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Evaluation of the Physical and Chemical Properties of Vehicles Brake Pad Particles

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Abstract

Air pollution is a major environmental problem, due to the increasing number of vehicles in Baghdad city streets and their direct impact on the process of air pollution resulting from an exhaust and non-exhaust pollutants (brake, clutch, tire wear, road surface wear and corrosion of vehicle components).

The aim of this study is to detect the chemical and physical properties of brake pad particles as well as the concentrations of heavy metals found in these pad particles. This study included, a collection of eleven (11) samples of brake pads belong to different types of cars, most of these cars were used commonly in Baghdad city streets. The size of break pads particles was examined under Scanning Electron Microscopy (SEM). The results showed that the brake pad particle size with diameters ranged (particle ≥ 0.5 µm). While the concentrations of metallic elements with oxide form (Al, Sb, Cr, Cu, Cd, Fe, Pb, Mg, Mo, Ni, Si, S, Sn, and Zn) which examined in X-ray Fluorescence Spectroscopy (XRF), indicated high concentrations of (Fe> Cu > Si > S >Sb> Zn > Mg > Al >Sn> Cr > Mo) respectively and other examined elements concentrations within the range of World Health Organization (WHO).

Keywords: Brake pad particles, Metallic elements,X-Ray Fluorescence Spectroscopy (XRF).

تقييم الخصائص الفيزيائية والكيميائية لدقائق وسائد مكابح السيارات

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الخلاصة

يعد تلوث الهواء من المشاكل البيئية المهمة، نظراً لزيادة عدد السيارات في شوارع مدينة بغداد وتأثيرها المباشر في عملية تلوث الهواء الناتج من عوادم السيارات ومن غير عوادم السيارات (مكابح السيارات، والإطارات، والقابض، غبار سطح الطريق، وتآكل مكونات السيارة).

الهدف من هذه الدراسة هو التحري عن الخصائص الفيزيائية والكيميائية لدقائق وسائد المكابح وكذلك تراكيز المعادن الثقيلة الموجودة في تركيبها.لتحقيق هدف الدراسة ،حيث تم جمع العينات وكانت (11) عينة من وسائد مكابح السيارات والتي تعود إلى أنواع مختلفة من السيارات ، معظم هذه السيارات شائعة الأستخدام في شوارع مدينة بغداد، فضلا عن قياس اقطار الدقائق لوسائد مكابح السيارات بواسطة المجهر الألكتروني.وأظهرت النتائج أن أقطار جزيئات وسائد مكابح السيارة مساوية أو أكبر من (0.5) ميكرومتر.بينما وجد ان تراكيز المعادن الثقيلة والتي تم فحصها بأستخدام طريقة فلورية الأشعة السينية، أشارت النتائج ان

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وسائد مكابح السيارات اظهرت تراكيز عالية لكل من (الحديد>النحاس> السليكون>الكبريت > الأنتيمون> الزنك>المغنسيوم>الألمنيوم>القصدير>الكروم>الموليبدنوم) بالترتيب أما العناصر المفحوصة الأخرى كانت ضمن حدود منظمة الصحة العالمية.

1. Introduction

Road traffic emissions are a major contributor to ambient particulate matter concentrations (both PM_{10} and $PM_{2.5}$) and these emissions are targeted through increasingly stringent European emission standards. These legal restrictions succeed in reducing exhaust emissions, but do not treat "non-exhaust" emissions from brake wear in an air of road dust. Several studies were done to understand the synthesis, composition, and distribution of brake pad dust because of the growing realization of environmental and health effects [1]. In the 2000 year, the World Health Organization (WHO) and the Environmental Protection Agency (EPA) are reporting exceeded limits of air pollutants, leading to reverse effects on public health and on ecosystems, where the pressures of air pollution impair vegetation growth and damage biodiversity [2].

The brake pads for vehicles have a complex composition containing even more than thirty different components, some of them more dangerous to health than others. The range of such emissions depends on their chemical and physical properties and on the tribological interactions with the surface disc (rotor) during the braking stages [3]. The majority of the braking system for a vehicle consisting of three parts: first; A disc (rotor), second; Pads and third; Caliper, Disc (rotor) usually are made of grey cast iron or aluminum used in passenger vehicles, while brake pads linings generally include five main complex components: fillers, binders, fibers, frictional additives or lubricants and abrasives. The structural of lining brake pad made under mechanical and thermal stress. The different five of reinforcing fibers present in the lining of brake pad types are usually found in passenger vehicles: metallic, semi-metallic, low metallic, non-asbestos organic (NAO), and ceramic brake pads. The brake pad lining contains metallic elements contents such as Fe, Cu, Zn, Cd, Al, Cr, Pb, and other [4]. The vehicle brake function transforms vehicle kinetic energy into thermal energy. The frictional contact between the disc (rotor) and the brake pad generates particles of different sizes. Number distribution of airborne brake pad particles range between (100-300) nm, and particles sizes range between (1-10 μm), [5]. Or range between (2-15 μm), while the number distribution of airborne brake pad particles range (320) nm [6]. The aims of the present work are to evaluate the physical and chemical of brake pads particles for the car present in Iraq by Scanning Electron Microscope (SEM) and X-ray Fluorescence Spectroscopy (XRF).

2.Materials and Methods:

2.1 Collection of samples:

Eleven (11) samples of brake pads belong to different types of cars, were collected to determine the physical and chemical constituents concentrations in these pads. Most of these cars were used commonly in Baghdad Street. Brake pad samples number (1- 10) were converted from compact state to powder state by using file metal device and(the sample 11) taken from a wheel of the car after friction of brake pad, Table (1-1).

Table (1-1)-Types of common cars and brake pads

Numbering of samples	Types of common cars	Origin of brake pads
1	Chevrolet optra (2008-2015)	USA
2	Geely (2009-2016)	China
3	Khodrosamand (2012-2017)	Korea
4	Mitsubishi lancer (2007-2017)	Japan
5	Peugeot roa (2006-2010)	Iran
6	Samand (2012-2015)	Iran
7	Samand (2007-2009)	Iran
8	Saipa 1 (2012-2018)	Iran
9	Saipa 2 (2012-2018)	Korea
10	Saipa 3 (2014)	Iran
11	Saipa 4 (2015)	Iran

2.2 Laboratory work

The brake pads samples that collected from different common cars were examined in the laboratories, all samples followed the same analysis procedures in order to determine the physical properties and its chemical constituents.

2.2.1 Determination of brake pads particles diameters:

The purpose of this examination was to determine brake pads particles diameters (size) and shape which considered as the most important physical properties[7], by using two methods: First Scanning Electron Microscopy (SEM)-(TESCAN - VEGA3, Czech Republic: origin) in a magnification power of (500x,1.00kx,5.00kx and 10.0kx) that available in the laboratories of the Environmental Research Center of the Ministry of Science and Technology. The second method to determine the diameters of particles in the laboratory by using a light microscope provides with oculometer (the stage micrometer is simply a microscope slide with a scale etched on the surface) [8]. Particles diameters were calculated after dividing into three sizes ranging from sequentially (particle ≤1 µm, particle between 1-5 µm, particle ≥ 5µm).

2.2.2 Chemical measurements of brake pads components:

The method was used to detect the chemical constituents of the samples was X-Ray Fluorescence Spectroscopy (XRF) examination, the method of detecting metallic elements of brake pads powder is achieved by using the X-Ray Fluorescence Spectroscopy (XRF) device. Measurement of elements in the oxides form, the weights of each examined sample were (3) gm [9]. Different of metallic elements are detected by this method (Fe, Cu, Sb, Zn, Cr, Mg, Sn, Mo, Al, Cd, Pb, Ni, Si, and S) and others.

3-Results and Discussion:

3.1 Physical properties brake pad particles under Scanning Electron Microscopy (SEM):

The examination of (SEM) for brake pad particles showed that some particles had smooth edges (nearly spherical) others had few sharp edges (amorphous shape) Figures (1-1), (1-2). Fibrous shapes could be detected in Figure (1-1C) some particles were less than (0.5 µm) in diameter and others were larger. This result agreed with they observed in visual magnification of (500x) organic particles with fiber shape in the sample of brake pad particles [10].

Other study observed that brake pad particles under (SEM) figure can also easily be seen that the larger particles "attract" numerous smaller fractions to their surfaces. This is relevant when considering that inhalable particle fractions smaller than100 µm may "carry in" significant amounts of smaller particulates and enter a body by respiration or gastrointestinal tract after swallowing larger particles [11]. While in the other study referred that the SEM pictures showed brake pad particles size in the nanometer and micrometer range. Most frequent were semi-spherical agglomerates. No fibers could be detected and the particle number concentrations distribution, with a maximum diameter at (0.5–1) µm [12].

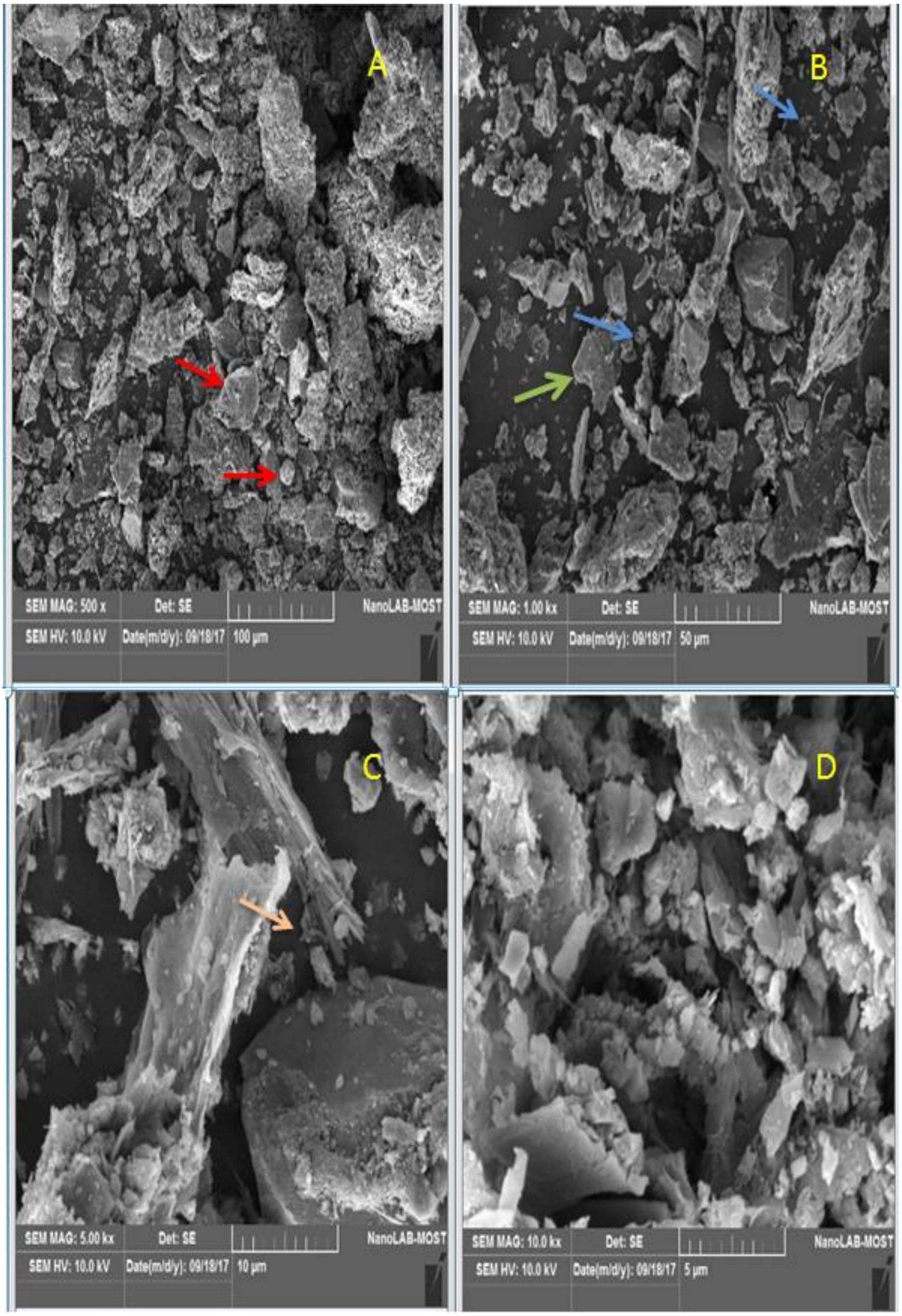

Figure (1-1)-Scanning electron microscopy pictures of brake pad before friction. (A)red arrow: semi-spherical shape (500x magnification); (B)blue arrow: amorphous shape, green arrow: Sharp edge (1.00 kx magnification);(C) fiber shape (5.00kx magnification);(D) 10.0kx magnification same sample.

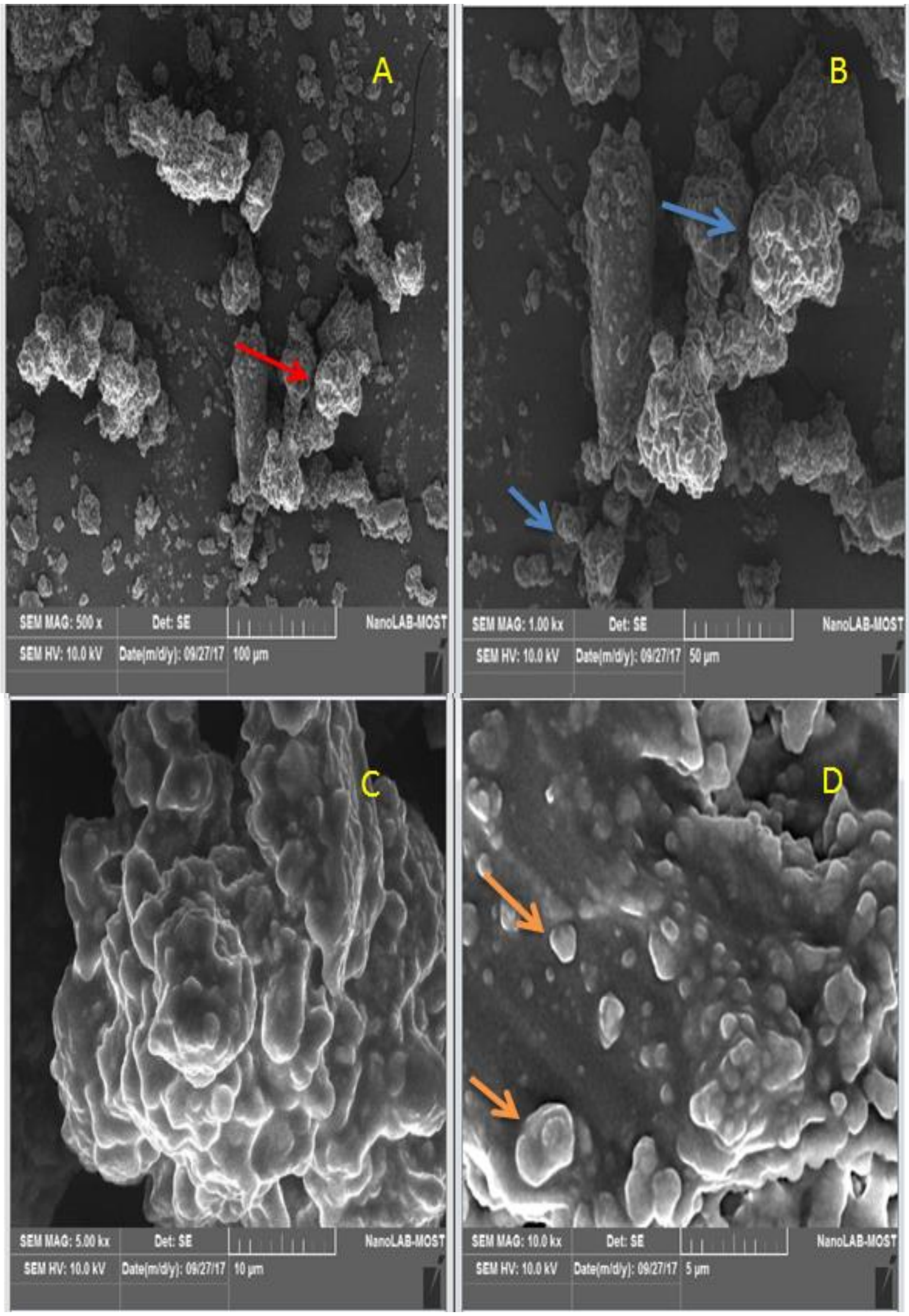

Figure (1-2)-Scanning electron microscopy pictures of brake pad particles accumulated after friction. (A) red arrow: aggregate shape (500x magnification); (B) blue arrow: amorphous shape (1.00 kx magnification); (C) 5.00kx magnification same sample; (D) semi-spherical shape (10.0kx magnification).

This study showed the analysis of the brake pads size using an Aerodynamic Particle Sizer (APS) spectrometer, they observed that the range of particles size between (0.5 μm to 20 μm), [13]. While in their study referred that SEM images of pad particles demonstrated that ultrafine and some of the fine particles seem to be smoother with fewer sharp edges compared to bigger particles, although the friction pad to produce particles processes during braking were not only accompanied with increases of temperature but also with the formation of considerable mechanical stress [8].

Samples of dust accumulated after friction from brake pads particles containing micron-sized particles, which had agglomerated to combine into a variety of shapes. A large proportion of these particles had a grain size of less than 5 µm. These observations match the findings, who ascertained that the action of breaking causes a reduction in the size of particles [14]. Other study mentioned that the particles concentration with a diameter larger than (1µm) decreased gradually and the increasing of submicron sized particles can easily be observed. The Thermo-gravimetric (TG) and Differential Scanning Calorimetry (DSC) analyses improved this observation as well as the character of chemical changes of the brake pad composition [15]. The results of current study referred that the accurate brake pad particles percentage (%) were calculated by using an optical light microscope for different sizes (particle ≤1, particle between1-5, particle ≥5) µm, Table-(1-2).

1) Particle ≤ 1----- (47.7) %
2) Between (1-5) ----- (22.9) %
3) Particle ≥ 5----- (29.4) %

In a previous study the tested different brake pads found that 63 % and 86% of the brake wear airborne particles mass was distributed in the PM_{10} and $PM_{2.5}$, respectively. A considerable 33 % (by mass) of brake pads particles was found with diameters smaller than 0.1µm [16]. In another study the tested different brake pads particles found that PM_{10} accounted for 63–85 % of the total brake wear mass, depending on the type of pad [17]. The previous two studies were compatible with the results of the current study.

Table (1-2)-Percentage (%) brake pad particles of samples used in this study.

No. of samples	(Particles ≤1µm) (%)	(Particles between1-5µm) (%)	(Particles ≥5 µm) (%)
1	42	33	25
2	63	21	16
3	48	31	21
4	55	25	20
5	48	13	39
6	41	22	37
7	31	28	41
8	45	24	31
9	45	13	42
10	59	19	22
Total sum	47.7	22.9	29.4

Other study reported that (56–70) % of total brake wear mass generated from three different Non-Asbestos Organic (NAO) pads emitted as $PM_{2.5}$ [18]. The previous study referred that the generation of brake pads particles (particle > 0.5µm) at low disc rotor temperature conditions is less as compared with the concentration of particles smaller than (0.1µm). The generating of small particles increased significantly increased with the increase of the cast iron disc temperature (up to 340 ˚C) [5].

3.2 Chemical characterization of brake pad particles

Several epidemiology studies have correlated adverse health responses with the presence of specific chemical species and trace elements (metallic elements) in the ambient PM which generated from brake pad [19]. Modern brakes are composites of many different and sometimes unknown ingredients, and even if the chemical composition of brake wears debris emission significantly differs from the chemical composition of the original pad lining material [5].

The test in the current study was shown the concentrations of elements in the oxides form of the twenty measured elements (Al, Sb, Cr, Cu, Cd, Fe, Pb, Mg, Mo, Ni, Si, S, Sn, and Zn) in the brake pads samples, Table-(1-3). Low concentrations of metallic elements found in brake pads samples detected using (XRF).

Table (1-3)-Trace elements (oxides form of elements) concentrations found in emitted brake pads dust using (XRF) method, (S): Sample, the yellow color refers to a values which are above WHO limits.

Unit	**(µg/m³)**					**WHO limits µg/m³ (1997,2000,2003, 2004, 2007, 2010 and 2017)**
Elements	**S1**	**S2**	**S3**	**S4**	**S5**	
Aluminum	1.46	2.81	2.07	4.49	2.93	0.0005-1), [20](
Antimony	0.00204	0.38000	0.01145	0.01145	0.00134	0.01-1), [21](
Barium	0.0072	0.3300	0.2600	1.4700	20.3000	0.005-1), [22](<
Calcium	38.59	35.03	38.93	11.23	35.39	Less (5), [23]
Chromium	0.03581	0.86000	0.02139	0.03375	0.00032	Less 0.1), [21](
Copper	0.0254	0.5900	0.0491	0.0246	0.0228	Less (1), [24]
Cadmium	0.00138	0.00092	0.00092	0.00092	0.00092	Less (0.3), [25]
Iron	48.88	17.52	7.26	75.99	30.77	Less (1), [21]
Lead	0.01305	0.13000	0.05178	0.02119	0.00966	0.5-1), [25](
Magnesium	7.37	5.14	1.53	0.16	3.93	(0.03-1), [25]
Manganese	0.34	0.25	0.14	0.54	0.37	0.01-0.03), [22](
Molybdenum	0.01008	0.00848	0.00530	0.00875	0.00836	(0.001-0.01), [23]
Nickel	0.02098	0.06405	0.01863	0.02247	0.03262	Less (0.5), [26]
Potassium	0.38	1.14	0.77	2.17	0.28	----
Silicon	16.38	13.51	8.12	18.30	10.84	0.05-0.1), [24](
Sulfur	0.78	1.32	2.50	1.92	7.34	Less (1), [22]
Tin	0.01020	0.02190	0.00913	0.00121	0.01122	Less (0.01), [24]
Titanium	0.34	0.73	0.69	0.49	0.52	Around (0.2), [23]
Zinc	0.3700	0.5200	0.4300	0.6500	0.0584	0.1-1), [21](
Zirconium	0.0075	0.0062	0.0162	0.0198	0.0230	Less (0.01), [26]

Unit	**(µg/m³)**						**WHO limits µg/m³ (1997, 2000, 2003, 2004, 2007, 2010 and 2017)**
Elements	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	
Aluminum	1.48	3.18	2.38	1.83	1.77	0.86	(0.0005-1), [20]
Antimony	17.5900	0.02530	2.77000	1.37000	0.26000	0.00199	(0.01-1), [21]
Barium	3.0400	14.0000	17.1200	10.0100	16.9200	1.5400	(<0.005-1), [22]
Calcium	6.90	25.59	21.69	24.18	36.96	18.21	Less (5), [23]
Chromium	0.06741	0.06933	1.15000	0.64000	0.15000	0.07214	Less (0.1), [21]
Copper	22.4600	0.1800	2.2500	1.1500	0.2800	0.0801	Less (1), [24]
Cadmium	0.00092	0.00092	0.00092	0.00092	0.00092	0.00092	Less (0.3), [25]
Iron	82.07	33.07	41.91	32.02	47.35	47.71	Less (1), [21]
Lead	0.17000	0.04500	0.10000	0.09152	0.15000	0.04152	0.5-1), [25](
Magnesium	2.44	2.15	7.15	7.46	2.13	3.04	(0.03-1), [25]
Manganese	0.70	0.41	0.44	0.32	0.40	0.28	(0.01-0.03), [22]
Molybdenum	0.05878	0.01036	0.02609	0.01730	0.00039	0.00455	(0.001-0.01), [23]
Nickel	0.02773	0.03313	0.04355	0.06496	0.01800	0.03798	Less (0.5), [26]
Potassium	0.76	1.32	0.77	0.57	0.96	0.27	----
Silicon	11.72	15.76	12.96	13.07	7.26	10.21	(0.05-0.1), [24]
Sulfur	18.29	8.49	6.38	4.01	3.80	2.99	Less (1), [22]
Tin	2.52000	0.01170	0.03573	0.02967	0.02680	0.01190	Less (0.01), [24]
Titanium	0.76	0.99	2.36	1.35	0.71	0.34	Around (0.2), [23]
Zinc	8.16	0.82	1.47	1.25	0.63	0.21	0.1-1), [21](
Zirconium	0.0131	0.0707	0.6700	0.4600	11.6800	0.0120	Less (0.01), [26]

The results of the current study compared with standards of WHO elements. The three elements (Cd, Pb and Ni) records normal limits in brake pads samples, the other elements such as aluminum (Al) its values range between (1.46-4.49) µg/m³in all examined samples except for sample (S11) which record values within the range of WHO. Chromium (Cr) values in S8 and S9 range between (0.64-1.15) µg/m³ and exceeded WHO limits while samples (S1,S3,S4,S5,S6,S7,S10, and S11) values within the range of WHO. Copper (Cu) values range (1.15-22.46) µg/m³ in (S6,S8, and S9) while samples (S1,S2,S3,S4,S5,S7,S10, and S11) values within range of WHO limits. Iron (Fe) values range between (7.26-82.07) µg/m³, Zinc (Zn) values (S6,S8, and S9) range between (1.25-8.16) µg/m³ while samples (S1,S2,S3,S4,S5,S7,S10, and S11) values within range of WHO. Magnesium (Mg) values range (1.53-7.46) µg/m³ except for sample (S4) within range of WHO, Tin (Sn) most samples within limit of WHO, except for sample (S6) value was (2.520) µg/m³, Molybdenum (Mo) most samples within limit of WHO, except for sample (S8) slightly high value was (0.026) µg/m³. Silicon (Si) values range between (7.26-18.30) µg/m³, Sulfur (S) values range (1.32-18.29) µg/m³ except for sample (S1) within range of WHO. Antimony (Sb) values (S6,S8, and S9) range between (1.37-17.59) µg/m³ while samples (S1,S2,S3,S4,S5,S7,S10, and S11) values within normal limit of WHO, dependent on the Table (1-3). This study shows the order of examined elements from high values which are Fe> Cu > Si > S >Sb> Zn > Mg > Al >Sn> Cr > Mo in brake pad dusts samples. Other elements (Ba, Ca, Mn, K, Ti, and Zr) could only be determined qualitatively due to the special matrix characteristics of brake pads.

The result indicated that iron (Fe) element concentrations were high as compared with range of WHO and with other elements, this result similar to previous study in which high concentration of Fe can reach between 1% and up to 60% in lining pad materials, this variety in concentrations according to the type of pad lining [27]. A further study mentioned that the braking process effects on the chemical composition of brake pad particles. Despite the large variation in the chemical composition of commercial lining materials, most researchers have reported Fe, Cu, Zn and Pb to be the most abundant metals in the brake pad lining [28]. Other elements Zn and Cu in test recorded high concentrations compared with standard values of WHO, but these values consider less than iron, this result agreed with the result, in which the Cu and Zn record high concentrations [13]. Lead (Pb) element observed which records normal limit, In the study [29], they mentioned that significant Pb content (up to 12% wt. from brake pad lining) has been reported in older studies while new studies showing a remarkable decrease (0.2% wt. from pad lining) due to the replacement of Pb in modern pads linings [5].

For Sb high values especially at samples (S6, S8, and S9) were observed, while the samples (S1, S2, S3, S4, S5, S7, S10, S11) values records concentrations within standard limits, Table-(1-3). The previous study referred that the brake pad particles emissions have been cited as a potentially important source of Sb. Brake linings contain (1–5% wt. from pad lining) Sb in the form of stibnite (Sb_2S_3), which is employed as a lubricant in order to reduce vibrations and improve friction stability [30]. For the elements (Al, Cd, Cr, Ni) and (Mg, Mo, Sn) which detected by (XRF) slightly high concentration of samples were recorded, While (Ni)values range between (0.027-0.180) µg/m³ within WHO limits. The previous study was compatible with the results of the current study, they mentioned in their studies metals such as (Mg, Mn, Ni, Sn, Cd, Cr) have also been found in concentrations lower than (0.1%wt.) from the pad lining material and depending on types of pads [5], [31].

Other study mentioned that the elements (Si, S) detected through (XRF) recorded high concentrations compared with WHO limits, and the researchers showed a higher content of Si range between (12.3-15.9)% wt. of pad lining materials [32]. Also, they found the primary silicon particles were very coarse and their distribution in the matrix is not uniform in shape. Also, they found the highest sulfur S (2.4-3.3) % wt. as compared with WHO limits [33].

The conclusion of the present study provided evidence of the high concentration of some heavy metals in the brake pad of vehicles. Therefore, break pad particle considered as an important non-exhaust air pollutant.

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