When the comparative XRD spectrums of AC/Ag-1-AC/Ag-4 in Figure 2 were examined, 2ɵ reflection peaks that support the existence of silver were showed at 38.039º, 44.180º, 64.360º. the index values were demonstrated silver level as (111), (200), (220) respectively [17]. The intensity was increased with the silver addition and activated carbons were passed to crystal structure from amorphous structure. It can be told metallic silver was existed in surface centered cubic structure. It was seen that XRD diffracted patterns that belong to AC/Ag mixtures; AgNO3 in the environment was in the structure as impurity.

By means of their enormous surfaces, the activated carbons best fit to hold metal nanoparticles. To evaluate the influence of Ag particles on the microporous structures of AC, the specific surface area (SBET) and pore volume of AC/Ag-1-AC/Ag-4 were determined. The results are listed in Table 2.

Table 2.BET parameters of AC/Ag-1-Ag-4 Nano-composites

Propreties	AC/Ag-1	AC/Ag-2	AC/Ag-3	AC/Ag-4
BET surface area (m^2 g^{-1})	658.488	540.837	386.360	205.051
t-Plot Micropore Area (m^2 g^{-1})	303.988	300.050	293.874	146.811
Average pore diameter (A)	30.644	30.487	28.978	27.383
pore volume (cm^3/g	0.091	0.0611	0.039	0.049
Silver content (wt%)	14.012	27.568	67.547	83.771

The silver ions coated on the activated carbon surface are reduced to metallic silver. [18]. As the amount of silver increases due to the direct trapping of silver particles in the pores, the BET surface area, total pore volume and average pore diameter of the AC/Ag nanoparticles decrease. A little amount of energy can help oxygen strongly attract silver toward itself because silver is extremely closer to the oxygen and the latter is superior to silver [19]. For this reason, the oxygen atoms can easily penetrate into the crystal cage and fill the octahedral void of silver which forms the nucleus for the silver crystals [20, 21].

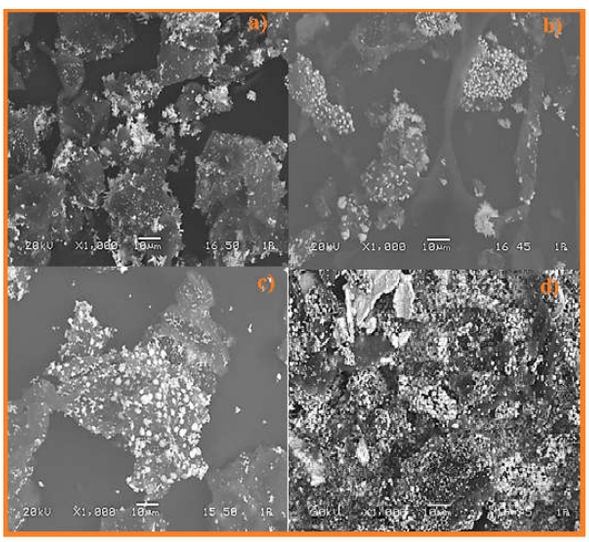

Figure. 3. SEM image of AC/Ag-1 and Ag/AC-4 nanosamples

SEM images display the morphological data of surface area as well as type and size of particles, and EDX analysis of elements. On the activated carbons are covering more silver in quantities, and the silver nanoparticles exhibit the characteristic of homogenous distribution over the AC surface. However, as seen in Figure 3, silver amounts varied between 200 and 400 nanometers.

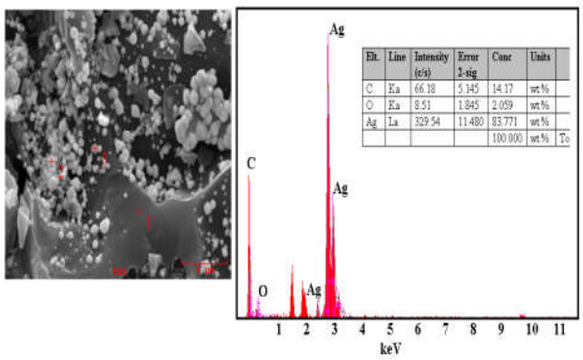

Figure 4.EDS analysis of the AC/Ag-4 sample

The result of the EDS analysis of the AC/Ag-4 sample is identified in Figure 4. For AC/Ag-4 sample, EDS analysis provides the recognition of the peak level of silver amount. The silver particles appear to be nanosized, in the range of<1.

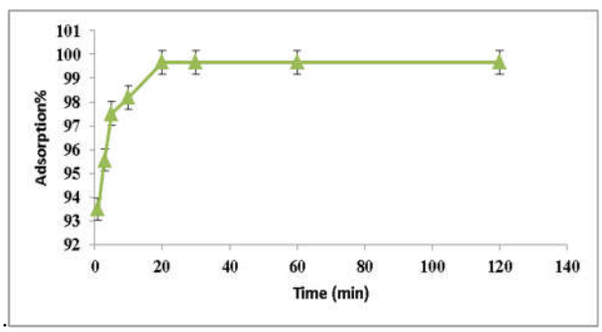

Figure. 5. The effect of mixing time on adsorption of MB (MB concentration: 100 mg/L, temperature: 298 K).

The adsorption process was performed by keeping all variables constant and taking samples in determined periods. Maximum dyestuff adsorption was observed within 30 minutes after the experiment started. The contact time required to reach equililibrium was found to be 60 minutes.

Adsorption studies

0.02 g of adsorbent was dispersed in solution by the agitation of the solution at 600 rpm, at room temperature, and at optimum pH 7. Langmuir and Freundlich isotherms were used for the calculation

of the adsorption studies. The Langmuir adsorption isotherm is shown below:

$$\frac{1}{q} = KL/qmax(\frac{1}{Ce}) + 1/qmax$$

Qmax = maximum adsorption capacity (mg/g)
Ce = liquid phase dyestuff concentration balanced with adsorbent (mg/L)
KL = Langmuir adsorption constant (mg/L)

In the line graph, the vertical axis is of 1/qe and the horizontal axis of 1/Ce, and the slope displays l/qmax and K/qmax values when transferred [22].

The Freundlich adsorption isotherm is shown below:

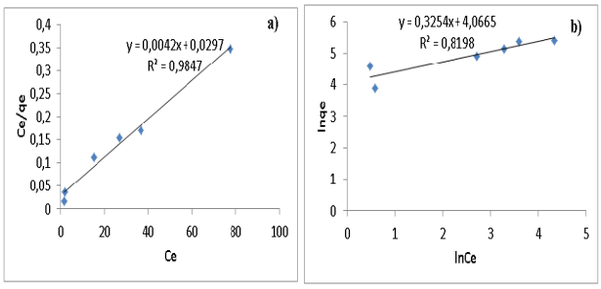

Figure. 6. AC/Ag-4 a) Langmiur and b) Freundlich Isotherms

Freundlich and Langmuir isotherm parameters were found when the experimental parameters at different concentrations were examined. It can be concluded from the studies that there is positive strong correlation between adsorption capacity and concentration amount. In the Freundlich isotherm equation, k represents the adsorption capacity, and n, a constant while in the Langmuir model Qmax is the adsorption capacity, and KL, a constant of energy need for adsorption. [24].

Table 3. Adsorption isotherms parameters of MB onto AC/Ag-4.

Sample	Langmuir Isotherms			Freundlich Isotherms		
	Qmax (mg g^{-1})	KL ×10 (L mg^{-1})	R^2	KF (mg g-1)	n	R^2
AC/Ag-4	416.66	0.028	0.87	1.091	1.517	0.97

The Table 3 shows that the AC/Ag-4 have highest adsorption capacity and shortest time to reach adsorption equilibrium compared with most of previous reports.

Table 4.Previous representative reports of adsorbents in application of MB removal.

Adsorbent	Amount of Adsorbent (g)	Initial (MB) concentration (mg/L)	Adsorption capacity (mg/g)	References
AgCl-NRs-AC	0.015	25	227.27	[25]
Ag NPs-AC	0.02	5	34.5	[26]
Ag/AC	0.2	500	240	[27]
Mn_2O_3/MCM-41	1	50	50	[28]
AgNP-CMSs	0.12	30	250	[29]
AC/Ag-4	0.2	100	416.66	This study

Desorption and recycling efficiency

Desorption studies were performed with water, 0.1 M HCl, 0.1 M NH3 and 0.1 M NaOH. AC/Ag-4 (100 mg/100 mL) saturated with 100 mg/L of MB was placed in different desorption media and was constantly stirred on a rotatory shaker at 100 rpm for one hour. The adsorbent was separated and washed with distilled water.

93.4% of MB was desorbed in 60 min using HCl as a desorption medium (Figure 7.).

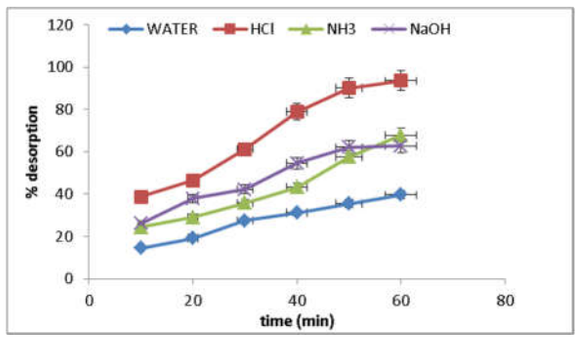

Figure. 7. Desorption studies of MB dye

In order to evaluate the possibility of regeneration and reuse of the AC/Ag-4 adsorbent, desorption experiments have been performed.

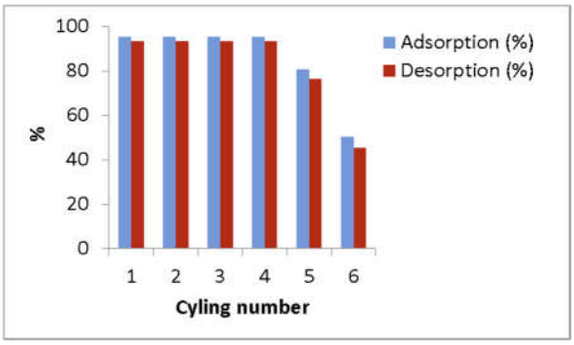

Figure 8. Recycling performance of the prepared AC/Ag-4 nanocomposites for MB removal (temperature: 298 K, adsorbent dosage: 0.1 g/100 mL), agitation: 120 rpm, contact time: 60 min, pH: 7).

Recycling efficiency of AC/Ag-4 was investigated for the removal of MB. After six cycles, the adsorption efficiency of AC/Ag-4 was reduced to 45% from 93.4% (Fig. 7). After every cycle, HCl was used as a desorption medium to remove adsorbed MB ions from the AC/Ag-4 surface.

SONUÇLAR (CONCLUSION)

In this study, the sol-gel method proved itself as an effective way to sythesize silver nanoparticles to cover the activate carbons. XRD, SEM and EDS were applied to characterize the adsorption process. The maximum level of AC/Ag-1 nano composites was determined as 416.66 mg/g by means of analyzing the adsorption. Langmuir and Freundlich techniques provided isotherms captured by observing various heat levels during MM adsorption. From the Langmuir model, higher levels of correlation coefficients in the adsorbents were an expected result because the surface was wider and homogenous. Therefore, AC-Ag composites can be preferable to remove dye thanks to the advantages of cost, efficiency and environment.

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