J. Water Environ. Nanotechnol., 7(1): 44-54 Winter 2022

ORIGINAL RESEARCH PAPER

Synthesis and characterization of modified resorcinol formaldehyde aerogel by graphene/m-phenylenediamine as a novel adsorbent to remove Tetracycline Antibiotics from Wastewater

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Received: 2021-10-22 Accepted: 2021-11-27 Published: 2022-02-01

ABSTRACT

Recently, there has been growing concern about the presence of pharmaceutical compounds and particularly antibiotics as emerging contaminants. This study employed high specific surface area organic aerogels to remove Tetracycline antibiotics. For this purpose, resorcinol formaldehyde aerogel (RF) was synthesized via the sol-gel process and dried under ambient drying conditions. The synthesized RF aerogel was modified by incorporating 1 wt.% graphene with 1 wt.% m-phenylenediamine during the synthesis process to prepare RF-G1/PmPDA1. Eventually, the performance of the synthesized samples as adsorbents was evaluated under various parameters such as the effects of pH values (2-12), adsorbent dose (4-10 mg), and adsorbent with antibiotics contact time (3-24 h). FTIR, FESEM, BET, CHN, and EDS tests were conducted to characterize the samples. Afterward, the adsorption rate of Tetracycline antibiotics was measured using UV-Vis. The BET test results revealed that the modification of the RF aerogel sample also increased the specific surface area from 96 to 308 m^2/g. The results also discovered that the removal rate of Tetracycline antibiotics for the RF aerogel and RF-G1/PmPDA1 was obtained to be 65.2% and 93.3% at optimal pH of 4 and 4, respectively.

Keywords: *Aerogel, Adsorbent, Antibiotic, Tetracycline, Modification.*

How to cite this article

Behzadi A., Yazdanbakhsh A. Synthesis and characterization of modified resorcinol formaldehyde aerogel by graphene/m-phenylenediamine as a novel adsorbent to remove Tetracycline Antibiotics from Wastewater. J. Water Environ. Nanotechnol., 2022; 7(1): 44-54.

DOI: 10.22090/jwent.2022.01.004

INTRODUCTION

The presence of antibiotics in drinking water can be a factor in increasing these compounds in the body. Antibiotics can reach the body tissues and cause different reactions. No thorough information is attained regarding the possible effect of small amounts or low concentrations of antibiotics on the human body. Nevertheless, even low concentrations may act as antibodies to bacteria and make the body resistant to the antibiotics used to treat bacterial diseases, which is a serious challenge for patients. Low concentrations of antibiotics needed to treat diseases play an important role in bacterial resistance, even being passed on to bacterial genetics. Studies demonstrate that the chronic effects of antibiotics are beyond their acute effects [1-3] Antibiotics can have an impact on the colony of bacteria in the sewer system. In the presence of antibiotics in wastewater treatment systems as well, the activity of bacteria is inhibited, which can seriously disrupt the decomposition of organic matter and the treatment process [4, 5]. Antibiotics not removed from the wastewater through treatment systems can enter the surface water sources and influence various food chain organisms. Algae, being very sensitive to diverse antibiotic types, are the basis of the food chain, and a fraction even in their amounts can impact the balance of the food chain. The concentration of

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Table 1. The properties of RF aerogel [18,19]

Property	Range
Density (g/cm^3)	0.2-1
Surface Area (m^2/g)	200-800
Average pore size (nm)	10-20

residual (untreated) antibiotics in water is observed to be very low (in nanograms or micrograms per liter). Nevertheless, their accumulation in poultry, livestock, and plants is considered a disease-cause in humans and animals [6, 7].

Pharmaceutical compounds are transported to aquatic environments through various sources such as the pharmaceutical industry, hospital effluents, and the excretion of humans and animals. The spread of antibiotic-resistant bacteria has increased in recent years. Many researchers believe that the indiscriminate use of antibiotics is the result of its increase. However, there is no possibility of using antibiotics; the health of the community depends on it. Therefore, various efforts and studies are being performed to find a proper way to remove them from water sources [8, 9]. In this study, performance removal of Tetracycline antibiotics (TCs), which are among the most widely used and common Tetracycline antibiotics, was investigated using graphene/m-phenylenediamine-modified resorcinol formaldehyde aerogel. Human and animal health care are the field of these widely-used antibiotics. They are employed to treat various bacterial infections of the skin, intestines, respiratory tract, urinary tract, genitals, lymph nodes, and other body systems; they are known as all-purpose antibiotics. The structure of these medicines consists of four aromatic rings with three different substitutions [10, 11].

Aerogels are low-density open-cell porous materials with large void space (above 98% porosity). They have unique properties such as high specific surface area and low thermal conductivity, making them suitable for special applications. Organic precursors producing strong covalently bonded (C-C) organic polymers have made it possible to synthesize a new class of integrated aerogels. Resorcinol formaldehyde (RF) aerogel observed among the most popular organic aerogels is first synthesized from condensation polymerization of resorcinol and formaldehyde at appropriate molar ratios in an aqueous medium using a catalyst (usually alkaline and in some cases acidic). The solution is then heated in a sealed container to a set temperature for a period to form a stable (cross-linked) wet gel. Wet gels are dried through supercritical fluid or other drying methods such as freeze and ambient drying. Resorcinol is highly reactive with three active sites (ring aromatics in positions 4, 2, and 6) and can react with formaldehyde at low temperatures. It leads to the formation of methylene bonds attached to two resorcinol molecules. The condensation polymerization mechanism of organic aerogel (RF) production is very different from the conventional synthesis mechanisms of mineral aerogel. However, the physicochemical processes resulting in wet RF gels are very similar to those in mineral gels such as silica and titanium [12-17]. The properties of RF aerogels are illustrated in Table 1

High energy consumption, cost-effectiveness, and the impossibility of mass production of aerogels are the limitations of supercritical drying; an ambient drying method is proposed to eliminate these shortcomings. Frick et al. were the first to introduce the ambient drying method of RF aerogel [20]. They observed a constant molar ratio of resorcinol to water (R/W), a constant weight ratio of resorcinol to formaldehyde (R/F), and a variable ratio of resorcinol to catalyst (R/C) result in gels that are dried under ambient conditions. The researchers found that even if the R/C ratio was above 1000, aerogels could be dried under these conditions. Dried aerogels in ambient conditions usually have a higher density. The ambient drying method is performed by changing the solvent with low surface tension and modifying the surface of wet gels. In this method, no high pressure is required throughout the drying process due to the use of organic solvents with low surface tension instead of supercritical fluids. Therefore, ambient drying does not require any autoclave or extraction, such as carbon dioxide [21]. RF aerogel does not necessitate pyrolysis to remove antibiotics and can be modified while synthesizing, compared to carbon aerogel. It is also synthesized at low temperatures and does not require high temperature and energy consumption.

RF Aerogels synthesis by the Pekala with alkaline catalyst is extensively studied for the effect of process parameters such as the concentration

of monomers, catalysts, and the solution's pH. Structure and properties such as density, surface area, and particle size are affected by these variables. Low density, high porosity (above 80%), high surface area, and proper pore size (micro, meso, and macro according to IUPAC standard) are included in RF aerogels synthesized by this method [22, 23].

The effect of the R/C ratio on the final structure of the aerogel has been a matter of focus. In the aquatic environment, this ratio typically varies from 50 to 1000. The formation of interconnected particles with large necks has been reported at low R/C ratios (approximately 50), while Cross-linked microspheres have been observed at high R/C ratios of about 1,500. Moreover, the final structure of the pores and the gelling time strongly depends on the pH of the solution, and gel formation occurs faster at low pH [24, 25].

In recent years, research into the use of aerogels to remove antibiotics from effluents has increased due to the special benefits and properties of aerogels. Unlike strategies such as reverse osmosis, membrane processes, and biological methods, aerogels do not destruction antibiotics but only move them from one phase to another phase. In the modification of aerogels, materials such as graphene with a very high specific surface area can increase the maximum removal percentage. M-Phenylenediamine worked as the amine-functionalized for RF aerogels to help further adsorption of antibiotics through the hydrogen bonding mechanism between the adsorbent and the adsorbate. Graphene, as a strong adsorbent, helps adsorb more antibiotics by creating mechanisms such as π-π stacking. The combination of the two mentioned substances was used as an RF aerogel modifier.

This study aims to improve the removal rate, increase the specific surface area, and functionalize the surface of RF aerogels to remove tetracycline antibiotics. Table 1 shows the chemical structure of tetracycline antibiotics. The carbon ring in tetracycline chemical structures and graphene hexagonal cells facilitates the π-π interaction between them; the π-cation bond most likely occurs among the amide groups in the tetracycline and the π-electron-enriched graphene regions. To this aim, first, mPDA was polymerized during synthesis, then synthesized functionalized using mPDA. Subsequently, the RF aerogels were modified during synthesis by the incorporation of 1 wt.% of graphene and 1 wt.% of m-phenylenediamine.

EXPERIMENTAL

Materials and Methods

In order to synthesize RF aerogel, condensation polymerization of resorcinol and formaldehyde monomers was used through the sol-gel process. Resorcinol is a white powder crystalline with the chemical formula $C_6H_4(OH)_2$. The presence of two hydroxyl groups of resorcinol causes a higher reactivity than formaldehyde and high ortho and para positions activity. In this research, 37 wt.% formaldehyde solution, produced by KBR India, was used and it contained 11 wt.% methanol as an inhibitor factor. Double distilled water has also been used as a solvent and sodium-hydrogen-carbonate ($NaHCO_3$) catalyst from DUKSAN, South Korea, for synthesizing the aerogels. Since catalysts have high activation energy, they should be utilized as a solution of 1 g of catalyst in 50 ml of distilled water to mix better [26]. To modify the RF aerogel, graphene/m-phenylenediamine was used with the chemical formula $C_6H_4(NH_4)_{2,}$ and it is a solid substance in the form of flakes and dark brown color.

Synthesis of RF Aerogel

To synthesize native RF aerogel (R/W=2, R/C=400), 6.25 g of resorcinol was first added to 21.8 g of double distilled water and stirred with a magnetic stirrer to completely dissolve the resorcinol solid particles in water. Afterward, 8.3 cc of formaldehyde was put in the RF solution and distilled water. Before adding the catalyst into the system, 0.015 g of sodium carbonate was dissolved in 0.755 ml of water for better mixing. Finally, the resulting solution was stirred with a magnetic stirrer for 15 minutes. In the next step, the solution was poured into a plastic container made of polypropylene and placed in the oven at the temperature of 80°C. After 48 hours of reaction, despite the gelling of the solution, there were some unreacted monomers in the system. In order to remove unreacted monomers, change the solvent in the gel, and reduce the pressure on the porous walls of the aerogels while ambient drying, a 4 wt.% hydrochloric acid solution was prepared, and then it was spread on the sample with a syringe to create a layer of the mentioned solution on the gel. The container was placed back in the oven at 100°C. After 24 hours, the gel was washed with acetone solution every 8 hours for one day (3 times a day).

The wet gel was placed in the oven at 100°C after the solvent replacement step, ambient drying was done, and native RF aerogel was obtained at the same temperature after 24 hours.

Synthesis of RF aerogel containing 1 wt.% graphene with 1 wt.% Poly-m-phenylenediamine

To synthesis RF aerogel containing 1 wt.% graphene with 1 wt.% Poly-m-phenylenediamine (RF-G1/PmPDA1) in (R/C=400, R/W=2), PmPDA uniform particles were synthesized at 25°C using ammonium persulfate (APS) as the oxidant. 0.38 g of mPDA was dissolved in 6.7 ml of distilled water and then stirred with a magnetic stirrer for 30 minutes to form a monomer solution. 1 ml of APS aqueous solution (molar ratio of oxidant/monomer=1) was added dropwise to the monomer solution for 20 minutes at one drop per second rate. The solution was stirred for more than 5 hours, filtration, and then washed with distilled water; 0.38 g of graphene was added to the homogeneous solution and stirred with a magnetic stirrer for 5 minutes. 6.25 g of resorcinol, 8.3 ml of 37% formaldehyde solution and 0.75 sodium-hydrogen-carbonate (diluted 1 cc sodium carbonate solution in water), 14.9 ml of double-distilled water, and graphene were added to the homogeneous solution of PmPDA. It was stirred with a magnetic stirrer for 15 minutes. Eventually, in order for the solution to turn into a gel, it was placed in an oven at 70°C, and the rest of the steps, such as the synthesis of native resorcinol formaldehyde aerogel, were performed. Fig. 1 illustrates a schematic of the RF-G1/PmPDA1 synthesis process.

Adsorption Tests

All antibiotic adsorption tests are performed intermittently in a 100 ml Erlenmeyer flask (covered with aluminum foil to prevent optical degradation of antibiotics) at 25°C using a magnetic stirrer at 140 rpm. The sample containers contained 8 mg of adsorbent, including native and modified aerogel and 40 mg/L of Tetracycline antibiotic. The pH of the samples could be adjusted by 0.1 M NaOH or 0.1 M HCl using a pH meter. The adsorbent solution was in contact with the antibiotic for 24 hours at 25°C. Finally, the supernatant was suspended from the solid phase and considered the residual concentration of antibiotics, determined by UV-Vis spectroscopy.

Removal percentage (R%) and the amount of the adsorbed antibiotic (Q_e, $mg.g^{-1}$) were calculated using Equations. 1 and 2.

$$\%R = \left[\frac{C_0 - C_e}{C_0}\right] \times 100 \quad (1)$$

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

C_0 is the initial concentration of antibiotic ($mg.l^{-1}$), C_e is the equilibrium concentration of antibiotic ($mg.l^{-1}$) read by UV-Vis, m is the amount of adsorbent (mg), and V is the volume of solution (L).

Characterization

BET (Belsorp mini II, Japan) and BJH tests were employed to measure the specific surface area, size, and distribution of pores. Morphology of the samples was evaluated through FESEM (Mira 3-XMU) test. To investigate the functional groups and bonds in the structures, FTIR (Avatar, Germany) test was used in the range of 400 to 4000 cm^{-1} wave number. EDX-CHN test (FlashEA1112, Thermo Finnigan) was conducted to evaluate the elements and their distribution percentage on the surface of the samples. UV-Vis device (GBC, Australia) at a maximum wavelength of 357 nm was used to measure the adsorption of antibiotics by the synthesized samples.

RESULTS AND DISCUSSION

Characterization of Samples

FTIR analysis was done to evaluate the formation of functional groups and chemical bonds formed in native and modified aerogels. In

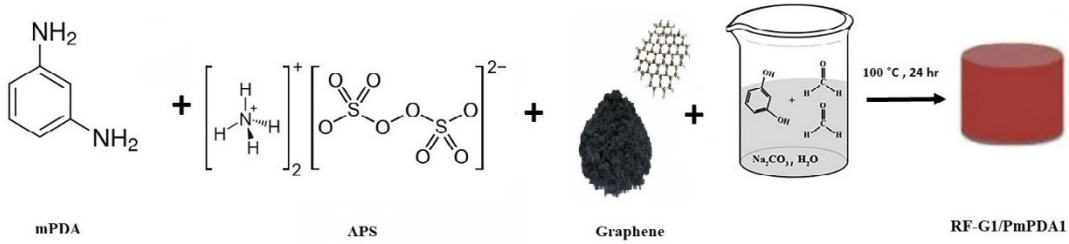

Fig. 1. Schematic of the synthesis process of RF-G1/PmPDA1 aerogel

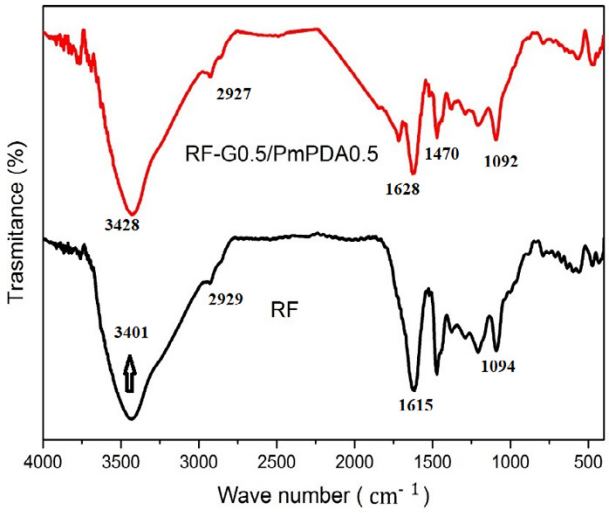

Fig. 2. FTIR spectra of RF and RF-G1/PmPDA1 aerogels

all samples of native and modified aerogels, the wide peak formed in the range of 3400-3430 cm^{-1} belongs to the OH group of the benzene ring [27]. Besides, in the range of 2860 cm^{-1} and 2920 cm^{-1} wavenumbers, the observed peaks were due to the symmetric tensile vibrations of CH_2, and hydroxyl groups, respectively [28]. The peak observed in the range of 1615 cm^{-1} wave number refers to the C=C group. The wavenumber around 1092 cm^{-1} was related to the methylene ether bridges between resorcinol [29]. The wavelength peak range 1216-1220 cm^{-1} confirms the formation of C-N tensile bonds of aliphatic amines in the RF-G1/PmPDA1 sample. The peak corresponding to the wavenumber 1723 cm^{-1} in the RF-G1/PmPDA1 sample also confirmed the NH tensile amide bond. In the modified sample, the peak formed at 1620 cm^{-1} refers to the quinoid rings, and the 1470 cm^{-1} peak refers to the CN bonds in the benzoid rings [12, 27]. The peak at wavelengths 3401 and 1615 cm^{-1} in the native aerogel sample shifted to wavelengths 3428 and 1628 cm^{-1} in the RF-G1/PmPDA1 aerogel, indicating a change in vibration frequency. Also, in RF-G1/PmPDA1 aerogel, the intensity of peaks at wavelengths 3428 and 1628 cm^{-1} has increased, which indicates an increase in the amount of OH and C=C functional groups. These functional groups are suitable for absorption, and with increasing their number, the removal of tetracycline antibiotics increases.

Fig. 2 illustrates the FTIR spectrum of the synthesized samples.

Fig. 3a-c indicates the FESEM image of a native RF aerogel in various magnifications (25K, 100K, and 200K). This figure confirms the existence of a three-dimensional porous structure and interconnected networks composed of many nanoparticles. The dimensions of the particles formed in the samples and the porosity created between them are in nanometers. The created structure is related to how the aerogel samples are synthesized; it also refers to parameters such as ratios of R/C, R/W, and R/F [19]. The network consists of small spherical particles connected. Therefore, the structure created is a cluster RF aerogel consisting of small spheres connected, and the interconnected microspheres are distributed almost uniformly on the aerogel matrix. Figs. 3d-f depicts the FESEM image of the RF-G1/PmPDA1 sample at various magnifications and the formation of graphene plates next to spherical particles.

Image J software based on the Gaussian model was used to determine the particle size. Each particle was measured in four directions; the particle size distribution histogram for the synthesized samples is indicated in Fig. 4. The particle size of the aerogel depends on the R/C ratio. Due to the selection of $NaHCO_3$ as an alkaline catalyst and the selection of R/C=400, according to 4a, the size was in the range of 30-100 nm and the average particle size was 52.4. The standard deviation of these values was also calculated to be 7.4.

According to Fig. 4b, the RF-G1/PmPDA1 structure is generally out of the cluster, and the particle size range, average particle size, and standard deviation of 10-45 nm, 18.5 nm, and 5.8 are obtained, respectively. The formed structure is denser and more compact, the spherical particles

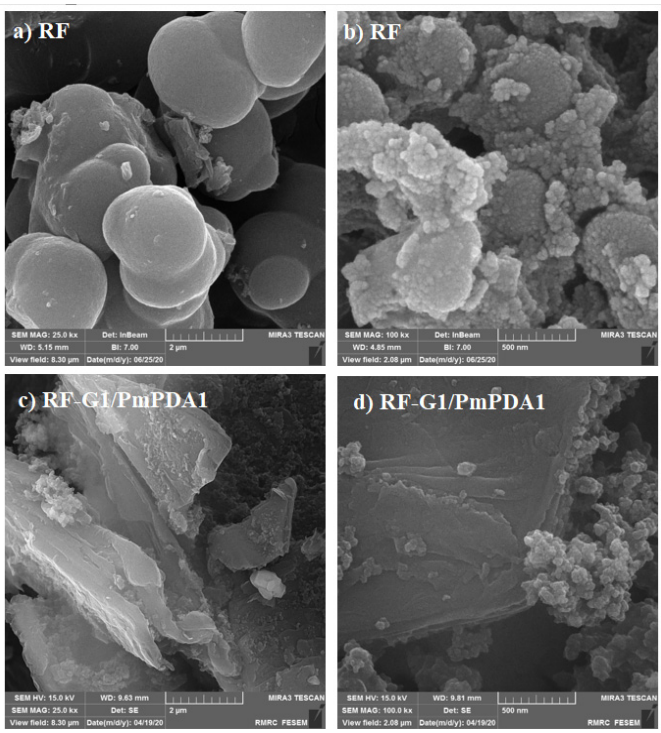

Fig. 3. The FESEM images of RF and RF-G1/PmPDA1 aerogels at a, c)25K and b, d)100K magnification

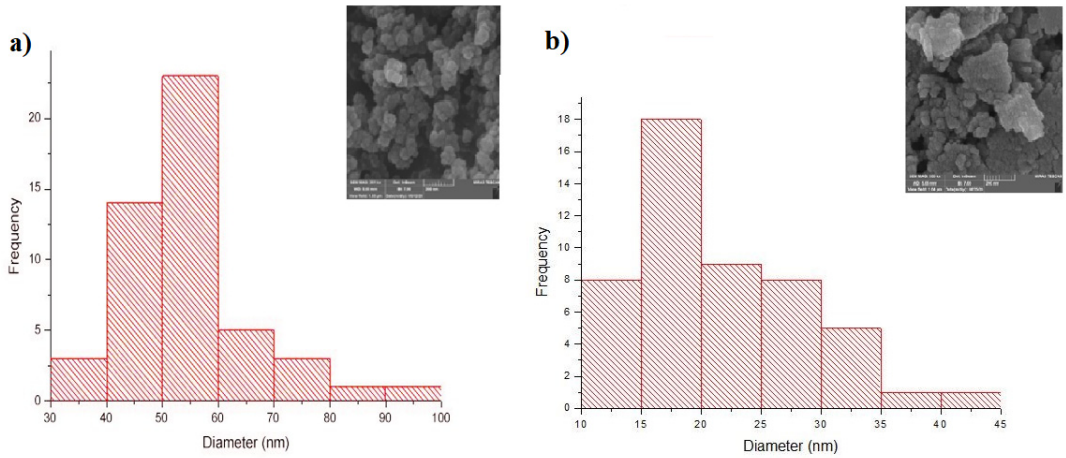

Fig. 4. The particle size distribution of a) RF, b) RF-G1/PmPDA1

are larger, and the particle size is smaller than the native aerogel based on the particle size distribution histogram. Spherical particles are joined together by smaller necks. The particle size distribution histogram results show that the modified sample has smaller particles, which increases the number of particles per gram of sample and consequently its specific surface area; it confirms the results of the BET test, which is examined below. Due to the nanometer particle size of antibiotics, meso, and macropores are suitable for removing Tetracycline antibiotics by filling pores mechanism.

Using EDS test for native RF aerogel sample, the weight ratio of C/O element is approximately 3. Therefore, this ratio should be equal to 3 in the CHN test while CHN for element C was measured to be 72 wt.% and element O was measured 24 wt.%. Accordingly, a combination of C, O, N, and H elements was obtained for native and modified RF aerogels via two EDS and CHN tests.

Table 2. The weight percentage of the present elements on the surface of RF and RF-G1/PmPDA1 aerogels

	C (%)	H (%)	N (%)	O (%)
RF	72	4	-	24
RF-G1/PmPDA1	60	6	4	30

Table 3. Surface area, pore size, and pore volume parameters for RF and RF-G1/PmPDA1 aerogels

Sample	Special surface area (m^2/g)	Porosity size (nm)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	V_{total} (cm^3/g)	S_{mes} (m^2/g)	S_{ext} (m^2/g)
RF	96	47	0.015	0.95	0.965	15	81
RF-G1/PmPDA1	308	3	0.07	0.13	0.2	133	175

One of the mechanisms in the adsorption of antibiotics by aerogels is forming a hydrogen bond between the aerogel and the antibiotic. Hydrogen bonding occurs between elements F, O, N with hydrogen. Among the synthesized samples, according to the weight percentage of the presented elements, the possibility of forming a hydrogen bond with the Tetracycline antibiotic is more than other samples in the RF-G1/PmPDA1 sample. Additionally, a high weight percentage of hydrogen increases the possibility of hydrogen bonding between antibiotics and aerogels since the Tetracycline antibiotic contains oxygen and nitrogen on its surface and can form a hydrogen bond with the hydrogen present on the native and modified RF aerogels. The results in Table 2 represent that the modification of aerogels improves the adsorption requirements of antibiotics, including the formation of hydrogen bonds. The formation of amide and hydroxyl groups on the surface of aerogels is confirmed according to the results of the FTIR test. Therefore, it is possible to have chemical reactions of amide groups on antibiotics and synthesized aerogels and the formation of hydrogen bonds between hydroxyl and amide groups between antibiotics and aerogels.

The BET method was used to measure the specific surface area of the samples, the effect of the parameters on the specific surface area, and the size of the pores. In addition, the BJH method was applied in distributing the size, diameter, and volume of the porosity. Then the volume of pores in micro and meso scales was calculated using the T-PLOT method. Table 3 indicates the information obtained from these tests. Generally, suppose the total volume of pores is reported in BET. In that case, this number will be the total volume of meso and micropores, and the volume of micropores is calculated using the T-plot diagram. Therefore, if the volume of pores is reported in this section, it is the same micro-pores covering the range below 2 nm.

The general properties of aerogels depend on two ratios: R/C (resorcinol/catalyst), and R/W ratio (resorcinol/water). The first one affects the density, specific surface area, and mechanical properties of aerogels. The latter plays a crucial role in pore size distribution and porosity percentage.

In this study, the R/C ratio is considered between 50 and 1000, and R/W=2 is constant in all samples. Therefore, native RF aerogel was produced in different R/C ratios. The synthesized sample with the highest specific surface area was considered the optimal R/C ratio, and the aerogels were modified at this R/C ratio.

Fig. 5 shows the adsorption-desorption diagrams of N_2 and the diameter distribution of aerogels. Native RF and modified aerogels adsorption isotherms were attributed to type IV adsorption isotherms according to IUPAC classification [12].

The adsorption-desorption diagram of the RF-G1/PmPDA1 sample based on the IUPAC classification in Fig. 5a indicates that the formed loop is related to the H_3 classification. According to this figure, mesopores are mainly layered in shape and are formed between layers of graphite, which is consistent with the results obtained through FESEM images. The information that the hysteresis loop gives about the geometry of the pores, which

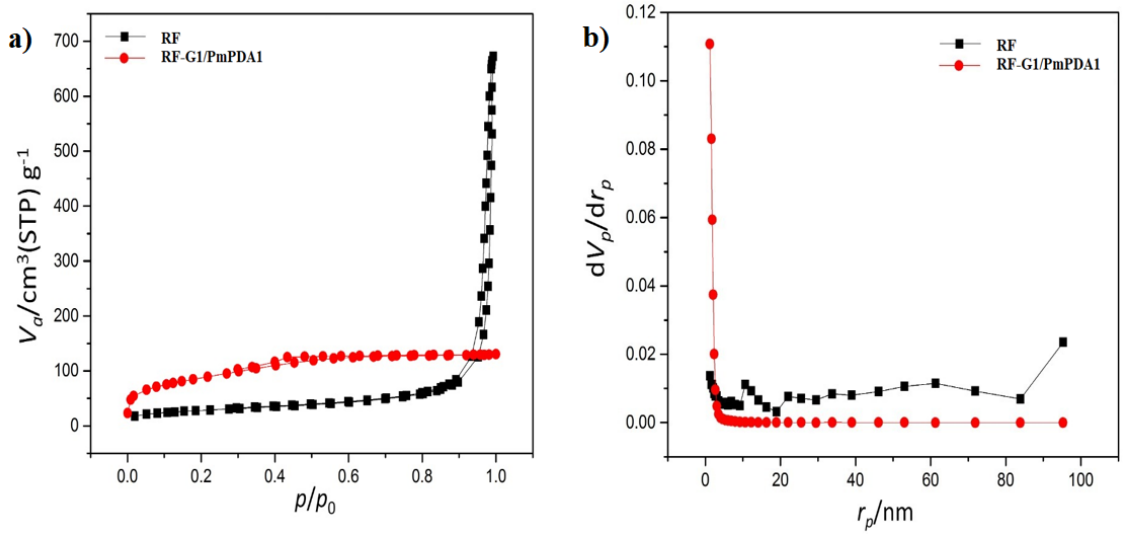

Fig. 5. a) absorption-desorption diagram of RF and RF-G1/PmPDA1 aerogels, b) The total volume of pores in different porosity sizes

according to the hysteresis loop, the pores in the RF-G1/PmPDA1 are cylindrical.

The pore size distribution in Fig. 5b illustrates that the pores are in the range of 1.21-100 nm, which indicates the formation of micro, meso, and macropores in the synthesized aerogels and the size distribution of the pores mainly occurs in the meso range. The specific surface area does not necessarily adsorb more antibiotics because it may be impossible for the sample to adsorb the antibiotics due to the unavailability of pores (close pore) and the low pore volume.

Adsorption mechanisms

The interaction between the Tetracycline antibiotic and RF-G1/PmPDA1 is also due to the π-π stacking. This type of interaction is of the non-covalent type, which includes the π system that is rich in electrons and can interact with one molecule or even another π system. In the case of aromatic-aromatic interactions, also called π stacking, this phenomenon results from the stack of two aromatic groups such as graphene and Tetracycline cyclic structures [30]. The molecular structure of the hexagonal ring is defined as π rings, which accelerate the adsorption on carbonaceous materials by increasing the number of antibiotic rings. The π-π stacking donor-acceptor electron interaction, the electrostatic interaction, and the π-cation interaction are usually considered as the main driving force of adsorption between Tetracycline antibiotics and graphene.

Graphene has electron conjugated π and many oxygen atoms in the form of hydroxyl, epoxy, and carboxyl groups. The Tetracycline ring structure and the modified aerogel surface can easily facilitate the stacking π-π interaction. In addition, by cation-induced polarization and electrostatic interaction, π-cation bonding occurs between amide groups and π-electron-enriched graphene regions. The adsorption capacity of the modified sample changes with changing Tetracycline charges, and when the Tetracycline antibiotic is present in the cationic species; it also remains unchanged when the antibiotic species is a zwitterion. It means that the effect of electrostatic interaction has a significant effect on the adsorption performance of Tetracycline antibiotics on RF-G1/PmPDA1. Mechanisms of strong adsorption interaction between Antibiotic and graphene in the modified sample include van der Waals forces (permanent induced dipole-bipolar forces and Landing scattering forces), the donor-acceptor of the π-π electron, and the π-cation bond between the given amine proton groups and the π graphene electrons.

The intensity of an adsorbent molecule's van der Waals forces is proportional to its contact surface and the specific van der Waals index for the adsorbent surface. The graphene surface is a carbon adsorbent with a very high van der Waals index, and Tetracycline molecules have a plane-shaped ring structure. Therefore, strong van der Waals forces probably occur between the Tetracycline molecules and the graphene surface

as the adsorbent. π-π stacking and van der Waals interactions are considered a kind of non-covalent physical adsorption. The adsorbed molecules of the Tetracycline must be oriented parallel to the graphene surface and form head-to-head complexes to maximize the van der Waals forces and the donor-acceptor stacking interactions of the π-π electrons. Nevertheless, since ring C (4) is hybrid-sp^3, the attached amino group can still bond effectively through graphene surface interaction via π-cation bonding without interfering with tail-to-tail geometry. In contrast, the protons of phenols, enols, and amide groups are aligned with the Tetracycline rings. Therefore, the formation of π-H bonds with the graphene surface is prohibited (the proton must also be perpendicular to the surface of the ring to form the π-H complex). A nitrogen atom has a single electron pair that can be effective by bonding to different types of antibiotics by sharing electron pairs and forming a complex with the Tetracycline antibiotic. Another route for antibiotic adsorption in a phenylamine-modified sample is ion exchange between antibiotic species and H^+ ions from the group $=N^+H^-$.

Antibiotic removal performance

Figs. 6a and 6b show the calibration curves of antibiotics at different concentrations in acidic and alkaline media. Figs. 6c and 6d also show the antibiotic absorption curves with RF and RF-G1 / PmPDA1 samples, respectively.

Table 4 illustrates the percentage of Tetracycline removal by RF and modified aerogels at different pH conditions.

The antibiotic charges of Tetracycline depend on the pH value and can exist as cationic, zwitterionic, and anionic species in acidic, neutral, and alkaline conditions [31]. At high pH, a negatively charged Tetracycline antibiotic species appears in the solution, which leads to electrostatic repulsion with

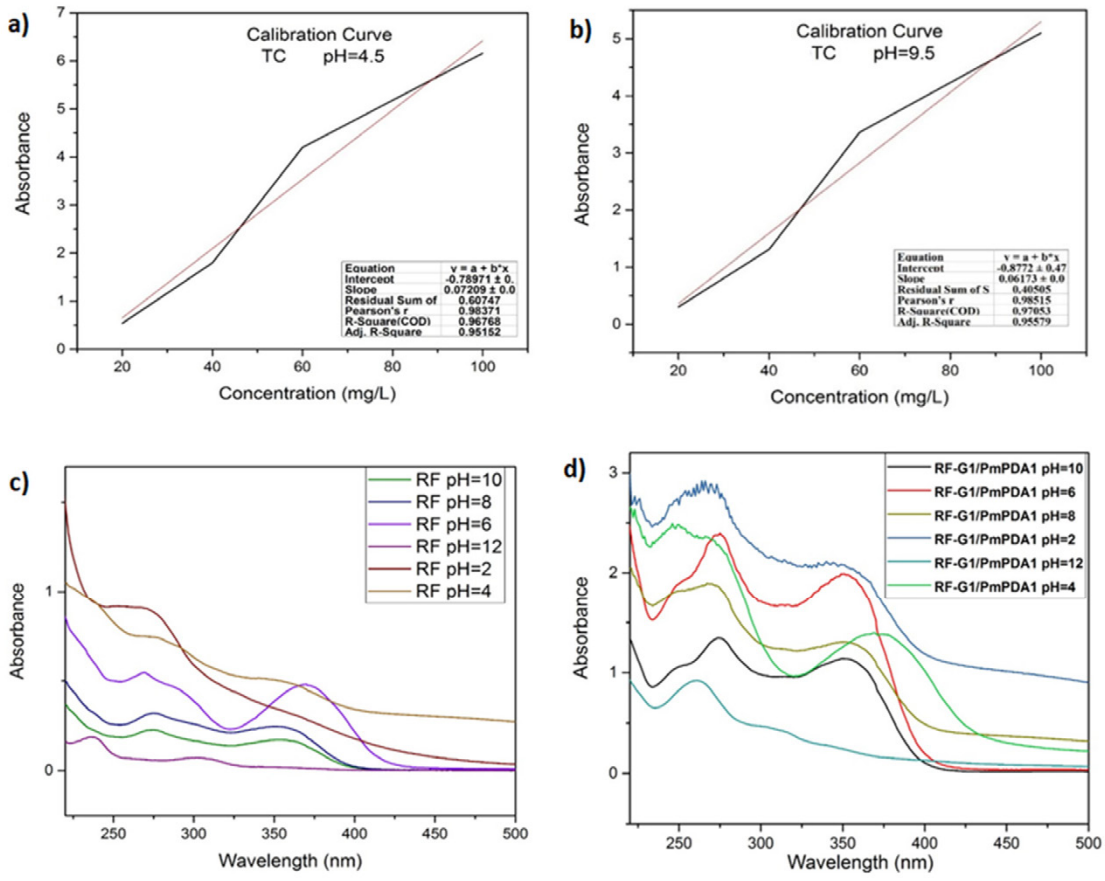

Fig. 6. a) Calibration curve in acidic media, b) Calibration curve in alkaline media, c) Absorption curve for RF samples, and d) Absorption curve for RF-G1/PmPDA1 samples

Table 4. The absorption amounts of the Tetracycline

Sample	pH	Tetracycline	
		Final concentration after absorption	R%
RF	2	17.30±1.2	65.75
	4	13.92±1.1	65.20
	6	15.06±0.8	62.35
	8	17.61±1.4	55.97
	10	33.45±2	16.37
	12	36.25±1.1	9.37
RF-G1/PmPDA1	2	3.74±0.6	90.65
	4	2.68±0.4	93.3
	6	9.55±0.5	76.12
	8	10.33±1.2	74.12
	10	11.74±1.7	70.65
	12	13.10±1	67.25

negative charges at the surface of the RF or modified aerogels, decreasing the amount of removal. In addition, double bonds (unsaturated bonds), conjugated structures, and hydroxyl groups in the RF-G1/PmPDA1 sample structure are also suitable for Tetracycline antibiotics' adsorption [32].

In the RF-G1/PmPDA1, the formation of the complex between the antibiotic and the modified aerogel surface, and the presence of NH_2 groups on the PmDA chain, leads to higher antibiotic adsorption, forming hydrogen bond and chemical reaction between antibiotic and modified aerogel.

As the pH increases, the cationic species decrease as well as the anionic and zwitterionic species of the tetracycline antibiotic increase. When the pH of the solution is in acidic condition, the number of $=N^+H^-$ groups decreases, and the number of neutral $=N^-$ groups increases on the surface of the particles, increasing the adsorption of Tetracycline in acidic conditions.

Generally, the percentage of antibiotic removal by RF and modified aerogels at acidic conditions increased with increasing pH and decreased at alkaline conditions due to repulsion of electrostatic interaction (Table 4). In the early days, the number of active sites on the adsorbent in solution is high, increasing the removal percentage of antibiotics. However, after 8 hours, due to the irreversibility of saturated active sites and adsorption of antibiotics by the adsorbent, the increased removal percentage of antibiotics was less severe. Furthermore, the number of active sites for adsorption increased due to increasing the amount of adsorbent and the removal of Tetracycline antibiotics. Eventually, it is found that with increasing the amount of adsorbent and the contact time of adsorbent and adsorbate, the removal rate of Tetracycline antibiotics increases.

CONCLUSION

In this study, an RF aerogel with a three-dimensional interconnected porous structure was synthesized to absorb the antibiotic Tetracycline. RF aerogels were effectively modified by graphene and m-phenylenediamine, which increased the adsorption of Tetracycline antibiotics. The aerogels were synthesized through the sol-gel process; the resulting wet gels were dried under ambient conditions. Characterization results indicated that amide groups were successfully formed on the surface of RF aerogel. Also, the presence of modifiers increased the specific surface area of RF aerogel, which led to better adsorb antibiotics by the modified samples. The highest removal percentages of Tetracycline antibiotics by RF and RF-G1/PmPDA1 aerogels were at optimal pH 4 and 4, respectively, with removal percentages of 65.2% and 93.3%. Possible mechanisms for removing Tetracycline antibiotics by modified samples include hydrogen bonding, pore filling, donor-acceptor π-π electron stacking, π-cation bonding, electrostatic interaction, and complex formation. It was also found that increasing the duration of contact of the adsorbent and adsorbate and increasing the amount of adsorbent increased the removal percentage of Tetracycline antibiotics.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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