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Synthesis of a Novel CuFe₂O₄@Schiff Base Magnetic Nanocomposite for the Removal of Cu(II) from Water Samples

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Traditional techniques for adding chelating agents to solids take time, energy, and materials. This study focuses on the preparation of a quick and easy solid-phase extraction approach using microwave-enforced green synthesis. $CuFe_2O_4$ magnetic nanoparticles (CFO-NPs) were modified chemically by bis(salicylaldehyde) phenylenediamine (BSAPhD) investigated for Cu(II) removal from aqueous solutions. The modification conditions (power and time) of the process are optimized. The performance of the resulting magnetic composite nanoparticles (BSAPhD@CFO-NPs) was compared with that of those prepared using a conventional reflux method (BSAPhD/reflux@CFO). BSAPhD@CFO-NPs was characterized using Fourier-transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM). All the data confirmed the success of the preparation of BSAPhD and modification for CFO with BSAPhD*wia* microwave synthesis. The experimental adsorption conditions including pH, contact time, and adsorbent mass were also optimized. BSAPhD@CFO-NPs has an adsorption capacity of 429.8 mg-Cu(II) g⁻¹, which is more than that of BSAPhD/reflux@CFO (287 mg g⁻¹) at pH 8 with 15 min contact time. The Freundlich, Langmuir, and Temkin isotherm models were used to describe adsorption equilibrium. It was found that the Langmuir model (R² = 0.9988) best fits Cu(II) adsorption on the BSAPhD@CFO-NPs adsorbent surface. The application of the BSAPhD@CFO-NPs adsorbent for the removal of Cu(II) from various water samples was performed. The results showed good recovery with high sensitivity.

Keywords: Cu(II), Magnetic nanocomposite CuFe2O4, Microwave-enforced green synthesis, Removal, Schiff bases

INTRODUCTION

Solid-phase extraction (SPE) is a straightforward, popular, reasonably affordable, and efficient means of extracting and concentrating metal ions. The traditional form of SPE is not in much demand, so many automation and miniaturization modifications have been investigated in recent years. One of the most recent methods is magnetic solid-phase extraction (MSPE), a type of dispersive solidphase extraction in which magnetic nanoparticles (MNPs) are used in place of conventional SP adsorbents. MNPs' distinguishing characteristics include high adsorptive surface area, low diffusion resistance, short equilibrium times, and rapid volumetric separation from large quantities under an external magnetic field [1]. Different metal elements, either alone or in composites, and oxides with magnetic properties, including superparamagnetic magnetite, are used to create MNPs *e.g.*, superparamagnetic magnetite (Fe₃O₄) [2]. Spinel ferrites have a structure with the formula MFe₂O₄, where M is commonly a transition metal (a divalent cation) such as manganese ferrite [3], nanocrystals of zinc ferrite (ZnFe₂O₄) [4] and copper ferrite CuFe₂O₄ nanoparticles [5]. Possible use in water filtration has led to significant interest in CuFe₂O₄ magnetic nanoparticles (CFO-NPs), which are low-cost and stable in various environments and can be retrieved easily from treated water using an external magnetic field and recycled numerous times [6].

Chelating agents that can adsorb metal ions are also used to modify MNPs, to boost their adsorption capacity. Schiff's bases function as chelating agents and bind to various metal

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ions, forming complexes with them. The Schiff base, bis(salicylaldehyde)phenylenediamine (BSAPhD) was considered a noble analytical reagent for chelating with metal ions [7]. Conventional Schiff foundation preparation techniques required a lot of time, energy, and resources, so, finding a quick and efficient approach was important. Microwave green synthesis was selected and used successfully in the modification processes of many adsorbents. This technique has many advantages such as time-saving, low cost, and less energy, moreover, its reactions can be carried out on solid supports without the use of solvents [1].

Cu(II) is used commonly in a variety of sectors and is regarded as hazardous [8]. Effluents from the industries concerned frequently contain high levels of copper, which, when it enters the environment causes risks to human health. Overexposure to Cu(II) can result in severe mucosal irritation, hepatic and renal damage, and central nervous system irritation followed by depression [9-11]. Many methods were used for the removal of Cu(II) from water samples [12].

To our knowledge, there is no study on the modification of CuFe₂O₄ with the Schiff base or through microwave synthesis. Moreover, there is no study using CuFe₂O₄ as an adsorbent for the removal of Cu(II), as well as a result of the strong bond between the Schiff base and metal ions such as Cu(II). So, the aim of this study is the fabrication of CuFe₂O₄ magnetic nanoparticles (CFO-NPs) with bis(salicylaldehyde)phenylenediamine (BSAPhD). The fabrication of CFO-NPs was performed with a time-saving method through microwave-assisted solvent-free synthesis. The resultant adsorbent was used for the removal of Cu(II) from the aqueous solution.

METHODOLOGY

Reagents and Solutions

Analytical reagent grade ferric nitrate (Fe(NO₃)₃.9H₂O) and copper nitrate (Cu(NO₃)₂.5H₂O) were purchased from Aldrich Chemical Co., USA. Salicylaldehyde and pphenylenediamine were purchased from Merck, Germany. Sodium hydroxide (NaOH) was purchased from BDH, UK. Double distilled water was used in all experiments. A stock 0.1 M solution of Cu(NO₃)₂. was prepared by dissolving the salt in double-distilled water (DDW). 0.01 M sodium ethylenediamine tetraacetic acid (Na₂EDTA) was prepared by dissolution in DDW. The 0.1 M HCl and 0.2 M ammonia buffer (NH₄OH and NH₄Cl) used to justify pH were purchased from Aldrich Chemical Co., USA.

Instruments

The infrared spectrum of BSAPhD@CFO-NPs was obtained using FT-IR (410 JASCO, Japan). Transmission electron microscopy (TEM) analysis was done using a JSM-5400 LV (JEOL, Japan). A microwave oven (Daewoo KOR-131G, Korea) emitting 2.450 GHz microwave frequency, 200-240 V, 50 Hz, microwave input power: 1350 W, microwave energy output: 1000 W, was used for CFO-NPs modification. A Wrist-Action Model 75 mechanical shaker (Burrell Corporation, Pittsburgh, PA, USA) was used for shaking. Cu(II) was determined in environmental water samples by a Perkin-Elmer MHS-10 spectroscopy that permits the determination of Cu(II) by AAS.

Synthesis of CuFe₂O₄ Magnetic Nanoparticles

CFO-NPs were prepared by thermal decomposition [5]. A 50.0 ml of 2.0 M Cu(NO₃)₂ was added to 200 ml of 1.0 M Fe(NO₃)₃. Then 500 ml of 0.7 M NaOH was added to the previous mixture at room temperature. A reddish-black precipitate was formed (pH = 13), then the mixture was heated at 95 °C for 30 min. After cooling to room temperature, the product was separated magnetically from the supernatant, washed repeatedly with distilled water, and redisposed in an aqueous solution at least three times until the pH was 7.0 [13].

A weight of 1.0 g of CFO-NPs was mixed homogenously with 50.0 mg of p-phenylenediamine, and irradiated in a microwave for 5 min at 10 W. The resulting phase was washed with hot water (60 °C) to remove excess pphenylenediamine and dried at room temperature. The resulting product was mixed thoroughly with 0.5 ml salicylaldehyde, and the mixture was irradiated for 5 min at 10 W in a microwave to produce BSAPhD@CFO-NPs, which was washed with hot DDW to remove excess salicylaldehyde and dried at room temperature, yielding a dark brown product.

Conventional CuFe₂O₄ Modification by the (Salicylaldehyde) Phenylenediamine Schiff Base

Preparation of salicylaldehyde-phenylenediamine Schiff base. For the preparation of salicylaldehydephenylenediamine Schiff base, 10.0 mmol of pphenylenediamine were dissolved in 10.0 ml of ethanol and added to 10.0 mmol of salicylaldehyde dissolved in 10.0 ml ethanol, before refluxing in methanol for 1 h at 50 °C. The product formed was cooled and then collected by filtration, then the BSAPhD/reflux product was washed with DDW and ethanol several times. Finally, it was recrystallized in ethanol by heating and left to dry overnight [13].

CuFe₂O₄ modification by (salicylaldehyde) phenylenediamine Schiff base. A certain weight of CFO-NPs (1.0 g) was mixed homogeneously with 50.0 mg of BSAPhD/reflux and irradiated in a microwave oven for 5 min at 10 W. The resulting phase was washed with hot DDW to remove excess BSAPhD/reflux and dried at room temperature. The resulting BSAPhD/reflux@CFO-NPs was dark brown.

Batch Adsorption Method

The proportional extraction of Cu(II) using BSAPhD@CFO-NPs and BSAPhD/reflux@CFO-NPs was determined in triplicate under static conditions by the batch equilibrium technique. A fixed weight of each adsorbent was added to a 50.0 ml solution containing 0.5 ml of 0.1 M Cu(NO₃)₂. Different additions of either the ammonia buffer (2.0 M) or 1.0 M HCl solutions were used to justify pH values in the range of 2.0 to 8.0 before adding the adsorbent. The mixture was shaken mechanically for 30 min at room temperature to attain equilibrium, after which the adsorbent was separated using an external magnetic field and the metalion-free solution was transferred to a conical flask. The Cu(II) concentration was determined by complexometric EDTA titration [14]. This method was implemented to examine the effects of contact time, amount of adsorbent, and metal ion concentration.

Cu(II) Determination in Real Water Samples

We collected and stored various real water samples, including Nile River water (NRW), drinking tap water (DTW), mineral drinking water (MDW), and firstly distilled water (DW), in clean plastic bottles. The analysis was performed after filtering NRW to remove suspended particles. After adjusting the pH of 50.0 ml of each sample to the optimum pH value (pH 8.0), 50.0 mg of BSAPhD@CFO-NPs was added to each water sample spiked with an aliquot of Cu(II) with a concentration of 5 mg l⁻¹ and shaking for 15 min. After that the magnetic adsorbent was separated using an external magnetic field and the concentration of Cu(II) was determined using the AAS technique.

RESULTS AND DISCUSSION

Microwave-enforced Green Synthesis for BSAPhD@CFO-NPs

Microwave heating for BSAPhD@CFO-NPs reduced the reaction time considerably compared to conventional heating, from 60 to 10 min. In a microwave oven, energy is supplied directly to the material with an electromagnetic field, causing rapid heating throughout the material with reduced thermal gradients [7].

Adsorbent Characterization

FT-IR. The adsorbent (BSAPhD@CFO-NPs) was characterized by FT-IR. As shown in Fig. 1a, the main bands of CuFe₂O₄ in the BSAPhD@CFO-NPs adsorbent appear at 3412 and 1626 cm⁻¹ and are assigned to stretching and bending vibrations of surface –OH. The bands at 601 and 430 cm⁻¹ are assigned to FeO and CuO stretching vibration respectively.

Figure 1b shows the BSAPhD spectrum, with a broad and weak band in the 3000-2800 cm⁻¹ region, confirming the intramolecular hydrogen-bonded OH. The strong absorption peak at 3447 cm⁻¹ can be attributed to the phenolic hydroxyl group OH, and the characteristic FT-IR absorption peaks at 1608 and 1280 cm⁻¹ are assigned to stretching vibration of C=N and phenolic C-O bonds, respectively [8].

Figure 1c shows the spectrum for BSAPhD@CFO-NP, after modification. The band assigned to –OH in CuFe₂O₄ has a lower intensity and has shifted to a higher frequency due to the formation of a hydrogen bond between CFO and BSAPhD, Fig. 2. The peak also appears at 1611 cm⁻¹, assigned to C=N stretching of BSAPhD, which confirms the success of preparation of BSAPhD and modification for CFO with BSAPhD using microwave synthesis.



Fig. 1. FT-IR spectra of (a) CFO-NPs, (b) BSAPhD, and (c) BSAPhD@CFO-NPs.



Fig. 2. Suggested synthesis mechanism for microwaveenforced green synthesis of BSAPhD@CFO-NPs.

The synthesis and adsorption mechanism of BSAPhD@CFO-NPs and Cu(II). Figure 2 clarifies the synthesis reactions BSAPhD@CFO-NPs through microwave-enforced green synthesis and its binding with Cu(II). There is a hydrogen bond formed between CFO and BSAPhD through synthesis. Moreover, there is a complex formed between BSAPhD@CFO-NPs and Cu(II), where Cu(II) binds to oxygen and nitrogen, and forms a stable hexaheterocycle compound.

TEM. The CuFe₂O₄ and BSAPhD@CFO-NPs particle sizes were determined by TEM. Figure 3a shows the adsorbent CFO-NPs particles are spherical and the particle size ranges from 12.5 to 16.9 nm. Figure 3b shows that, after modification, the BSAPhD@CFO-NP particles are in cluster form, with a particle size range of about 12.4 to 15.4 nm.

Adsorption Experiments

Effect of solution pH. The influence of solution pH on Cu(II) adsorption was evaluated in parallel tests in which 50.0 mg solutions of each of BSAPhD@CFO-NPs and BSAPhD/reflux@CFO-NPs were added to 50.0 ml Cu(II) solutions whose initial Cu(II) concentration was 6.45 mg l⁻¹. The solution's pH was adjusted to the desired value at the start of each experiment so that the effect of pH was investigated

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Fig. 3. TEM images of (a) CFO-NPs and (b) BSAPhD@CFO-NPs.

in the range of 2.0 to 8.0, with all other parameters remaining constant, Fig. 4. At low pH (2.0 to 4.0) the Cu(II) adsorption capacity was very small for both adsorbents. At low pH, the acidic medium proton competes with Cu(II) for binding to the adsorbent, decreasing extraction efficiency [14]. When the pH was above 4, adsorption capacity increased, rising to 429.8 mg g⁻¹ at pH = 8.0. As can be seen in Fig. 4, the Cu(II) adsorption capacity of BSAPhD@CFO-NPs exceeds that of BSAPhD/reflux@CFO-NPs where it was 429.8



Fig. 4. Effect of pH on Cu(II) adsorption onto the two adsorbents.

and 287 mg g⁻¹ for BSAPhD@CFO-NPs and BSAPhD/reflux@CFO-NPs, respectively.

Effect of adsorbent dose. The effect of the adsorbent dose on Cu(II) extraction is shown in Fig. 5. Cu(II) adsorption capacity increased as the adsorbent mass used increased from 10.0 to 50.0 mg. This occurred because more adsorption sites became available for Cu(II) [14]. When the adsorbent mass exceeded 50.0 mg, adsorption efficiency decreased slightly, which can be attributed to the surface saturation of the adsorbent with Cu(II), probably indicating the presence of another type of adsorbate/adsorbent interaction. It is possible that this could be caused by competition between those molecules retaining fractions of the adsorbate and free adsorbent molecules, which attract it, bringing it back into the solution. It was also found that the Cu(II) adsorption capacity of BSAPhD@CFO-NPs exceeds that of BSAPhD/reflux@CFO-NPs.

Effect of contact time. Figure 6 shows the effect of time on Cu(II) adsorption for both adsorbents. Contact times ranged from 5 to 60 min. A mechanical shaker was used, with a fixed adsorbent weight of 50.0 mg and pH = 8.0. BSAPhD@CFO-NPs needed a shorter adsorption time for maximum adsorption of Cu(II) than BSAPhD/reflux@CFO-NPs. However, the adsorption capacity can decrease after about 15 min, when both adsorbents are saturated with



Fig. 5. Effect of the mass of the new adsorbents on Cu(II) adsorption.



Fig. 6. Effect of time on Cu(II) adsorption by 50.0 mg of each newly developed adsorbent.

Cu(II), due to the mass transfer barrier. This may result from multilayer adsorption. This confirmed that microwaveenforced green synthesis modification of BSAPhD with CFO-NPs produces a good metal ion adsorbent, which operates quite quickly.

Adsorption Isotherm

The quantity of Cu(II) adsorbed per unit mass of BSAPhD@CFO-NPs is shown by the adsorption isotherm as a function of the equilibrium concentration of Cu(II). This behavior can be explained by Langmuir and Freundlich's isotherm models. The Langmuir isotherm is represented in linear form by Eq. (1):

$$\frac{C_{e}}{q_{e}} = \frac{1}{q_{max.}K_{L}} + \frac{C_{e}}{q_{max.}}$$
(1)

where $q_e \text{ (mg g}^{-1}\text{)}$ is the adsorption capacity at equilibrium, $q_{max.} \text{ (mg g}^{-1}\text{)}$ the saturated adsorption capacity, $C_e \text{ (mg ml}^{-1}\text{)}$ the Cu(II) concentration at equilibrium, and K_L the Langmuir constant related to adsorption capacity (mg g}^{-1}\text{)}. K_L can be correlated with variation in the adsorbent's suitable area and porosity, implying that a large surface area and pore volume will result in higher adsorption capacity.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor R_L [15] As in Eq. (2):

$$R_L = \frac{1}{1 + K_L C_o} \tag{2}$$

where K_L is the Langmuir constant (mg g⁻¹) and C_o the initial concentration of Cu(II) (mg g⁻¹).

Adsorption is favored when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$, and irreversible when $R_L = 0$. For BSAPhD@CFO-NPs $R_L = 0.912$, indicating that Cu(II) adsorption is favorable on the adsorbent's surface.

The Freundlich isotherm is applicable for adsorption processes on heterogeneous surfaces. The surface heterogeneity, and the exponential distribution of active sites and their energy are defined by the isotherm [15].

The linear form of the Freundlich isotherm [16] is represented by Eq. (3):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F is the adsorption capacity (l mg⁻¹) and 1/n the adsorption intensity (also indicating the relative energy distribution and the heterogeneity of the adsorbent sites.

Figure 7 is a plot of C_e/q_e vs. C_e for BSAPhD@CFO-NPs. The straight lines suggest that Cu(II) adsorption obeys the Langmuir isotherm over the entire range studied, with $R^2 =$ 0.9988. As shown in Table 1, K_L and R_L are 0.95 and 0.912, respectively, which confirms that adsorption is favorable. A comparison of R^2 in the two isotherm models shows that the Langmuir model is the best fit for Cu(II) adsorption on the surface of both BSAPhD@CFO-NPs adsorbents. However, the value of n in the Freundlich model shows that active site distribution is both homogeneous and heterogeneous on the BSAPhD@CFO-NPs adsorbent surface.

Using the Temkin isotherm model [15], which is represented by the following equation, the heat of adsorption and the interaction between the adsorbent and adsorbate were evaluated.

$$Temkin \ isotherm: q_e = B_1 \ln K_T + B_1 \ln C_e \tag{4}$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), K_T is the equilibrium binding constant (l mg⁻¹), B_1 is the Temkin constant related to the heat of adsorption (J mol⁻¹), T is the absolute temperature (K). Lower than the Freundlich values are the Temkin constant values and the correlation coefficient ($R^2 = 0.9778$). Because of this, the Temkin isotherm reflects a weaker match of experimental data than the Langmuir isotherm [16].

Limit of Detection (LOD) and Limit of Quantification (LOQ)

The calibration curve for adsorption capacity values of BSAPhD@CFO-NPs towards Cu(II) in the linear range of 1.0 to 10.0 mg ml⁻¹, Fig. 8 showed regression coefficient values 0.99447. The limit of detection (LOD) and the limit of quantification (LOQ) for the determination of Cu(II) were determined during analytical calibration. LOD and LOQ were evaluated to be 1.3 and 1.7 mg l⁻¹, respectively. These

values show analytical performance and the validity of the developed method.



Fig. 7. Langmuir and Freundlich isotherm plots of Cu(II) adsorption on BSAPhD@CFO-NPs

Table 1. Langmuir and Freundlich Isotherm Parameters for Cu(II) Adsorption onto BSAPhD@CFO-NPs

Langmuir				Freundlich			Temkin		
K _L	q _{max}	\mathbb{R}^2	$R_{\rm L}$	K _F	\mathbb{R}^2	Ν	K _T	\mathbb{R}^2	
(mg g ⁻¹)				(l mg ⁻¹)			(l mg ⁻¹)		
0.95	0.7019	0.9988	0.912	199.7	0.9934	2.46	186.5	0.9778	



Fig. 8. Calibration curve for adsorption capacity of Cu(II).

Removal of Cu(II) in Real Water Samples

In four water samples, including Nile River water (NRW), drinking tap water (DTW), mineral drinking water (MDW), and first distilled water (DW), 5 mg l⁻¹ of Cu(II)

was removed using 50.0 mg of the BSAPhD@CFO-NPs. The results are reported in Table 2. The results show that the SP-extractor was effective in removing the low concentration of Cu(II) that was spiked without causing any matrix effects. The high metal capacity values for Cu(II) absorption utilizing the novel SP-extractors are explained by the high recovery of Cu(II) from the DW, DTW, MDW, and NRW samples using a small mass of the adsorbent.

Comparison with other Literature

Adsorption of Cu(II) sing BSAPhD@CFO-NP was compared to those employing other solid phase extraction techniques and more complex adsorbents. According to Table 3, BSAPhD@CFO-NP has a higher capacity for Cu(II) adsorption than the other adsorbents.

CONCLUSION

Bis(salicylaldehyde) phenylenediamine was used to establish a solid-phase extraction process for Cu(II) removal from an aqueous solution using chemically-modified magnetic nanoparticles. In this context, BSAPhD-

Table 2. Removal of Cu(II) from Real Samples Spiked with Cu(II) Using BSAPhD@CFO-NPs

Water samples	Spiked Cu(II) (mg l ⁻¹)	Mass of the adsorbent (mg)	Percentage recovery*
Nile river water (NRW)	2.5	50	96.5 ± 0.5
Drinking tap water (DTW)	2.5	50	96.8 ± 0.5
Mineral drinking water (MDW),	2.5	50	98.5 ± 0.5
First distilled water (DW)	2.5	50	99.0 ± 1.0

*Average of three triplicate runs.

Table 3. Comparison of BSAPhD@CFO-NPs with other Adsorbents Used for Removal of Cu(II)

Adsorbent	pН	Adsorption capacity	Ref.
		$(mg g^{-1})$	
Covalently attached bis(salicylaldimine) to silica gel	8	31.6	[18]
Silica gel/bis(diazoimine) (L2)	7	37.21	[19]
Polyhydroxybutyrate-b-polyethyleneglycol block copolymer	6	18.7	[20]
Alumina modified with indane-1,2,3-trione 1,2-dioxime	9	2.41×10^{-3}	[21]
BSAPhD@CFO-NPs	8	429.8	Present study

functionalized CuFe₂O₄ was prepared using microwaveenforced green synthesis. This new method of synthesis of modified adsorbents has many advantages such as being quick, easy, and solvent free. These advantages have been achieved when it was found that BSAPhD@CFO-NPs have higher Cu(II) adsorption capacity than that one synthesized using a conventional reflux method (BSAPhD/reflux@CFO). It has an adsorption capacity of 429.8 mg-Cu(II) g⁻¹, which is more than that of BSAPhD/reflux@CFO (287 mg g^{-1}) at pH = 8.0 with 5.0 mg of adsorbent and 15-min contact time. A mechanism was derived which clarifies the net reactions occurring during BSAPhD@CFO-NPs synthesis. Moreover, it explains the bonds between BSAPhD@CFO-NPs and Cu(II), where Cu(II) binds to oxygen and nitrogen, forming a stable Hexaheterocycle compound. This also was supported by performing FT-IR and TEM analysis which show the changes that occur for CFO-NPs before and after modification with BSAPhD using microwave-enforced green synthesis. The adsorption isotherm was studied using Freundlich and Langmuir isotherms. It was found that the Langmuir model is the best fit for Cu(II) adsorption on the surface of both BSAPhD@CFO-NP adsorbents where $R^2 =$ 0.9988.

REFERENCES

- [1] S.A. Ahmed, E.M. Soliman, Anal Sci, 31 (2015) 1047.
- [2] K.K. Kefeni, T.A.M. Msagati, B.B. Mamba, Mater. Sci. Eng., B 215 (2017) 37.
- [3] X. Guang, K. Shengyan, L. Qiangang, Z. Guangming, Z. Ningyu, D. Hongbiao, N. Lijun, Frontiers in Chemistry 8 (2020).
- [4] A. Meidanchi, O. Akhavan, Carbon 69 (2014) 230.

- [5] A. Dandia, A.K. Jain, S. Sharma, RSC Adv. 3 (2013) 2924.
- [6] N. Bahar, T.M. Nawaz, M. Panthöfer, G. Haitao, T.D. Schladt, G. Teuta, K. Vadim, B. Robert, W. Stefan, K. Ute, S.L. Maria T. Wolfgang, J. Mater. Chem. 21 (2011) 6909.
- [7] R. Soomro, M.J. Ahmed, N. Memon, H. Khan, Anal. Chem. Insights (2008) 3.
- [8] M.N. Uddin, M.A. Salam, Research 1 (2014) 777.
- [9] R.G. Renmin, Z. Jiajing, L. Xingyan, N. Shoujun, J. Health Sci. 54 (2008) 174.
- [10] M. Arbabi, N. Golshani, Epidemiology and Health System J. 3 (2016) 283.
- [11] C.S. Zhu, L.-P. Wang, W.B. Chen, J. Hazard. Mater. 168 (2009) 739.
- [12] S.A. Al-Saydeh, M.H. El-Naas, S.J. Zaidi, J. Ind. Eng. Chem. 56 (2017) 35.
- [13] H.H. Al-Hmedawi, S.A. Alfahdi, JKU 13 (2015) 156.
- [14] S.A. Ahmed, A.A.A. Gaber, A.M.A. Rahim, J. Mater. Environ. Sci. 10 (2019) 163.
- [15] S.A. Ahmed, A.A.A. Gaber, A.M.A. Rahim, Appl. Water Sci. 7 (2017) 677.
- [16] M. Roosta, M. Ghaedi, N. Shokri *et al.*, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 118 (2014) 55.
- [17] S.A. Ahmed, A.A.A. Gaber, A.M.A. Rahim, Eur. J. Mater. Sci. Eng. 4 (2019) 173.
- [18] S. Sivrikaya, M. Imamoglua, Anal. Lett. 51 (2018) 773.
- [19] S. Urus, S. Purtas, G. Ceyhan, T. Erkenez, Sep. Purif. Technol. 118 (2013) 432.
- [20] S.K. Wadhwa, M. Tuzen, T.G. Kazi, M. Soylak, B. Hazer, Food Chem. 152 (2014) 75.
- [21] M. Hossein, N. Dalali, A. Karimi, K. Dastanra, Turk. J. Chem. 34 (2010) 805.