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The Journal of the Turkish Chemical Society, Section A: Chemistry (JOTCSA) was founded in February 2014, under the Turkish Chemical Society. Respected scholars in Turkey were invited to serve in the editorial board, and we are doing our best to cover all aspects of chemistry. **Dr. Sinem GÖKTÜRK** (Physical Chemistry), **Dr. Alev KARAGÖZLER** (Biochemistry), **Dr. Ersin KARAGÖZLER** (Electrochemistry), **Dr. Dursun Ali KÖSE** (Inorganic Chemistry), **Dr. F. Zehra KÜÇÜKBAY** (Analytical Chemistry), **Dr. M. Atilla TAŞDELEN** (Polymer Chemistry), and myself (Organic Chemistry) are dedicated to work hard to make this humble effort of scholarly publishing a good example of the open-access spirit in chemistry. We are looking forward to receiving even more submissions to our journal to introduce them into our high-quality peer-reviewing system, composed of many scholars from different countries, and work hard to make a high-quality scientific output.

While thanking the authors of papers published in the first and second issues, we invite the researchers working in all fields of applied and theoretical chemistry to consider our Journal for publication of their manuscripts.

You can get more information about our journal, at http://dergipark.ulakbim.gov.tr/public/journals/5106/kimlik.pdf, where much information is available to satisfy your taste. Please do not hesitate to contact me at hkucukbay@inonu.edu.tr or Dr. Barbaros AKKURT, our managing editor, at jotcsa@turchemsoc.org, for further details.

On behalf of all my co-workers in this journal, I sincerely hope that the year 2015 will be a prosperous one for chemistry in general, for Turkish Chemical Society, and for the publication efforts in Turkey.

Sincerely,
Dr. Hasan KÜÇÜKBAY, PhD
Chief editor, JOTCSA

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Erratum to Vol. 1, Issue 1

1) The abstract submission, "Production of Aerogels with Fuller's Earth", has listed a wrong number of authors. The full list of authors are as follows: Semanur YAVUZ, Esra TANRISEVEN, Berrin SAYGI YALÇIN, and Hanifi SARAÇ.

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MICROWAVE-ASSISTED SYNTHESIS OF SOME HALO-SUBSTITUTED CHALCONES

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Abstract

An efficient microwave-assisted synthesis of halosubstituted chalcones were presented by the condensation of halosubstituted ketones and substituted aldehydes. These reactions were found to be economically cheap in comparison with classical synthesis.

Keywords: Synthesis, halosubstituted chalcones, microwave technique.

1. Introduction

Microwave organic reaction enhancement (MORE) has captured the interest of researchers as a non- conventional technique towards the rapid synthesis of novel biological compounds [1]. Many researchers have described accelerated organic reactions towards proving the synthetic utility of MORE chemistry in routine organic synthesis. It can be termed as '4e-chemistry' because it is easy, effective, economical, and eco-friendly and is believed to be a step towards green chemistry [2].

The presence of α, β – unsaturated carbonyl compounds is one of the main structural components in various naturally occurring biologically active substances known as chalcones, analogs of 1,3-diarylprop-2-ene-1-one form a wide class of compounds containing two aromatic rings bound with vinyl ketone fragment. It is well known that most natural or synthetic chalcones are highly active with extensive pharmaceutical and medicinal applications. Chalcones are found to be effective as antitumor [3], anticancer [4], antibacterial [5], antioxidant [6], antileishmanial [7], cytotoxicity [8], antiproliferative [9], anti-inflammatory [10], antimicrobial [11], tyrosinase inhibitory [12], and insecticidal [13] activities.

In view of application of microwave organic reaction enhancement chemistry and importance of chalcones, we plan to synthesize some novel halo-substituted chalcones. The condensation of 1-(1-hydroxy-4-halonaphthalen-2-yl)ethanone and differently substituted aromatic aldehydes using mild basic conditions under microwave irradiation gives halo-substituted chalcones (Scheme 1).

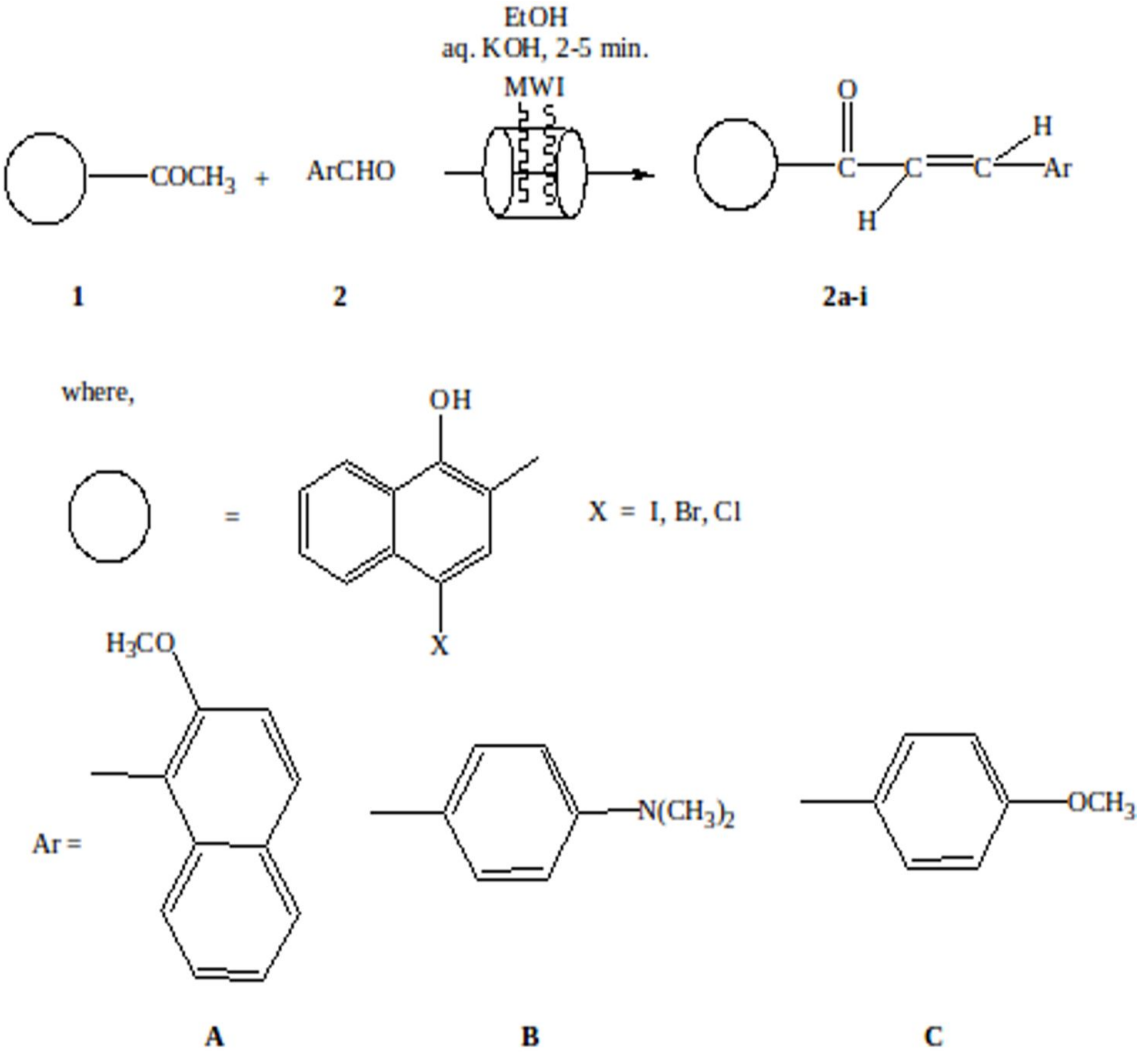
2. Materials and Methods

2.1. Chemicals and apparatus

Melting points were uncorrected and determined in an open capillary tube. FT-IR spectra were recorded on FT-IR Shimadzu spectrometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ on an Avance 300 MHz spectrometer using TMS as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC-MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 Perkin-Elmer model 240 analyzer. Synthos-3000, Anton Paar reaction system was used for microwave syntheses.

2.2. Typical procedure for synthesis of chalcones

An equimolar mixture of 1 and 2 were dissolved in 15 mL of ethanol with stirring and the aqueous solution of potassium hydroxide (50% 10 mL) was added drop wise. Resulting reaction mixtures were irradiated in microwave for 2-5 minutes, with a short interval of time for 10 sec. to avoid evaporation of excess solvent. Reaction progress was monitored on TLC using n-hexane/ethyl acetate/petroleum ether combination (1:1:1, v/v/v) as the mobile phase. On completion of reaction, the reaction mixture was diluted with cold water and acidified with 10% HCl. The separated solid was filtered and crystallized from a mixture of ethanol and DMF to obtain the pure samples **2a-i**.



Scheme 1. Microwave-assisted synthesis of chalcones.

1-(1-Hydroxy-4-iodonaphthalen-2-yl)-3-(2-methoxynaphthalen-1-yl) propenone, **2a**: FT-IR (KBr, ν, cm^{-1}): 3410 (OH), 1630 (C=O), 1455, 1550 (C=C), 1278 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.8 (s, 1H, OH), 6.7-7.4 (m, 11H, ArH), 6.9 (d, J=16 Hz, 1H, H_α), 7.6 (d, J= 16 Hz, 1H, H_β), 3.8 (s, 3H, OCH_3). (EI, m/z (%): 480 (M^+, 42%). Anal. calcd. for $C_{24}H_{17}IO_3$: C, 60.0; H, 3.54; I, 26.45. Found: C, 60.13; H, 3.57; I, 26.56.

1-(4-Bromo-1-hydroxynaphthalen-2-yl)-3-(2-methoxynaphthalen-1-yl) propenone, **2b**: FT-IR (KBr, ν, cm^{-1}): 3412 (OH), 1633 (C=O), 1467, 1542 (C=C), 1274 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.9 (s, 1H, OH), 6.7-7.4 (m, 11H, ArH), 6.8 (d, J=16.5 Hz, 1H, H_α), 7.6 (d, J= 16 Hz, 1H, H_β), 3.9 (s, 3H, OCH_3). (EI, m/z (%): 433 (M^+, 70%). Anal. calcd. for $C_{24}H_{17}BrO_3$: C, 66.51; H, 3.92; Br, 18.47. Found: C, 66.62; H, 3.90; Br, 18.46.

1-(4-Chloro-1-hydroxynaphthalen-2-yl)-3-(2-methoxynaphthalen-1-yl) propenone, **2c**: FT-IR (KBr, ν, cm^{-1}): 3412 (OH), 1634 (C=O), 1470, 1557 (C=C), 1276 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.9 (s, 1H, OH), 6.7-7.4 (m, 11H, ArH), 6.9 (d, J=16 Hz, 1H, H_α), 7.7 (d, J= 16.5 Hz, 1H, H_β), 3.8 (s, 3H, OCH_3). (EI, m/z (%): 388 (M^+, 63%). Anal. calcd. for $C_{24}H_{17}ClO_3$: C, 74.22; H, 4.38; Cl, 9.02. Found: C, 74.27; H, 4.40; Cl, 8.98.

3-(4-Dimethylaminophenyl)-1-(1-hydroxy-4-iodonaphthalen-2-yl)propenone, **2d:** FT-IR (KBr, ν, cm^{-1}): 3416 (OH), 1629 (C=O), 1448, 1578 (C=C), 1275 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.8 (s, 1H, OH), 6.7-7.3 (m, 9H, ArH), 6.9 (d, J=16 Hz, 1H, H_α), 7.6 (d, J= 16 Hz, 1H, H_β), 3.3 (s, 6H, two CH_3). (EI, m/z (%): 443 (M^+, 60%). Anal. calcd. for $C_{21}H_{18}INO_2$: C, 56.88; H, 4.06, I, 28.66. found: C, 56.96; H, 4.10; I, 28.71.

1-(4-Bromo-1-hydroxynaphthalen-2-yl)-3-(4-dimethylaminophenyl)propenone, **2e:** FT-IR (KBr, ν, cm^{-1}): 3414 (OH), 1629 (C=O), 1443, 1575 (C=C), 1272 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.8 (s, 1H, OH), 6.7-7.3 (m, 9H, ArH), 6.8 (d, J=16 Hz, 1H, H_α), 7.6 (d, J= 16.5 Hz, 1H, H_β), 3.3 (s, 6H, two CH_3). (EI, m/z (%): 396 (M^+, 82%). Anal. calcd. for $C_{21}H_{18}BrNO_2$: C, 63.63; H, 4.54; Br, 20.28. Found: C, 63.67; H, 4.58; Br, 20.24.

1-(4-Chloro-1-hydroxynaphthalen-2-yl)-3-(4-dimethylaminophenyl)propenone, **2f:** FT-IR (KBr, ν, cm^{-1}): 3415 (OH), 1629 (C=O), 1452, 1572 (C=C), 1274 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.9 (s, 1H, OH), 6.7-7.4 (m, 9H, ArH), 6.9 (d, J=16.5 Hz, 1H, H_α), 7.6 (d, J= 16.5 Hz, 1H, H_β), 3.3 (s, 6H, two CH_3). (EI, m/z (%): 351 (M^+, 70%). Anal. calcd. for $C_{21}H_{18}ClNO_2$: C, 71.79; H, 5.12; Cl, 9.97. Found: C, 71.83; H, 5.15; Cl, 9.94.

1-(1-Hydroxy-4-iodonaphthalen-2-yl)-3-(4-methoxyphenyl)propenone, **2g:** FT-IR (KBr, ν, cm^{-1}): 3412 (OH), 1631 (C=O), 1450, 1565 (C=C), 1270 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.9 (s, 1H, OH), 6.7-7.3 (m, 9H, ArH), 6.9 (d, J=16.5 Hz, 1H, H_α), 7.6 (d, J= 16.5 Hz, 1H, H_β), 3.9 (s, 3H, OCH_3). (EI, m/z (%): 430 (M^+, 85%). Anal. calcd. for $C_{20}H_{15}INO_3$: C, 55.81; H, 3.48; I, 29.53. Found: C, 55.78; H, 3.51; I, 29.57.

1-(4-Bromo-1-hydroxynaphthalen-2-yl)-3-(4-methoxyphenyl)propenone, **2h:** FT-IR (KBr, ν, cm^{-1}): 3414 (OH), 1634 (C=O), 1457, 1562 (C=C), 1271 (C-O-C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm: 11.9 (s, 1H, OH), 6.7-7.3 (m, 9H, ArH), 6.9 (d, J=16.5 Hz, 1H, H_α), 7.6 (d, J= 16.5 Hz, 1H, H_β), 3.8 (s, 3H, OCH_3). (EI, m/z (%): 383 (M^+, 58%). Anal. calcd. for $C_{20}H_{15}BrNO_3$: C, 62.66; H, 3.91; Br, 20.88 Found: C, 62.62; H, 3.94; Br, 20.84.

1-(4-Chloro-1-hydroxynaphthalen-2-yl)-3-(4-methoxyphenyl)propenone, **2i:** FT-IR (KBr, ν, cm^{-1}): 3416 (OH), 1634 (C=O), 1462, 1570 (C=C), 1273 (C-O-C). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm: 11.9 (s, 1H, OH), 6.7-7.3 (m, 9H, ArH), 6.9 (d, J=16.5 Hz, 1H, H_α), 7.6 (d, J= 16.5 Hz, 1H, H_β), 3.8 (s, 3H, OCH_3). (EI, m/z (%): 339 (M^+, 58%). Anal. calcd. for $C_{20}H_{15}ClNO_3$: C, 70.79; H, 4.42; Cl, 10.32. Found: C, 70.87; H, 4.47; Cl, 10.39.

3. Results and Discussion

The classical Claisen-Schmidt condensation synthesis of chalcones involves aldehyde reacted with acetophenone in the presence of aqueous bases, $Ba(OH)_2$ / LiOH [14, 15]. Chalcones are also synthesized by using microwave irradiation, ultrasound irradiation [16] and by Suzuki reaction [17]. Various modified methods for synthesis of chalcones has been reported using different catalyst such as $SOCl_2$ [18], natural phosphate / lithium nitrate [19], KF / natural phosphate [20], acyclic acidic ionic liquid [21], Na_2CO_3 [22], high-temperature water [23], sodium carbonate [24], $ZrCl_4$ and ionic liquid [25],

silica-sulfuric acid [26], NaOH / Al_2O_3 [27], and silica chloride [28].

Table 1. Microwave assisted synthesis of halosubstituted chalcones, **2a-i.**

Compound	Color	Conventional	Method[a]	Microwave	Method[b]	Melting Point (°C)
		Time (h)	Yield (%)	Time (min)	Yield (%)	
2a	Yellow	14	68	2	90	143-147
2b	Yellow	14	72	4	87	137-139
2c	Yellow	12	70	5	91	153-156
2d	Orange	14	65	4	85	163-165
2e	Red	12	67	3	82	160-162
2f	Red	14	70	5	84	155-157
2g	Yellow	12	74	4	88	167-169
2h	Yellow	13	72	3	90	146-148
2i	Orange	12	67	4	86	173-175

A classical synthesis of these compounds involves the condensation of acetophenones and aldehydes to give chalcones. The combination of solvents and long reaction time, costly chemicals / catalyst makes this method environmentally hazardous. This provided the stimulus to synthesize some new chalcones using microwave irradiation technique [29]. Microwave irradiation has been used to accelerate organic reactions because of high heating efficiency, providing remarkable rate enhancement, dramatic reduction in reaction times with improvement in yield and quality of products. Reactions that require hours or even days by conventional heating can often be accomplished in seconds or minutes by microwave heating [30]. Initially, we attempted the condensation of 1-(1-hydroxy-4-iodonaphthalen-2-yl)ethanone (**1**) with 2-methoxy-naphthalene-1-carbaldehyde (**2**) using an aqueous solution of KOH in ethanol as the reaction solvent. The reaction went to completion within 2 minutes and the corresponding product **2a** was obtained in 90% yield.

In order to optimize the reaction conditions, we carried out the same condensation reaction using conventional Claisen-Schmidt method [11]. We found that microwave technique [30] has several advantages including clean reaction conditions, not expensive nature, yields and environmentally eco-friendliness. The structures of newly synthesized compounds **2a-i** were established on the basis of spectroscopic data and elemental analysis. In the FT-IR spectra of condensed products, it displays the absorption band near 1632 cm^{-1} due to α,β-unsaturated carbonyl stretching. The ^{1}H-NMR spectroscopic analysis display the singlet due to –OH proton appears at δ 11.9 ppm. The α,β-unsaturated olefinic proton shows trans configuration with J value 16.5 Hz and display a doublet near δ 6.9 for H_α and δ 7.6 for H_β.

4. Conclusion

In summary, we have carried out a simple Claisen-Schmidt condensation between halo-substituted ketones with different aldehydes using aq. KOH under microwave irradiation technique. The advantages of present protocol are simplicity of operation, time saving, high yields of products, avoidance of expensive catalyst, and usage of volatile organic solvent.

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BENZYLOXYPHENYL-BASED SYNTHESES OF SOME NOVEL N-ACETYLPYRAZOLINES

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Abstract

Substituted benzyloxyphenyl chalcones **1a-j** on reaction with hydrazine hydrate **2** and glacial acetic acid **3** in 2-methoxyethanol as reaction medium gave novel substituted N-acetylpyrazolines **4a-j**. Newly obtained N-acetylpyrazolines were characterized on the basis of FT-IR, ^{1}H-NMR, GC-MS, and elemental analysis.

Keywords: Benzyloxyphenyl chalcones, N-acetylpyrazolines, 2-methoxyethanol.

1. Introduction

Pyrazolines are well known, and important nitrogen-containing 5-membered heterocyclic compounds and various methods have been adopted for their synthesis. Numerous pyrazoline derivatives have been found to possess notable biological activities, which stimulated the research activity in this field. They have several prominent effects, such as antimicrobial, anti-mycobacterial, anti-inflammatory, analgesic and antidepressant activities [1-5]. Pyrazolines also exhibit excellent film-forming, fluorescent and luminescent properties [6-8]. After the pioneering work of Fischer and Knoevenagel in the late nineteenth century, the reaction of α, β-unsaturated aldehydes and ketones with hydrazines have become one of the most popular methods for the preparation of 2-pyrazolines [9]. In view of these observations, we wish to synthesize some novel benzyloxyphenyl based N-acetylpyrazolines by the condensation of substituted benzyloxyphenyl chalcones with hydrazine hydrate and glacial acetic acid in 2-methoxyethanol (Scheme 1).

2. Material and Methods

2.1 Chemicals and apparatus

Melting points were determined in an open capillary tube and are uncorrected. FT-IR spectra were recorded in KBr on a Perkin-Elmer spectrometer. ^{1}H-NMR spectra were recorded on a Gemini 300-MHz instrument in DMSO-d_6 as solvent and TMS as an internal standard. The mass spectra were recorded on a Shimadzu EI-GC-MS spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 CHN elemental analyzer. The purity of the compounds was confirmed using TLC (petroleum ether / ethyl acetate / n-hexane in 1: 1: 1 volume proportion as mobile phase).

a. Typical procedure for synthesis of N-acetylpyrazolines

A mixture of 3-[2-benzyloxyphenyl]-1-[3,5-dichloro-2-hydroxyphenyl]-propenone (0.01 mole), hydrazine hydrate (0.02 mole) and glacial acetic acid (0.01 mole) in 2-methoxyethanol (15 mL) were refluxed for 3 hours. The progress of reaction was monitored with TLC. The reaction mixture was cooled and poured into ice-cold water. The separated solid was filtered, washed with ethanol and then with water, dried and crystallized from ethanol to give a pure sample of N-acetylpyrazoline.

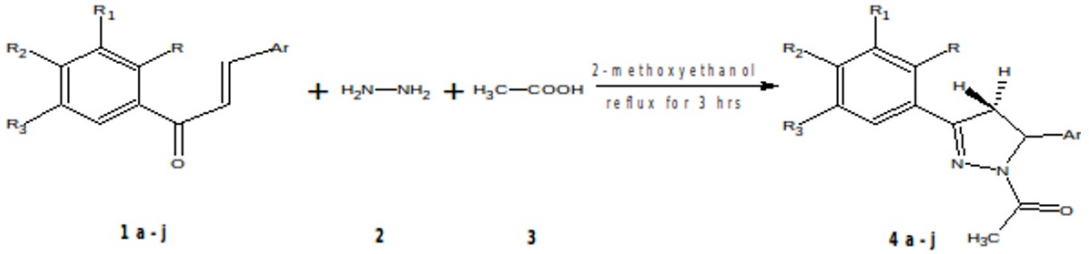
Similar other substituted derivatives were prepared by using the same reaction procedure. The physical and analytical data of **4a-j** N-acetylpyrazolines are reported in Table 1.

Table 1. Physical and analytical data of N-acetyl pyrazolines **4a-j**.

Entry	Mol. formula	Melting point (°C)	Yield (%)		Elemental analysis	
				C %	H%	N%
4a	$C_{24}H_{20}O_3N_2Cl_2$	110	76	63.33 (63.29)	4.21 (4.39)	6.21 (6.15)
4b	$C_{26}H_{25}O_4N_2Br$	198	78	61.41 (61.20)	4.80 (4.91)	5.60 (5.20)
4c	$C_{26}H_{25}O_4N_2Cl_2$	64	67	62.51 (62.40)	5.12 (5.00)	5.55 (5.60)
4d	$C_{25}H_{22}O_4Cl_2N_2$	142	80	61.68 (61.85)	4.41 (4.53)	5.61 (5.77)
4e	$C_{25}H_{21}O_3N_2Cl_3$	137	66	59.41 (59.58)	4.07 (4.17)	5.32 (5.56)
4f	$C_{26}H_{24}O_4N_2ClBr$	206	77	57.51 (57.40)	4.43 (4.41)	5.25 (5.15)
4g	$C_{25}H_{22}O_3N_2Cl_2$	153	72	63.88 (63.96)	4.56 (4.69)	5.93 (5.97)
4h	$C_{25}H_{22}O_4Cl_2N_2$	152	68	61.68 (61.85)	4.41 (4.53)	5.61 (5.77)
4i	$C_{26}H_{25}O_4N_2Cl$	181	71	67.30 (67.16)	5.41 (5.38)	6.18 (6.02)
4j	$C_{26}H_{24}O_5N_2$	140	73	70.38 (70.27)	5.34 (5.40)	6.44 (6.30)

Table 2. Explanations to the substituents used in the compounds **4a-j**.

		Substituents		
Entry	**R**	**R_1**	**R_2**	**R_3**
4a	OH	Cl	H	Cl
4b	OH	Br	H	CH_3
4c	OH	H	CH_3	Cl
4d	OH	Cl	H	Cl
4e	Cl	Cl	Cl	H
4f	OH	Br	CH_3	Cl
4g	Cl	H	Cl	H
4h	OH	Cl	H	Cl
4i	OH	H	CH_3	Cl
4j	H	$H_2C(O^-)_2$		H



Scheme 1. Synthesis of some novel N-acetylpyrazolines.

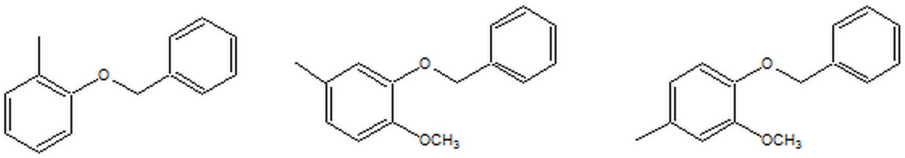


Figure 1. Designation of Ar groups in Scheme 1.

4a. 1-[5-(2-Benzyloxyphenyl)-3-(3,5-dichloro-2-hydroxyphenyl)-4,5-dihydro-pyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1670 (C=O), 1590 (C=N), 1477, 1540 (C=C), 1232 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.8-7.6 (m, 11H, Ar-H), 5.1 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.2 Hz, 1H, H_A), 3.4 (s, 3H, CH_3), 3.6 (dd, J = 12.0, 17.3 Hz, 1H, H_B), 4.8 (dd, J = 5.1, 12.0 Hz, 1H, H_X). MS (EI, m/z: 454 [M^+, 60%].

4b. 1-[5-(3-Benzyloxy-4-methoxyphenyl)-3-(3-bromo-2-hydroxy-5-methylphenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1674 (C=O), 1592 (C=N), 1457, 1544 (C=C), 1235 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.7-7.5 (m, 10H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.0, 17.2 Hz, 1H, H_B), 3.1 (s, 3H, Ar-CH_3), 3.8 (s, 3H, OCH_3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, H_X). MS (EI, m/z: 509 [M^+, 48%].

4c. 1-[5-(4-Benzyloxy-3-methoxyphenyl)-3-(5-chloro-2-hydroxy-4-methylphenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1672 (C=O), 1590 (C=N), 1480, 1552 (C=C), 1233 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.7-7.6 (m, 10H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.0, 17.2 Hz, 1H, H_B), 3.1 (s, 3H, Ar-CH_3), 3.7 (s, 3H, OCH^3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, H^X). MS (EI, m/z: 464 [M^+, 42%].

4d. 1-[5-(3-Benzyloxy-4-methoxyphenyl)-3-(3,5-dichloro-2-hydroxyphenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1670 (C=O), 1591 (C=N), 1465, 1543 (C=C), 1232 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.6-7.6 (m, 10H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.0, 17.2 Hz, 1H, H_B), 3.7 (s, 3H, OCH_3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, H_X). MS (EI, m/z: 464 [M^+, 80%].

4e. 1-[5-(3-Benzyloxy-4-methoxyphenyl)-3-(2,3,4-trichlorophenyl)-4,5-dihydro-pyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1674 (C=O), 1592 (C=N), 1480, 1554 (C=C), 1232 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) 6.7-7.7 (m, 10H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.1, 17.1 Hz, 1H, H_A), 3.5 (dd, J = 12.0, 17.2 Hz, 1H, H_B), 3.7 (s, 3H, OCH_3), 3.2 (s, 3H, CH_3), 4.9 (dd, J = 5.1, 12.2 Hz, 1H, H_X). MS (EI), m/z: [M^+, 55%].

4f. 1-[5-(3-Benzyloxy-4-methoxyphenyl)-3-(3-bromo-5-chloro-2-hydroxy-4-methyl-phenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1672 (C=O), 1590 (C=N), 1470, 1565 (C=C), 1233 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.7-7.6 (m, 9H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.0, 17.2 Hz, 1H, H_B), 3.1 (s, 3H, Ar-CH_3), 3.7 (s, 3H, OCH_3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, HX). MS (EI), m/z: 543 [M_+, 60%].

4g. 1-[5-(3-Benzyloxy-4-methoxyphenyl)-3-(2,4-dichlorophenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1670 (C=O), 1591 (C=N), 1476, 1564 (C=C), 1233 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) 6.6-7.5 (m, 11H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.1, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.1, 17.2 Hz, 1H, H_B), 3.7 (s, 3H, OCH_3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, H_X). MS (EI), m/z: 468 [M^+, 86%].

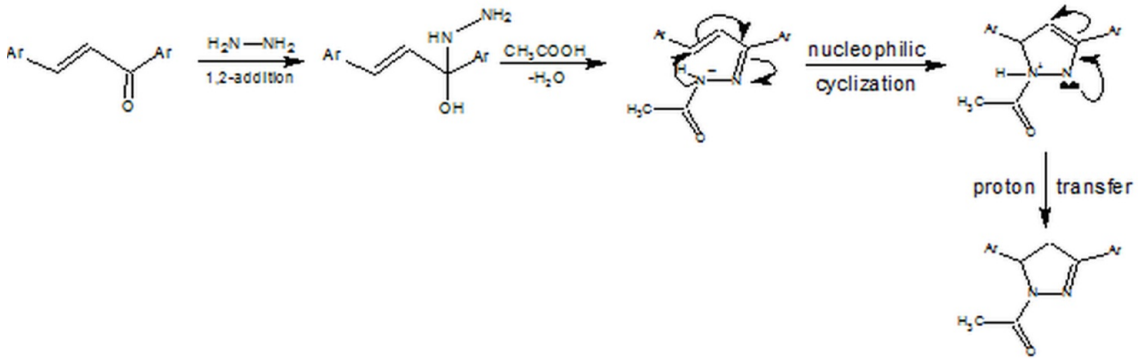
4h. 1-[5-(4-Benzyloxy-3-methoxyphenyl)-3-(3,5-dichloro-2-hydroxyphenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1672 (C=O), 1592 (C=N), 1480, 1558 (C=C), 1230 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.6-7.5 (m, 10H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.1, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.1, 17.2 Hz, 1H, H_B), 3.7 (s, 3H, OCH_3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, H_X). MS (EI), m/z: 484 [M^+, 38%].

4i. 1-[5-(3-Benzyloxy-4-methoxyphenyl)-3-(5-chloro-2-hydroxy-4-methylphenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1672 (C=O), 1590 (C=N), 1474, 1562 (C=C), 1233 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.8 (s, 1H, OH), 6.7-7.6 (m, 10H, Ar-H), 5.2 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.1 Hz, 1H, H_A), 3.2 (s, 3H, CH_3), 3.5 (dd, J = 12.0, 17.2 Hz, 1H, H_B), 3.1 (s, 3H, Ar-CH_3), 3.8 (s, 3H, OCH_3), 4.8 (dd, J = 5.1, 12.2 Hz, 1H, H_X). MS (EI), m/z: 464 [M^+, 65%].

4j. 1-[3-Benzo[1,3]dioxol-5-yl-5-(4-benzyloxy-3-methoxyphenyl)-4,5-dihydropyrazol-1-yl]-ethanone. FT-IR (KBr pellets): 1673 (C=O), 1590 (C=N), 1467, 1541 (C=C), 1232 (C-N) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 6.8-7.6 (m, 11H, Ar-H), 5.1 (s, 2H, OCH_2), 3.2 (dd, J = 5.0, 17.2 Hz, 1H, H_A), 3.4 (s, 3H, CH_3), 3.6 (dd, J = 12.0, 17.3 Hz, 1H, H_B), 3.8 (s, 3H, OCH_3), 4.3 (s, 2H, ring OCH_2), 4.8 (dd, J = 5.1, 12.0 Hz, 1H, H_X). MS (EI), m/z: 444 [M^+, 47%].

3. Results and Discussion

A classical synthesis of these compounds involves the condensation of α, β-unsaturated carbonyl compounds with hydrazines. Pyrazoline is also synthesized by using microwave irradiation [10], tungsten light irradiation [11], and ultrasound irradiation [12]. Recently, various modified methods have been reported for synthesis of 2-pyrazolines by using different catalysts such as $KHSO_4.H_2O/SiO_2$, porous calcium hydroxyapatite, mercury(II) acetate, $Bi(NO_3)_3.5H_2O$, Zn, $H_3PW_{12}O_{40}$, and Lewis acid / Lewis bases [13-19]. Greener and environmentally benign syntheses of 2-pyrazolines using solvent-free grindstone technique were reported [20]. In keeping with these observations, we focus towards the reactivity of various substituted benzyloxyphenyl chalcones for the synthesis of novel N-acetyl pyrazolines. The experimental procedure for the syntheses of the compounds **4a-j** involves refluxing the mixture of substituted benzyloxyphenyl chalcones **1a-j**, hydrazine hydrate **2** and glacial acetic acid **3** in 2-methoxyethanol as the reaction medium for 3 hrs.



Scheme 2. Proposed mechanism for the conversion of chalcones into N-acetylpyrazolines.

The obtained 2-pyrazolines were characterized using spectroscopic techniques, their FT-IR spectra showed the absence of carbonyl absorption band and the appearance of characteristic absorption band for ν C=N at 1592-1588 cm^{-1} and a band at 1130 cm^{-1} for C-N. In the ^{1}H-NMR spectrum, an ABX pattern was observable, H_A, H_B and H_X appear as double doublets at δ 3.10–3.30, 3.75–3.80 and 4.90–5.0 ppm with J_{AB} = 17.1 Hz, J_{AX} = 5.1 Hz, and J_{BX} = 12.0 Hz. The appearance of ABX pattern and disappearance of chalcone peaks in ^{1}H-NMR spectrum reveal the cyclization of α, β-unsaturated carbonyl compounds into five membered rings. The singlet of OH and OCH_3 observed at δ 11.8 and 3.8 ppm, respectively. Aromatic protons appear near the region δ 6.7-7.6 ppm.

4. Conclusion

In summary we have synthesized a series of novel benzyloxyphenyl based N-acetylpyrazolines, **4a-j**, by the condensation of substituted benzyloxyphenyl chalcones **1a-j** with hydrazine hydrate **2** and glacial acetic acid **3** in 2-methoxyethanol.

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FACTORS AFFECTING THE REMOVAL OF A BASIC AND AN AZO DYE FROM ARTIFICIAL SOLUTIONS BY ADSORPTION USING ACTIVATED CARBON

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Abstract

Decolourisation of wastewater, particularly from textile industries, is one of the major environmental concerns these days. Current methods for removing dyes from wastewater are costly and cannot effectively be used to treat wide range of such wastewater. This work describes the use of commercially available granular activated carbon (GAC) as an efficient adsorbent material for dyes' removal. Aqueous solutions of various concentrations of the basic dye Methylene Blue (MB) and the azo-dye Tartrazine at 5-20 $mg.L^{-1}$ and 10-100 $mg.L^{-1}$, respectively, were shaken with certain amount of GAC to determine the adsorption capacity and removal efficiencies. The effects of adsorbent dose, initial pH, initial dye concentration, agitation speed, and contact time on dyes' removal efficiencies have been studied. Maximum dye concentration was removed from the solution within 60-90 min. after the beginning of every experiment. Adsorption parameters were found to fit well into Langmuir and Freundlich adsorption isotherm models with correlation coefficient ($R^2 > 0.99$) in the concentration range of MB and TZ studied.

Keywords: Activated carbon, Adsorption, Methylene Blue, Tartrazine.

1. Introduction

A large number of synthetic dyes have been produced for the purpose of industrial and domestic applications for many years. Most of them have been found to be toxic and carcinogenic. These dyes may enter the aquatic environment from industrial and municipal effluent [1].

The decolourisation of industrial effluents is a challenging and fundamental task related to pollution control, mainly in textile industries. However, the textile industry plays a part in the economy of several countries around the world. The process of dyeing causes the production of more or less coloured wastewater [2]. Effluents discharged from textile and dyeing industries are of low biological oxygen demand (BOD) and high chemical oxygen demand (COD). Disposal of highly coloured waste into receiving water can be toxic to aquatic life. The dyes impede light penetration and upset the biological activity [3]. Dyes also pose a problem because it may be toxic to some organisms and can cause severe damage to human beings, such as dysfunction of kidney, liver, and central nervous system [4, 5]. The treatment of dye bearing effluents is considered to be very complicated process because of its heterogeneous mixtures of many pollutant substances ranging from organic pesticides to heavy metals. In addition, these substances are considered to be non-biodegradable and persistent [6].

Various treatment methods have been applied and investigated by many researchers for treating dye-bearing effluents including, physical, physico-chemical, and chemical processes [7-10]. All these methods have different colour removal capabilities, capital costs, and operating rates. Among these processes, adsorption has been found to be superior compared to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation, and insensitivity of toxic substances [11]. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity comparable to its low cost of production [12].

Activated carbons are multilateral adsorbents and have wide range of applications most of which is dedicated to the removal of pollutant species by adsorption from the liquid and gas phases.

Activated carbons are highly effective in removal of contaminants because of their large surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity. The importance of activated carbons' applications is related to its use in removal of colour, odour, taste, and other undesirable organic impurities from potable water, in the treatment of domestic and industrial wastewater, solvent recovery, air purification in inhabited spaces such as restaurants, food processing and chemical industries, in air pollution control, and in a variety of gas-phase applications [13-16].

The present study was undertaken to evaluate and compare the efficiency of the activated carbon for the removal of the basic dye (Methylene Blue, MB) and the azo-dye (Tartrazine, TZ) from aqueous solution. The removal efficiency was determined to study the effects of contact time, initial concentration of dye solution, pH, adsorbent dosage, and agitation rate.

2. Experimental

2.1. Materials and apparatus

The dyes used in this study were methylene blue dye (molecular formula: $C_{16}H_{18}N_3ClS$, Fig. 1,. left) and Tartrazine (molecular formula: $C_{16}H_9N_4Na_3O_9S_2$, Fig. 1, right) supplied by Morgan Chemical Company and were used without further purification. Other reagents include diluted HCl and NaOH solutions. All reagents were of analytical grade. Distilled water was used throughout the experiments. The dyes' concentrations were determined using Agilent UV-Vis Cary 60 PC scan double beam recording spectrophotometer using 1-cm glass cells. A digital pH meter, type 720 WTW 82362, was used to monitor the pH value during adjusting with either the acidic or basic solution.

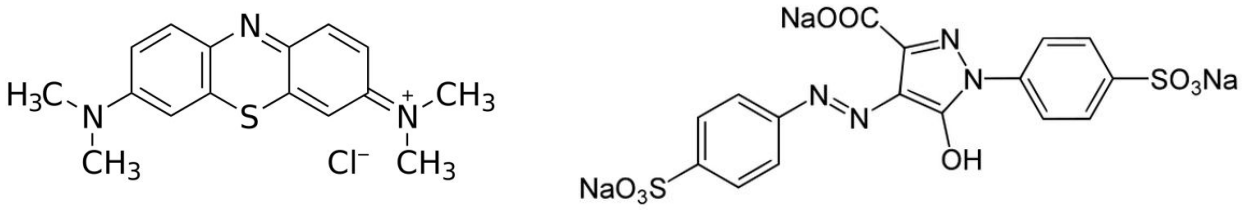

Figure 1. Chemical structures of methylene blue (MB, left) and tartrazine (Tz, right).

2.2. Preparation of the adsorbent

Commercially available activated carbon (500 µm ≤ D ≤ 2mm), supplied by Morgan Chemical Company, was used as the adsorbent without further chemical treatment. A measured quantity of the sample was immersed in hot water for three hours. The washed activated carbon was filtered and oven-dried at 60 °C for 2 hours and then heated to 200 °C for 3 hours under N_2 flow.

2.3. Physical characterisation of activated carbon

The properties of the activated carbon adsorbent including particle size, density, pore volume, and porosity were determined according to the method of American Standard for Testing & Materials (ASTM). The apparent surface area was measured from N_2 adsorption at 77 K in a Quantrachrome Autosorb I-CLP. Total surface areas were calculated using the BET equation [12]. The values for density, total pore volume and BET surface area are 0.447 g cm^{-3}, 0.124 cm^3 g^{-1} and 776 m^2 g^{-1} respectively.

2.4. Preparation of dye solution

A stock solution of the dye was prepared by dissolving 1.0 g of the dye in 1000 mL of distilled water to make a stock solution of 1000 mg L^{-1}. The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. For absorbance measurements, UV-Vis double beam spectrophotometer with PC-scanning facility (Agilent, Inc) was employed;

the activated carbon was filtered before sampling. The maximum wavelength λ_{max} for the methylene blue was measured at 664 nm, while for tartrazine it was at 425 nm. Concentrations were determined from a standard calibration curve.

2.5. Adsorption procedure

The adsorption isotherms have been determined by mixing dyes' solution (100 mL) of known initial concentration of MB (2-20 ppm) and TZ (10-100 ppm) with varied amounts of adsorbents (0.2-1.5 g) using several volumetric flasks. The adsorption behaviours of the samples were studied by evaluating the percentage removal efficiency of methylene blue and tartrazine calculated as the following:

$$\text{Removal efficiency} = [\frac{(C_0 - C)}{(C_0)}] x 100 \quad (1)$$

Where C_0 is the initial concentration of methylene blue, C is the solution concentration after adsorption at any time.

The amount of dye adsorbed per gram of adsorbent (q_e) was calculated as follows:

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

Where C_o and C_e are initial and equilibrium dye concentrations, respectively (mg L^{-1}), V is dye solution volume (L); m is the mass of adsorbent (g).

The effect of adsorption time on the dye removal at various predetermined intervals from (10-120 min.) using a double beam UV-Vis spectrophotometer with PC scanning facility for measurement of concentration at λ_{max}= 664 nm for methylene blue and λ_{max}= 425 nm for tartrazine was monitored by shaking the reaction mixture and analysing for the dye content at the end of each contact time. The removal efficiency was determined to study the effects of contact time, initial concentration of dye solution and pH, adsorbent dosage, temperature, and agitation rate.

3. Results and Discussion

3.1. Effect of the contact time

The effect of contact time on the adsorption capacity of two dyes by activated carbon was conducted through batch experiments to achieve the equilibrium as shown in Fig. 3. The mechanism of colour removal can be described by the migration of the dye molecule from the solution to the adsorbents particle and diffusion through the surface. The results showed that equilibrium was reached within 90 min. of operation for activated carbon. The adsorption capacity was constant thereafter in the case of both adsorbate observed.

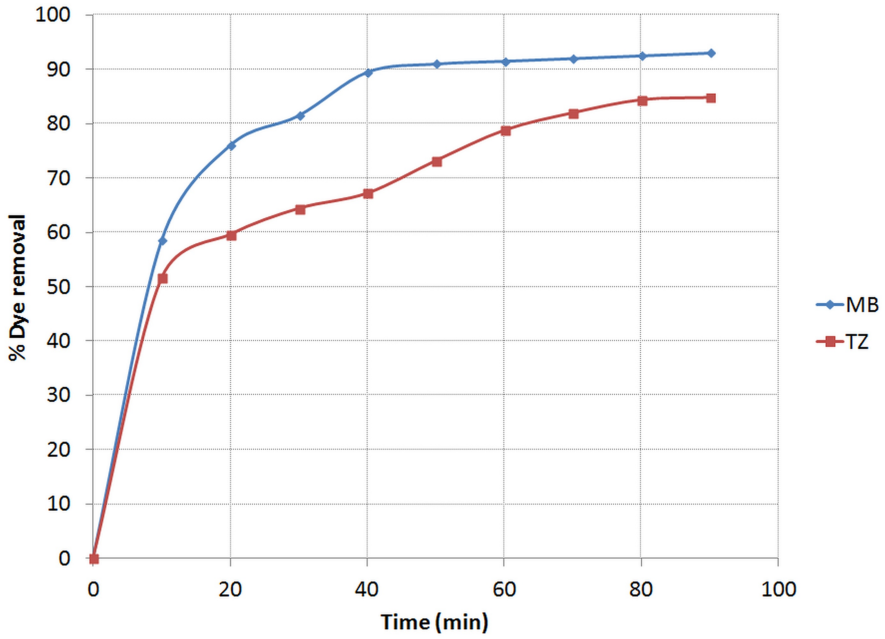

Figure 3. Effect of contact time on the percent removal of MB (20 ppm) and TZ (100 ppm) with activated carbon, 0.5 g of AC, agitation speed, 100 rpm,T= 25 °C and 100 mL solution.

3.2. Effect of initial concentration

The effect of initial concentration of methylene blue (5-20 mg L^{-1}) and tartrazine (25-100 mg L^{-1}) on the removal efficiency using activated carbon are shown in Figs. 4 and 5. The experiments were carried out at fixed adsorbent dose (0.5 g), at room temperature (25 ±1 ºC), neutral pH (7.0), and 100 rpm agitation speed.

The effect of the initial dye concentration depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface [17]. Figs. 4 and 5 show the effect of initial dye concentration. Generally the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [11]. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will disappear [18]. However, the increase in the initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration [19]. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration.

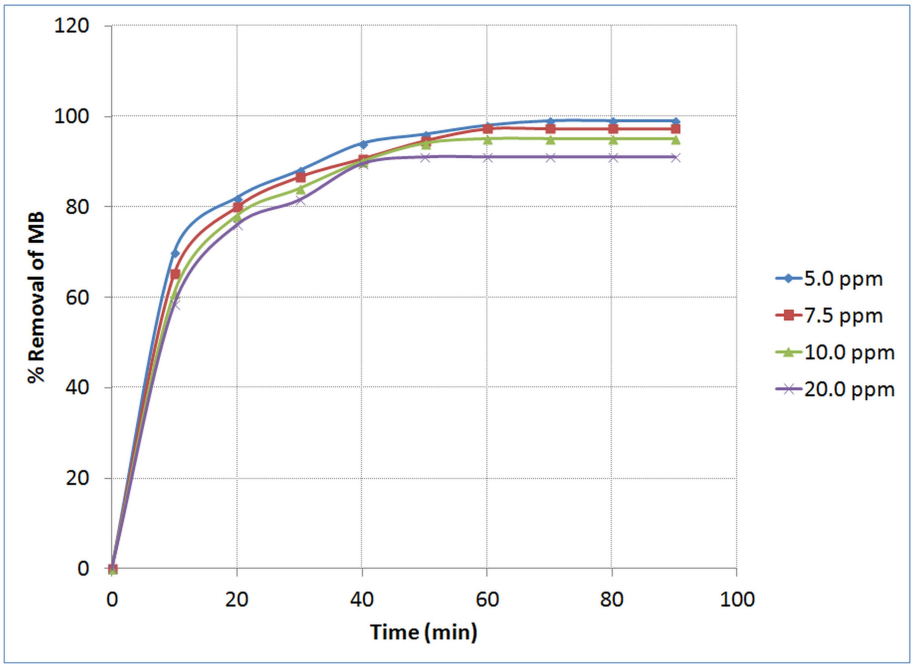

Figure 4. Effect of initial MB concentration on the dye removal efficiency, 0.5 g of AC, agitation speed, 100 rpm,T= 25 °C, and 100 mL solution.

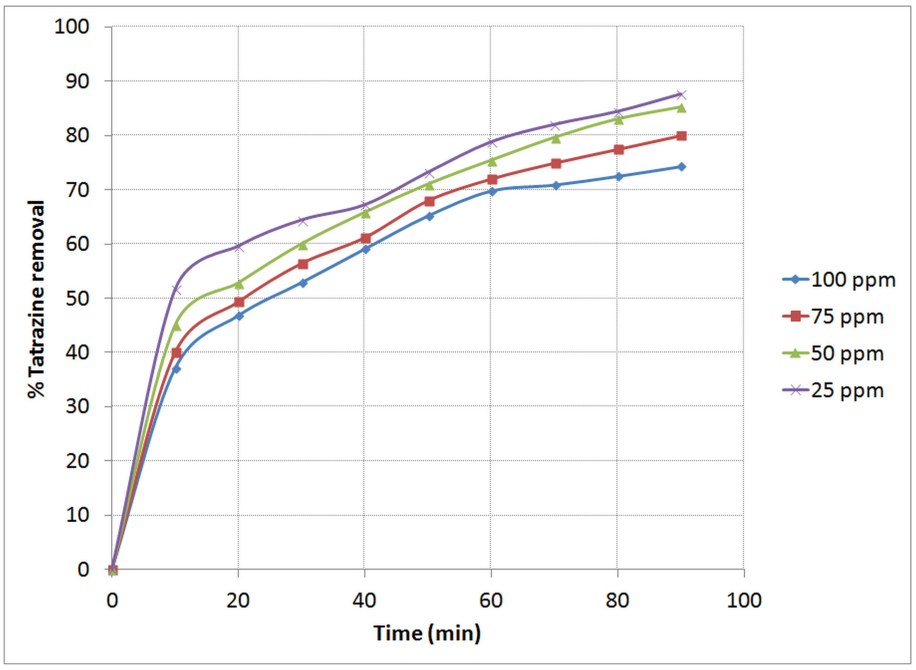

Figure 5. Effect of initial TZ concentration on the dye removal efficiency, 0.5 g of AC, agitation speed, 100 rpm,T= 25 °C, and 100 mL solution.

3.3. Effect of the adsorbent mass

The effect of Activated Carbon (AC) amount on the uptake of the dye was measured for dye concentration 10 mg L^{-1} of MB and 100 mg L^{-1} of TZ, different shaking time (10-120 min), and different quantity of AC (0.2, 0.5, 1.0, and 1.5 g) at pH = 7.0 and at room temperature (25±1 ºC). The results are shown in Figs. 6 and 7. In general, it was found that by increasing the amount of the adsorbent, the adsorption rate increased. This increase was most significant when the amount of adsorbent was increased (0.5-1.5 g). Maximum dye removal was achieved within 60-90 minutes after which a decrease in dye concentration was negligible. Increase in dye removal percentage with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. At the beginning of the process, the rate of dye removal by the AC was fast during the first 30 min and then decreased gradually.

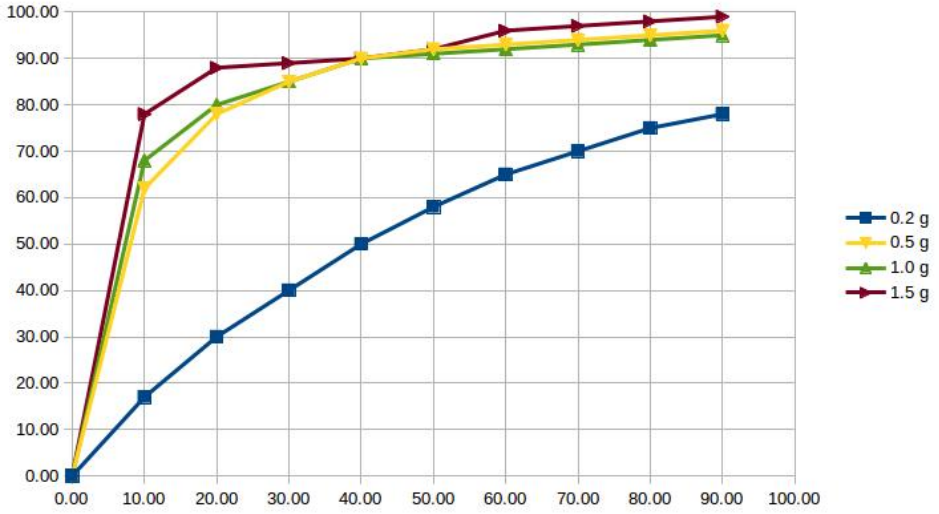

Figure 6. Effect of the amount of AC on the removal efficiency of MB, 10 ppm, 100 rpm, T=25 ^{O}C, and solution volume = 100 mL.

3.4. Effect of pH

The pH value of the solution is an important parametre for the adsorption processes, and the initial pH value of the solution has significant influence compared to the final pH. To study the effect of pH on MB and TZ adsorption, the experiments were carried out at 10 mg L^{-1} initial dye concentration of MB and 100 mg L^{-1} with 0.5 g of adsorbent dosage at (26 ±1 ºC). In this study, a selection among pH values 3.0, 6.8, and 10.0 was suggested based on the fact that most of practical applications are within this range (industries. workshops, etc.). Figs. 8 and 9 show the relationship between the pH value and the removal of MB and TZ.

It can be seen from Fig. 8 that as the solution pH increases, the removal increases as well. Increasing the solution pH increases the number of hydroxy groups, thus increases the number of negatively charged sites and enlarges the attraction between MB dye and adsorbent surface [3, 17].

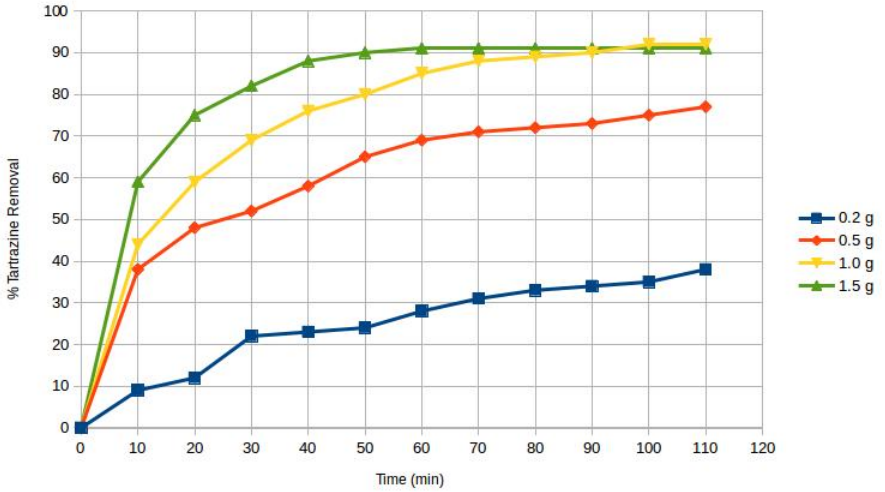

Figure 7. Effect of the amount of AC on the removal efficiency of TZ, 100 ppm, agitation speed, 100 rpm, T=25 °C, and solution volume = 100 mL.

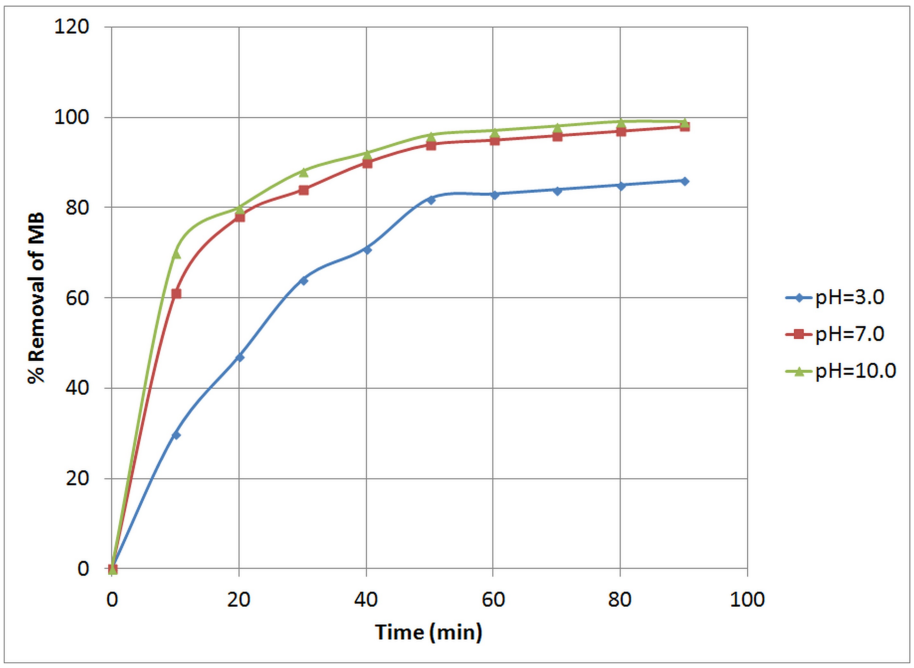

Figure 8. Effect of pH on the removal efficiency of MB,10 ppm, agitation speed, 100 rpm, T=25 °C, and 100 mL solution.

Tabrez *et al*. used fly ash as low-cost adsorbent for the removal of Methylene Blue, Malachite Green, and Rhodamine B dyes from textile wastewater [20]. In their work, they found that the adsorption of dyes increases from 0.426 to 0.467, and 0.232 to 0.394, and 0.286 to 0.367 mg g^{-1} for methylene blue, malachite green, and Rhodamine B, respectively, as the pH was increased from 3.0 to 9.0 [20]. Fig. 7 shows that as the pH increased, the efficiency of the TZ removal decreased. This may be attributed to the fact that the adsorption of TZ dye which contains OH functional group is favoured by the decrease in pH.

Therefore, adsorption may be due to hydrogen bonding, Van der Waals forces, and others. In general, initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value.

The variation of removal efficiency with pH can be explained by considering the difference in the structure of the two dyes. For MB, the acid-base equilibrium can be represented by the following equation:

$$MBH^{2+} \Leftrightarrow MB^{+} + H^{+} \quad (3)$$

In addition, MB has very low pK_a value (less than1.0) and its removal was mainly due to solubilised - unprotonated form MB^+ for all studied pH values. However, Tartrazine [21] has two strong sulphonic acid groups with pK_a = 2.0, one weak acidic acetate group with pK_a = 5.0 and one azo group with pK_a=10.9. Below pH 10.0, TZ should have different chemical forms according to pH, but chromophore (azo group) does not change. Hence, the measured removal concerns all these species. Adsorption experiments were avoided for pH >10.0.

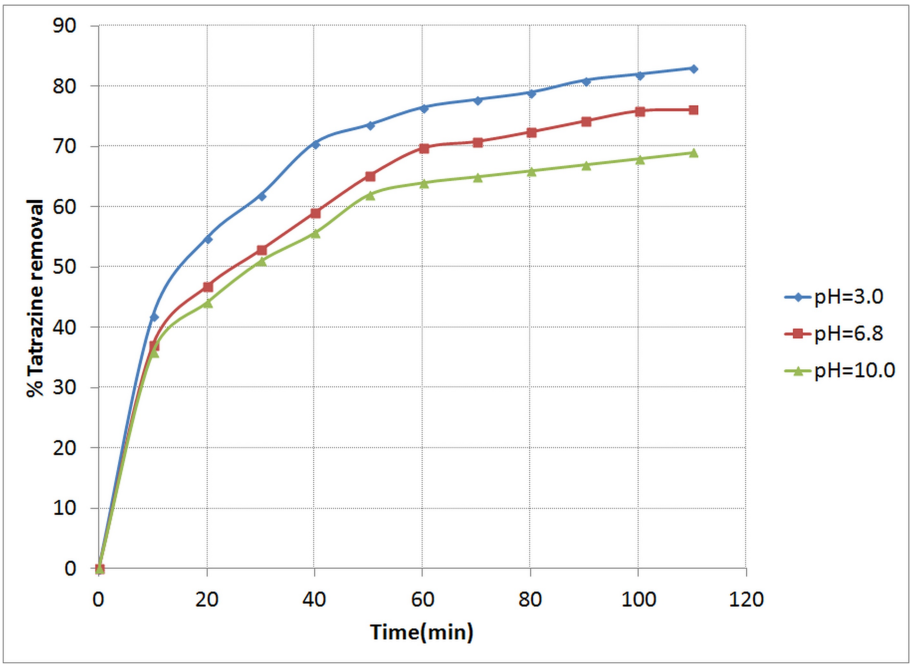

Figure 9. Effect of pH on the removal efficiency of TZ, 100 ppm, agitation speed, 100 rpm, T=25 °C, and 100 mL solution.

3.5. Effect of agitation speed

In a liquid adsorption system, the mass transfer rate of a solute to a particle is affected by liquid film thickness surrounding the particle and the film thickness depends on agitation speed. A series of experiments at different degrees of agitation (from 25 to 125 rpm) were undertaken for the adsorption of MB and TZ on activated carbon as shown in Figs. 10 and 11. The results indicate that the degree of agitation influences the removal efficiency as the agitation rate increases from 25 to 125 rpm. At agitation rates higher than 100 rpm the removal efficiency differs only to a quite small extent for MB adsorption, indicating that the film thickness has insignificant effect when the agitation rate is higher than 100 rpm. Hence, an agitation rate of 100 rpm was selected for all the experiments.

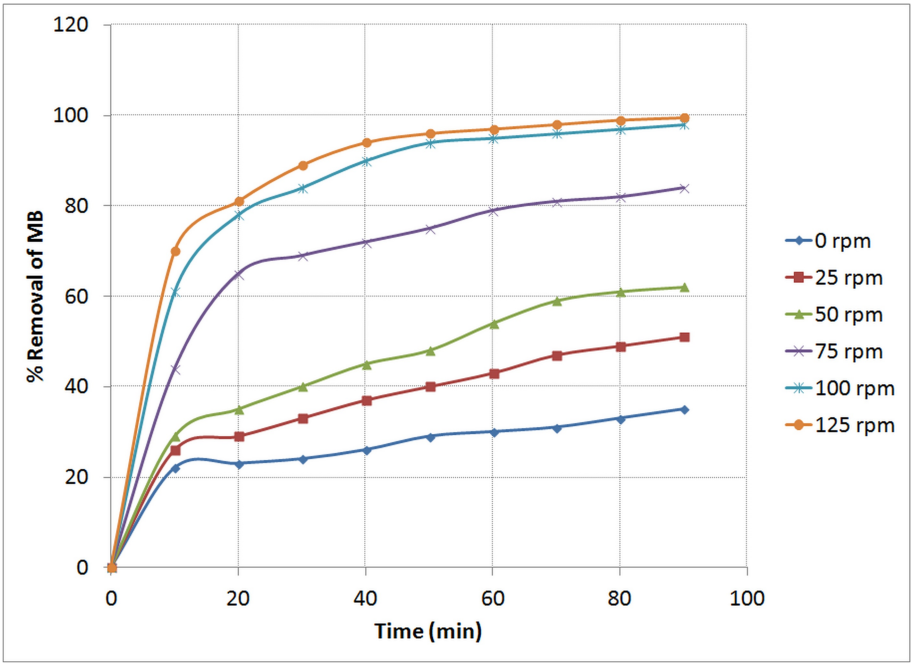

Figure 10. Effect of agitation speed on the removal efficiency of MB, 10 ppm, 0.5 g of AC, T=25 °C, and 100 mL solution.

3.6. Adsorption isotherm

For solid–liquid adsorption systems, adsorption isotherms are important models for the description of adsorption behaviour. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid phase and the liquid phase [22]. It is significant for understanding the adsorption behaviour to identify the most appropriate adsorption isotherm model. In this paper, Langmuir and Freundlich isotherms were employed to investigate the adsorption behaviour. Adsorption isotherms were studied at 298 K.

3.7. Langmuir isotherm

Langmuir isotherm is tested on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place. Thus, an equilibrium value can be reached and the saturated monolayer curve can be presented in the equation below which has been successful for the explanation of monolayer adsorption. The linear form of Langmuir equation is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (4)$$

where q_{max} is the maximum or monolayer adsorption capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}), which is related to the free energy of adsorption. Plots of C_e/q_e against C_e at different temperatures are shown in Fig. 12 and 13. The maximum adsorption capacity, q_{max}, and Langmuir constant, K_L were calculated from the slopes and intercepts of the plots respectively. Values obtained for the adsorption of MB and TZ onto the adsorbent are presented in Table 1.

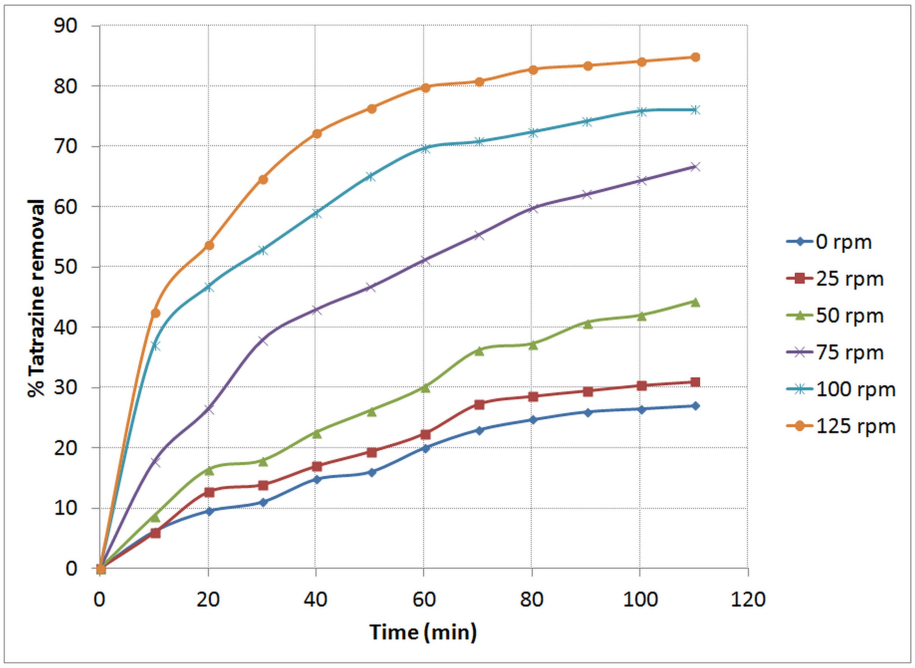

Figure 11. Effect of agitation speed on the removal efficiency of TZ, 100 ppm, 0.5 g of AC, T=25 °C, and 100 mL solution.

Agreement of the experimental data with Langmuir isotherm model indicates the homogeneous nature of activated carbon surface, *i.e.* each dye molecule/activated carbon adsorption has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of activated carbon. A similar observation was reported by the adsorption of acid orange 10 dye onto activated carbons prepared from agricultural waste bagasse [23] and by the adsorption of direct dyes on activated carbon prepared from sawdust [24] and adsorption of Congo Red dye on activated carbon from coir pith [25].

It can be predicted whether an adsorption system is favourable or unfavourable using the essential characteristic of the Langmuir isotherm expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter defined by (5):

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the highest initial concentration. This parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < RL < 1$) or unfavourable ($R_L > 1$). It can be seen from Table 1, the value of R_L is less 1 which suggests that the adsorption is favourable.

3.8. Freundlich isotherm

The Freundlich isotherm model is used to describe heterogeneous adsorption process, *i.e.* adsorption which takes place on a heterogeneous surface through a multilayer adsorption mechanism. Freundlich isotherm is expressed by the equation

$$q_e = K_f x C_e^{1/n} \quad (6)$$

This can be linearised to

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) x \log C_e \quad (7)$$

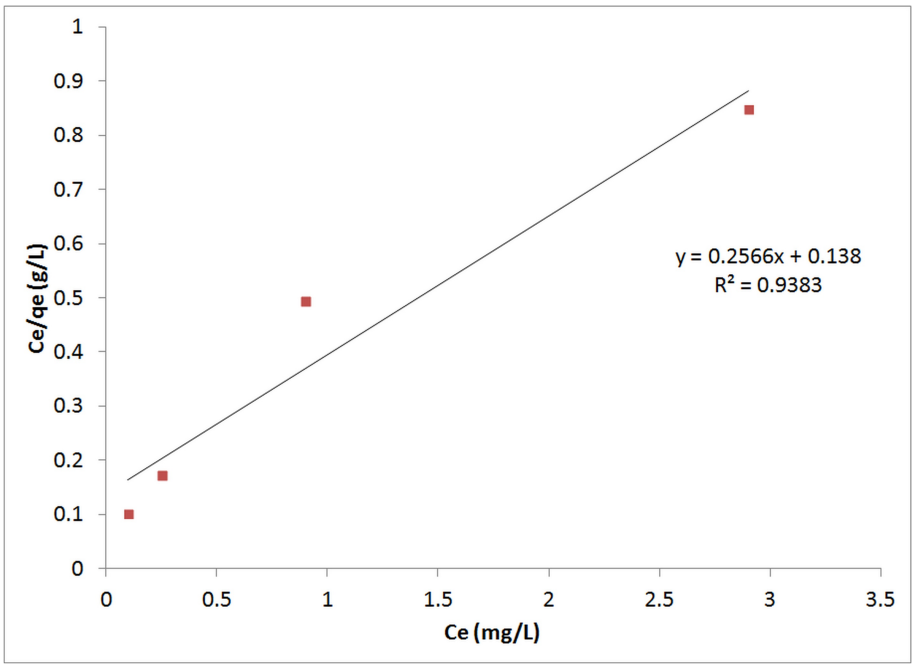

Figure 12. Langmuir adsorption isotherm of MB-activated carbon adsorption at 25°C.

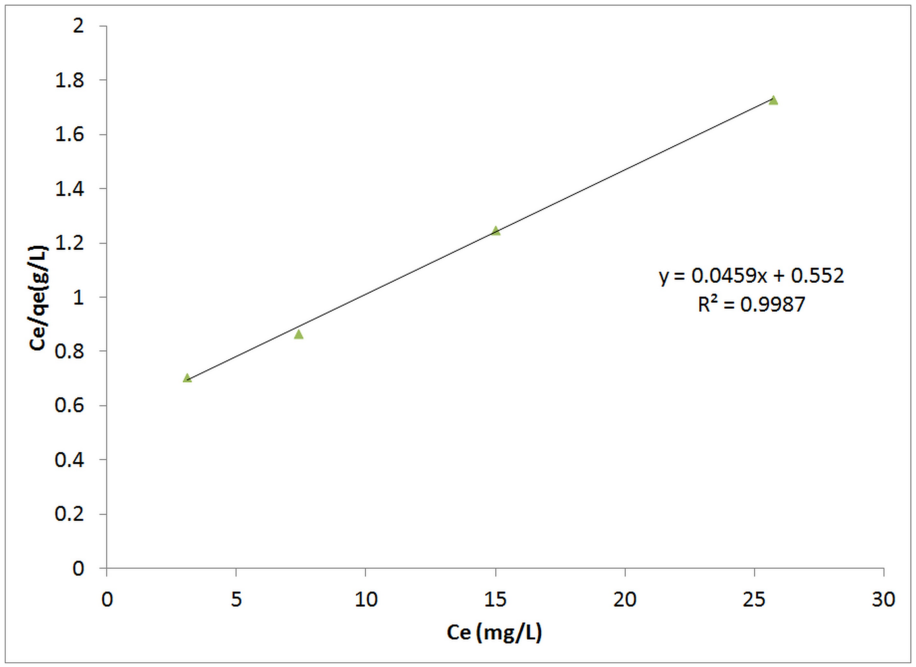

Figure 13. Langmuir adsorption isotherm of TZ-activated carbon adsorption at 25 °C.

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (MB and TZ) and K_F and n are Freundlich constants, n giving an indication of how favourable the adsorption process and KF (mg g^{-1} (L mg^{-1}), and n is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. The slope 1/n ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [7, 20]. A value for 1/n below unity indicates a normal Freundlich isotherm while 1/n above one is indicative of cooperative adsorption [23]. The plot of log q_e versus log C_e gives straight lines with slope '1/n' (Figs. 14 and 15), which shows the adsorption. The Freundlich parameters and correlation coefficients (R^2) evaluated from the plots are listed in Table 1. Accordingly, the Freundlich constants (K_F and n) and R^2 presented in Table 1, show that Freundlich model could also be used to explain the adsorption process.

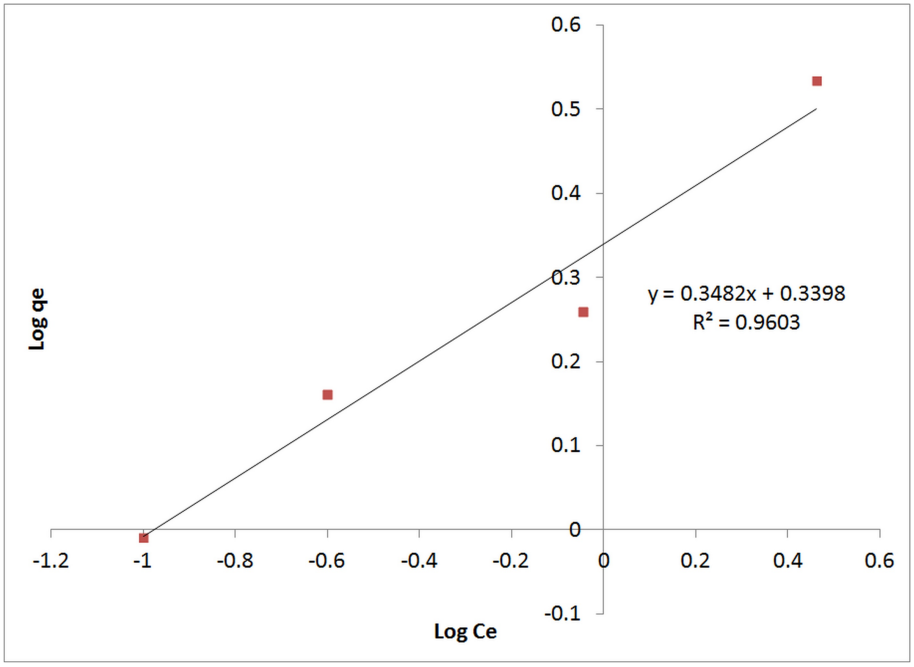

Figure 14. Freundlich adsorption isotherm of MB-activated carbon adsorption at 25 °C.

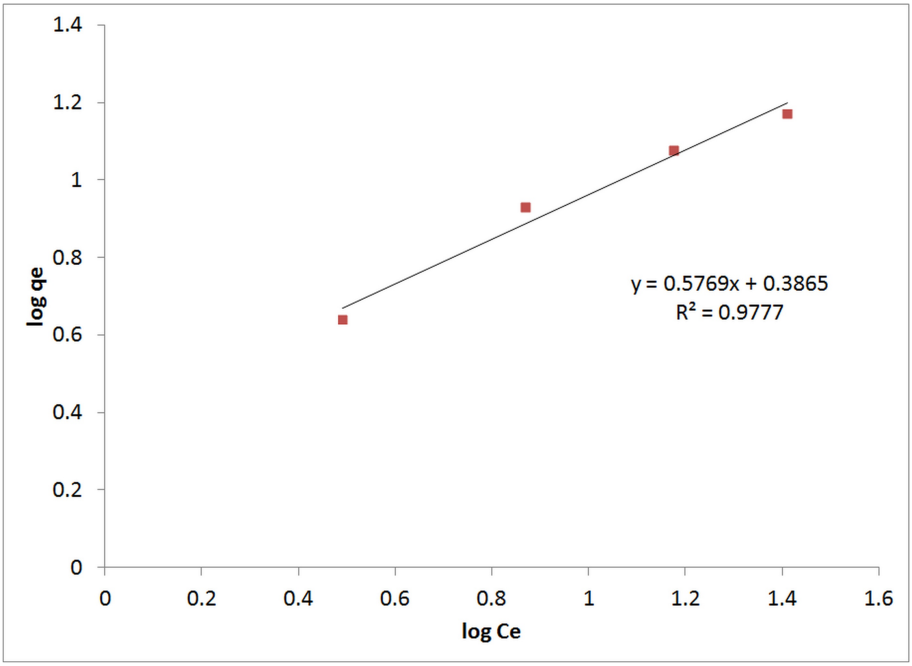

Table 1. Isothermal parameters for the adsorption of Methylene Blue (MB) and Tartrazine [21] on activated carbon.

The correlation coefficient values ($R^2 > 0.93$) (Table 1) show strong positive correlation indicating that the adsorption follows Langmuir isotherm. The maximum adsorption capacity, q_{max}, obtained from the Langmuir plot is 3.78 and 21.8 mg g^{-1} for MB and TZ, respectively. This value is higher than those reported by other researchers working on polymeric materials. For instance, Malana *et al.* [26], reported adsorption capacities of 1.017, 1.875 and 2.610 $mg.g^{-1}$ for Methylene Blue onto three novel polymeric gels.

Figure 15. Freundlich adsorption isotherm of TZ-activated carbon adsorption at 25 °C.

Models	Parameters	Methylene Blue (MB)	Tartrazine [21]
Langmuir Isotherm	q_{max} (mg g^{-1})	3.78	21.8
	K_L (L mg^{-1})	3.3	0.08
	R_L	0.015	0.11
	R^2	0.93	0.99
Freundlich Isotherm	K_F (mg g^{-1} (L mg^{-1})n)	0.39	0.38
	1/n	0.31	0.57
	R^2	0.96	0.97

4. Conclusion

Activated carbon is a promising adsorbent for the removal of the basic and azo-dyes. The removal of Methylene Blue and Tartrazine from artificial solutions using activated carbon has been investigated under different experimental conditions in batch mode. The adsorption of dye was dependent on adsorbent dose, agitation speed, and dyes' concentration in the solution. Initial pH of solution affected the adsorption of this dye. The optimum pH for the removal of Methylene Blue from aqueous solution under the experimental conditions used in this work was 10.0 while for Tartrazine was 3.0. The maximum dye removal was observed within 90 min from the beginning of each experiment. Adsorption data were observed to follow Langmuir and Freundlich isotherm models at the studied temperature.

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THE INVESTIGATION OF BIOCHEMICAL CONTENT OF *Elaeagnus angustifolia*

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ABSTRACT

Studies about herbal products are increasing every day due to their rich biochemical content. *Elaeagnus angustofolia* is one of the best known plant species to have a strong biochemical substance spectrum. This work was performed to identify the some biochemical content of Eleagnus angustofolia. In this study, vitamins A, E, and C, total sugar content, inverted sugar content, cellulose content, amount of total protein, and fatty acid properties were studied. Our investigations revealed that *Elaeagnus angustifolia* has a strong biochemical content.

Keywords: Eleagnus angustofolia, nutritional value.

Introduction

Elaeagnus angustifolia, which is in the family of Elaeagnaceae, is a usually thorny shrub or small tree that is able to grow up to 5–7 m in height. Its stems, buds, and leaves are densely covered by silvery to rusty scales. The plant has leaves that are alternate, lanceolate, having a length of 4–9 cm and width of 1-2.5 cm, along with a smooth margin. The flowers are of highly aromatic nature and grouped in clusters of 1-3, they possess a 1-cm long along with a four-lobed creamy yellow calyx; they begin to appear in the early periods of summer and are followed by a group fruit formation, the appearance being a small cherry-like drupe with a length of 1-1.7 cm, and orange-red formations are present, covered in silvery scales. The fruits are edible and have a sweet taste, though a dry, mealy texture is usually found [1]. This work was performed in order to determine the biochemical content of the species of *Eleagnus angustofolia*. In this study, we have performed the analyses of vitamins A, E, and C, total sugar content, inverted sugar content, cellulose content, total protein content, fatty acid content. Some relevant analyses were also performed and detailed in the experimental section.

Materials and methods

Reagents, chemicals, and instrumentation

Eleagnus angustifolia was obtained from a plant supplier in Elazığ district in Eastern Anatolia, Turkey. All solvents were of analytical-grade and were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, Missouri, USA). All the vitamin analyses were carried out with high-performance liquid chromatographic system (make of Shimadazu) consisting of LC–10 ADVP pumps, SIL-10ADVP, along with a degasser unit DGU-14A and Class VP software (Shimadzu, Kyoto Japan). The unit also has an autosampler, SIL-10ADVcolumn oven, a CTO-10ASVP UV-visible spectrophotometric detector SPD-10AVP. These instruments were connected via a communication module (model CBM-20A) and controlled by a Shimadzu LC solution workstation. As chromatographic column, a Supelcosil LC 18 (15 × 4,6 mm, 5 mm, Sigma, USA) was used. Vitamin A detection had a wavelength of 326 nm and 202 nm, whereas Vitamins E, D, and K were measured at 265 nm. For Vitamins A, D, E, and K, n-hexane, methanol, and acetonitrile were used as eluents in the chromatographic setting. For vitamin determinations, perchloric acid and distilled water were used. The wavelength to measure the absorption was 245 nm, and the chromatographic column used was a simply plain C_{18}. In order to perform the sugar analyses, methylene blue indicator, Fehling-1 reactant (copper(II) sulfate pentahydrate), Fehling-2 reactant (potassium sodium tartrate tetrahydrate) in sodium hydroxide, and phenolphthalein indicator dissolved in ethyl alcohol in 5% (w/w) were used; for cellulose analyses, potassium hydroxide, sulfuric acid, a desiccator to store the anhydrous material, and an incinerator were used. Total protein analyses were performed with the Folin's reagent. The fatty acid composition was elucidated with a Shimadzu gas chromatograph. Fatty acid methyl esters (FAMEs) were produced and introduced into the injection port of a Shimadzu GC 17 instrument (Kyoto, Japan). Machery-Nagel (Germany) capillary column of 25 m length, 0.25 µm inner diameter, and a Permo bond 25 µm thickness was used for this analysis. High-purity nitrogen was used as the carrier gas.

During analysis, mixtures of standard fatty acid methyl esters were injected and the retention time was determined for each fatty acid to learn the unique positions of standards included. After this process, mixtures of fatty acid methyl esters of the samples were analyzed. Examples of the solvents and reactants used include n-hexane, 5 mL of 2% $KHCO_3$, *etc*.

Vitamin A and E analyses

All the other parameters in this study were measured by high performance liquid chromatography (HPLC) using the methods previously described for these vitamins [2, 3]. Briefly describing, plant extracts produced from a mixture of 2:3 hexane – isopropanol (v/v) were divided into small portions and the supernatant was obtained by centrifuging the mixture. An aliquot of 5 mL was taken and put into capped tubes of 25 mL capacity. Then 5% KOH solution (w/w) was added. After vortexing the contents at 85 ºC for 15 min, the tube was allowed to stand. On cooling to room temperature, 5 mL of distilled water was added onto the tubes and then mixed. Unsaponifiable lipophilic molecules were extracted with 10 mL of a mixture of several hexanes. The hexane phase was evaporated under a stream of nitrogen. 1 mL (50%:50%, v/v) of acetonitrile / methanol mixture was used to dissolve the mixture and with the aid of the autosampler, the contents of the vial were introduced into the injection port of the HPLC instrument.

Vitamin C analysis

Vitamin C analysis was performed by using methods available in the literature [11]. 0.2 mL of plant extracts were taken. 0.5 M $HClO_4$ was used to precipitate the proteins. This mixture was vortexed and the total volume was completed up to 1 mL with distilled water. After 15 minutes, the mixture was centrifuged (2500 rpm / min) and then 20 µL of the supernatants was taken carefully to analyze with HPLC.

Total sugar, inverted sugar and sucrose analyses

Sugar analysis was performed according to the regulations outlined in TSE 1466 (Turkish standard), which is basically a volumetric method [12]. For inverted sugar measurements, an aliquot of 5 mL of extract solution was taken and was put into each flask, for a total of 4. The volume of the solution was completed to 50 mL by adding a sufficient amount of distilled water along with 5 drops of phenolphthalein solution. The mixture was neutralized with 0.1 N NaOH solution until the pink color of the solution persisted. The pH value was measured using a pH meter and the pH was adjusted to 7.0. A mixture of 5 mL of Fehling-1 solution and 5 mL of Fehling-2 solution was placed into a flask. 10 mL of distilled water was added. An aliquot of 5 mL of this solution was added into the previously prepared sample, which was being heated to boil. When boiling started, the flask was kept for 2 minutes. After 2 minutes, 10 drops of methylene blue solution were added. 5 mL of the sample solution was added to obtain a brick red color due to copper(I) oxide, which indicates the termination of the experiment. Inverted sugar content was calculated by using the formula below:

$$\text{Inverted sugar} = \frac{V_1 \times V_3 \times F \times 100}{V_4} \times \frac{V_2 \times g \text{ of sample}}{1000} \quad (1)$$

V_1 = volume of the solvent used to prepare the extract, $V_2 = V_{2.1} + V_{2.2}$, V_3 = the volume of solvent used to complete the final volume, F = factor of the solution used, V_4 = volume of the extract solution.

Total sugar analysis was performed by following the regulations of the Turkish Standards Institute with procedure number 1466 as the preferred volumetric analysis [12]. For inverted sugar, an aliquot of 5 mL from the extract solution (V_4) was taken and was added into each flask, for a total of 4. The total volume was made 50 mL by adding sufficient amount of distilled water. Another aliquot of 5 mL from this solution (V_4) was transferred into a conical flask and 2.5 mL of 2 M HCl was added. The flasks were placed in a container, into which a thermometer was submerged, and it was filled with hot water at 70 ºC, and the mixtures were kept for 5 minutes. Then they were cooled under tap water. A few drops of phenolphthalein were added, and the mixtured were neutralized with a solution of 0.1 N of NaOH. The pH value was measured by a pH meter to adjust to 7.0. Another 5.0 mL of sample from this solution received 5 mL of Fehling-1 solution and 5 mL Fehling-2 solution. Then 10 mL of distilled water was added. 5 mL of previously prepared sample ($V_{2.1}$) was added and the mixture was allowed to boil for two minutes after the initiation of boiling. Just through the end of this period, 10 drops of methylene blue solution were added. A portion of 5 mL of the sample was added to obtain brick red color owing to the formation of copper(I) oxide, and the experiment was terminated with the observation of the color. The calculation of total sugar content was performed by using the formula below:

$$\text{Total sugar} = \frac{V_1 \times V_3 \times F \times 100}{V_4} \times \frac{V_2 \times g \text{ of sample}}{1000} \quad (2)$$

V_1 = volume of the solvent used to prepare the extract, $V_2 = V_{2.1} + V_{2.2}$, V_3 = the volume of solvent used to complete the final volume, F = factor of the solution used, V_4 = volume of extract solution.

Sucrose levels were found by utilizing the following formula:

$$\text{Sucrose levels} = (\text{Total sugar} - \text{inverted sugar}) \times 0.95 \quad (3)$$

Determination of cellulose content

Cellulose analyses were measured according to TSE 4966 [6]. A certain amount of sample was taken, dried in an oven for 2 hours, and then crushed in a mortar. 3 grams (m) of the sample was taken and 60 mL of KOH was added. It was allowed to stand for half an hour under reflux. The samples were filtered into crucibles, which were treated with acetone for three times and two times with petroleum ether. The samples were oven-dried at 130 ^{0}C for 1 hour. A dessicator was employed for cooling and then the the crucibles were weighed (w_1). Then, another sample in the incinerator, which was kept at 500 ^{0}C for 1 hour, was cooled in a dessicator, and weighed (w_2).

The following formula was used to calculate the cellulose levels in the sample:

$$\text{Cellulose levels} = \frac{(w_1 - w_2)}{m} \quad (4)$$

Assessment of total protein amount

Protein amount was measured by spectrophotometric manner after Lowry et al [7]. 10 µL of the sample solution was added to the Lowry's reagent, and after waiting for 10 minutes, the sample was diluted with distilled water, and after the addition of Folin's reagent, the sample was measured at 760 nm.

Isolation of Fatty Acids and Gas Chromatographic Analyses of Fatty Acid Methyl Esters

Fatty acid composition was determined according to the method described in the literature [8]. Fatty acids were isolated by the addition of 10 mL of 3:2 (v / v) hexane / isopropanol mixture onto the liquid phase of the samples remaining after LPO measurement. Then the hexane phase was taken into separate test tubes and 5 mL 2% (w/w) methanolic sulfuric acid solution was added, followed by keeping at 55 °C for 12 hours. At the end of this time, 5 mL of 5% (w/w) sodium chloride solution was added and the fatty acid methyl esters were extracted with 5 mL of n-hexane. The mixture was treated with 5 mL of 2% $KHCO_3$ solution (w/w), then the n-hexane phase was evaporated under nitrogen stream [8], fatty acid methyl ester residues were dissolved in 1 mL of n-heptane and taken to autosampler vials. The analyses of fatty acid methyl esters were performed on a Shimadzu GC 17 instrument (Kyoto, Japan). A Machery-Nagel (Germany) capillary column of 25 m length, 0.25 µm inner diameter, and Permobond 25 µm thickness was used for this purpose. Nitrogen was used as the carrier gas. During the analysis, mixtures of standard fatty acid methyl esters were injected and the corresponding retention time was determined for each fatty acid. After this process, mixtures of fatty acid methyl esters of the samples were analyzed.

Statistical analysis

The results were expressed as mean± SD. Statistical analysis and relevant comparisons were performed by SPSS software (Version 17.0).

Findings

All data were presented in Table 4 and Figure 1.

Table 1. Vitamin analysis

Vitamin (N=3)	Vitamin C	Vitamin A (retinol)	Vitamin E (α-tocopherol)
$mg.mL^{-1}$	6.25 ± 0.14	10.1 ± 0.27	5.25 ± 0.24

Table 2. Total sugar, reducing sugar, sucrose, and cellulose levels in g per 100 g of total sugar in edible sources (N:3)

Sucrose	**Reducing sugar**	**Total sugar**	**Cellulose**
0.80 ± 0.81	29.77 ± 0.81	30.19 ± 0.58	4.5 ± 0.21

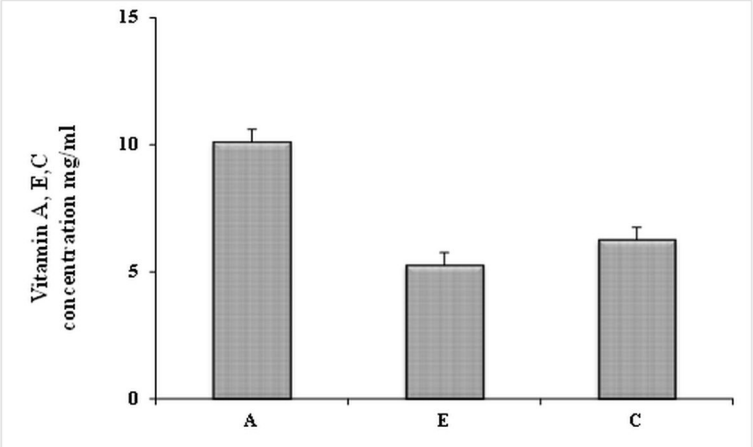

Figure 1. Vitamins used in the level of 20 µM.

Table 3. Total protein levels in mg/g protein of edible sources (N:3)

Total protein amount (N:3)	Value
$mg.g^{-1}$	0.66 ± 0.001

Table 4. Fatty acid composition (in percent) (N:1)

Detected fatty acid	Percentage
C16:0 palmitate	31.41
C16:1 ω-7 palmitoleate	10.40
C18:0 stearate	16.95
C18:1 ω-9 elaidate	8.64
C18:2;6,12, ω-6 linoleate	16.31
C18:3; 9,12.15, ω-3 linolenate	5.13
C20:4 ; 5, 8, 11, 14 ω-6 arachidonic acid	5.23

Discussion

In a previous communication, the authors have detected soluble sugars in *Elaeagnus angustifolia L* samples. The predominant sugars quantified were fructose at 27.1% and glucose at 22.3% of dry weight [9]. While we have found lower values of sucrose in the study, we have identified that the total sugar content was around 30%, which was clearly presented in Table 2. Vitamin A level was detected to be higher than that of vitamin E. Vitamin C was at the highest level among all vitamins present. The data were presented in Table 1 and Figure 1.

The chemical composition of lipophilic acid fractions from *E. angustifolia* cultivated in Russia were determined by GC-MS and HPLC. As a result, 13 species the fatty acid were determined in the extracts. These are namely lauric, tridecanoic, myristic, pentadecanoic, palmitic, palmitoleic, heptadecanoic, linoleic, linolenic, oleic, stearic, eicosanoic, and docosanoic acids [10]. While determining high levels of saturated fatty acids in our study; the unsaturated fatty acid content was observed to be at a lower level. We presented the data in Table 4.

Gonçarov *et al*. reported in their study about the determination of glycolipids and phospholipids of *Elaeagnus angustifiloia*; 9 glycolipids and 7 phospholipids were identified in seed fatty acid component. 8 glycolipids and 3 phospholipids have been identified as the fatty acid component in pericarp [11]. Also in their studies, they reported about the determination of some heavy metal content in *Elaeagnus angustifolia L.* According to their communication, Cu concentration was 25.39 µg / g, Fe concentration was 26.37 $\mu g.g^{-1}$, and Mn concentration was 11.70 $\mu g.mg^{-1}$. In this study, we have found a very low protein amount and the relevant data were presented in Table 3.

Conclusion

Our work and the literature information, in reference to the chemical and instrumental analyses, confirmed that *Elaeagnus angustifolia* has a strong content that might be useful in prospective studies which, we believe, can shed more light on this valuable herbaceous plant.

Declaration of interest

Contributing to our research, sugar and cellulose analyses were performed in Elazig Food Control laboratories for which the authors would like to express their thanks.

Conflict of Interest

We have no conflict of interest.

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