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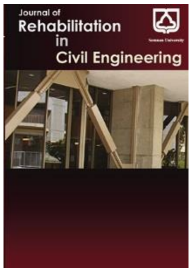

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Rehabilitation of Asphalt Pavement to Improvement the Mechanical and Environmental Properties of Asphalt Concrete by Using of Nano Particles

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ABSTRACT

Dealing with the pollution released into the air by vehicles is a major concern for many countries around the world. There is an increasing trend toward environmental considerations as well as road logistics issues, resulting in doing experiments on new materials, which can help reducing the amount of pollutants in the atmosphere. In this research, the photo catalytic properties of Nano TiO2/SiO2 used over the asphalt roads in order to absorb the pollution substances from the atmosphere are investigated. The above mentioned compound reacts with UV light and oxidizes the pollutant particles including nitrogen oxides (NOx) as well as volatile organic compounds (VOC). In this method, the sol-gel technique was used to produce photo catalyst based on TiO2/SiO2. One purpose of this research is to examine the photo catalytic properties of the compound when it is used in a hot mix asphalt (HMA). Another aim of the study is to find and describe both rheological and mechanical characteristics of the hot mix asphalt (HMA) as well as the Nano modified agents. The resulting asphalt would have the advantages of HMA, including lower energy requirements and less emission during production, while having photo catalytic characteristics of TiO2/SiO2 to absorb and decompose the organic and inorganic air pollutants. The outcomes of the tests showed that adding the Nano TiO2/SiO2 modifier to the asphalt binder effectively removed NOx particles from the air and enhanced the rheological properties of bitumen. It also enhanced the hardness and viscosity of the pavement, while reducing its penetration and fatigue life. When TiO2/SiO2 was sprayed as a water based coating, the efficiency of NOx reduction ranged between 41 and 63%.

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1. Introduction

There are many evidences that show the conventional asphalt we use today need to be improved. With increasing loads and number of axles on the roads, particularly those of overweight (OW) and superheavy loads (SHL), highway agencies need to adopt policies for accommodating this increase without jeopardizing pavement performance [1].

In the past decades, the demand for modified asphalt binder had a strong increasing trend [2].

Factors such as oxygen, ultraviolet (UV) light of sun, and heat, affect both physical properties and chemical structure of asphalt, and cause a phenomenon called aging.

The vast application of modified asphalt binder has led all Departments of Transportation (DOT) within U.S. to develop test specifications for modified asphalt binders [3] Almost all the countries faces a significant challenge in controlling air pollution resulting from transportation activities. Although attempts are made to lower vehicle emission standards, a method is needed to remove these pollutants once they are emitted to the atmosphere.

The potential of titanium dioxide (TiO_2) as an air purifier in urban and metropolitan areas, which suffer from high concentration of air pollutants, has been widely recognized in literature Nanotechnology deals with particles with at least one characteristics dimension in the length scale of 1 to 100 nm. In this length scale, asphalt binder particles have different physical and chemical properties mainly due to their high surface area and quantum effects [4, 5].

The latest studies done by the authors and other researchers showed that the concrete pavement treated with TiO2 gives excellent results, so that a thin layer of coating when applied close to the source of pollution can reduce a significant amount of pollutants such as nitrogen oxides (NOx) as well as volatile organic compounds (VOC) from the air. Shafabaskh et al. performed in-direct tensile fatigue (ITF) and repeated load axial (RLA) tests on nano-TiO2-modified and control SSMA samples, and showed a better fatigue cracking and rutting performance of the modified mixtures [4-7].

Because traffic growth is concentrated mainly in urban areas, it has increased the production and emissions of pollutants with higher concentrations in these regions. Increasing environmental pollutants has led thinkers of human societies to seek a solution to the rising problems of transportation. Share of energy-consuming sectors in pollutant emissions and share of fossil fuels in pollutant emissions in 2009 are presented in Table 1 and Table 2.

Intra-city traffic is one of the main sources of pollutants that is detrimental to human health and causes many environmental effects that air pollution caused by traffic and its impact on the health of pedestrians and cyclists can be summarily pointed out.The aim of the current research is to test the theory that Nano TiO2/SiO2 works as a photocatalytic agent when added to HMA mixture. For this purpose, a crystallized anatase-based titanium dioxide and silica dioxide powder were mixed with a 60/70 grade asphalt binder at four levels by weight of the binder (A, B, C and D). The resulting emulsion (TiO2/SiO2 binder) was sprayed onto the asphalt pavement by the amount of 0.25 kg/m^2. The properties of the prepared mixtures were evaluated by means of Superpave rheological tests, such as dynamic shear rheometer, rotational viscosity, and classical tests, as well as evaluating the effectiveness of the mixture in decomposing the percentage of NOx particles from the airflow. Even though there have been many studies on the asphalt mixtures made of Nano modified particles, little studied are done on bitumen that are modified by Nano composite particles.

Table 1. Share of energy-consuming sectors in pollutant emissions in 2009[5].

Portion/Gas	N_2O	CH_4	CO_2	SPM	CO	SO_3	SO_2	NO_x
Homestic, Commercial and Public	4.5	8	25.7	2.9	0.6	7.8	6.5	6.7
Industry	2.7	4.2	15.8	4.6	0.4	30.2	20.5	9.0
Transportation	48.0	87.7	24.9	78.1	96.9	38.9	32.4	49.6
Agronomical	40.2	1.6	2.5	8.0	0.3	2.6	4.4	3.9
Refinery	0.4	0.7	3.2	-	-	-	-	-
Powerhouse	4.2	6.6	27.9	6.3	1.8	20.4	36.3	30.7
Total	100	100	100	100	100	100	100	100

Table 2. Share of fossil fuels in pollutant emissions in 2009 [5].

Gas/ Fuel	N_2O	CH_4	CO_2	SPM	CO	SO_3	SO_2	NO_x
liquid gas	0.7	4.4	1.5	-	0.1	-	0.002	0.1
Benzene	21.2	52.9	10.4	7.8	95.6	-	0.5	17.4
Kerosene	1.2	1.4	3.2	-	0.1	-	0.9	0.2
Gas oil	67.3	9.2	18.0	75.8	1.8	38.7	31.8	38.6
Fuel oil	3.6	4.4	13.7	4.9	0.7	59.7	63.7	11.4

2. Background

When the TiO2 catalyst is exposed to a photon irradiation with energy equal to or higher than the energy gap (3.2 eV), an electron cavity that stimulates reactive oxygen groups such as radical hydroxyl and radical superoxide is produced. These radicals are directly involved in the oxidation process to decompose the pollutants and bacteria. The rate of reaction progress in heterogeneous catalytic reactions enhances with an increase in active surface area. Nano catalysts are much more effective than typical catalysts for two reasons: first, their very small size (generally from 10 to 80 nm), which produces an extremely large surface area. Second, when materials are made on a nanoscale, they acquire properties that are not found in their macroscopic counterpart that both of these reasons make the nanocatalysts more effective and versatile. In addition to nanocatalysts, mixed oxides can be raised for environmental applications such as the control of emissions from the chemical and petrochemical industries and automobile exhaust [8]. Studies show that ultraviolet light (UV) with k < 390 nm can stimulate the photocatalytic material for decomposing organic compounds such as dirt, smut, grime, oil, etc., microorganisms such as mold, algae, bacteria, and allergens, air pollutants including VOC, tobacco smoke, NOx, and Sox) as well as odors (chemical substances)[8]. The resulting products are O2, CO2, H2O, SO4-2, nitrate and other inorganic particles. One of the most widely material used as a photocatalyst suitable for pavement purposes and can help reducing pollutants emitted by the vehicles. TiO2 has many advantages when used as a photocatalytic material, such as its low cost and fast reaction time at standard ambient conditions (room temperature and atmospheric pressure). By activating TiO2 using UV light (< 378 nm), a variety of organic pollutants are converted to carbon dioxide and water. In this reaction no other chemical compounds has to be used and there is no side reactions take place [9].

The TiO2 existing on the pavement surface decomposes the motor vehicles exhaust using UV radiation from the sunlight. The pavement desorbs the reaction products. Self-cleaning is another application of photocatalytic materials. When surface pollutants are decomposed in the oxidation process, it results in a clean surface, which is extremely hydrophilic [10]. Some factors can exert influence on the efficiency of photocatalyst substance, including light wavelength and intensity, relative humidity, temperature and wind. High temperature and light intensity (>300 nm) improves the photocatalytic effect [11]. In a study done in Hong Kong, the blocks used for pavement were coated with TiO2 and left in the environment for a period of 4 and 12 months in five pedestrians [12]. The research on photocatalytic effect first began by Fujishima and Honda works when they studied photo-electrochemical solar energy conversion. Inspired by photosynthesis phenomenon in plants, the researchers tried to make redox reactions induced by light phonons, using a semiconductor exposed to UV light, in order to oxidize water and reduce carbon dioxide [13]. The interest in environmental photocatalysis has been increasing. This let to applying TiO2 on glass, tile, paper and pavements for a variety of applications such as self-cleaning substances, purifying water and air, sterilization and soil spill remediation. These researches revealed that the process could decompose both organic and inorganic materials and that surficial TiO2 is capable to regenerate itself [13]. Hydroxil radical and superoxides are produced by TiO2 when exposed to UV light. These two compounds oxidize and reduce pollutants such as VOC and NOx, respectively [14]. The following reactions show NOx oxidation through hydroxyl radicals. The reactions take place when photocatalyst is present.

$$NO + \dot{O}H \xrightarrow{TiO_2} NO_2 + \dot{H}$$
$$NO_2 + \dot{O}H \xrightarrow{TiO_2} NO_3 + \dot{H} \qquad \text{Eq. (1)}$$

Concerning the above different photocatalytic oxidation formulas, water-soluble nitrates are the products of NO_x oxidization, which run-off water from the rainfall can remove these substances. The crystallization of TiO_2 takes place in three types, including anatase, rutile, and brookite. At higher temperatures, anatase, which is a meta-stable phase, can be converted to rutile [15]. According to the studies, the anatase form of the TiO_2 has more power than rutile and brookite for purifying pollutants [16]. Hydrophobic characteristics are favorable when preparing TiO_2 coating, which creates a self-cleaning surface. Pollutants are attached to the rainwater droplets and are washed away from the surface.

TiO2 is mostly applied through pavements made of concrete composed of cement, sand, TiO2 and water, where the resulting concrete is used as a thin cover over the pavement surface. Not many researches are done on asphalt pavements. In this case, TiO2 is mixed with the asphalt binder to be used as pavement or be sprayed on the pavements [17, 18]. According to the studies, the NO_x reduction efficiency of Nano TiO_2 ranges between 20 and 57 percent. Chinese researchers used an asphalt containing 2.5% TiO_2 by weight in the emulsified binder [18]. In a research, by designing the UV irradiance, the compositions and the initial concentrations of automobile exhaust, an asphalt mixture test system – photocatalytic decomposition of automobile exhaust performance (AMTS-PDEP) was developed based on the photocatalytic mechanism of titanium dioxide (TiO2). The results show that the PDEP of anatase TiO2 is much better than Rutile TiO2. The PDEP of asphalt mixture with 0.3 μm TiO2 is better than other particle sizes. Affected by particle adhesion, the PDEP of asphalt mixtures with 3.5% content of TiO2 reaches the maximum value. It is recommended that anatase TiO2 (0.3 μm) is used as the photocatalyst, the optimum TiO2 content is 3.1%, TPS modified bitumen is used as the binder[19]. Another research carried out the NO2 degradation performance and asphalt pavement performance of SBS modified asphalt with different content (0%, 1%, 2%, 5%, 10%) of nano-TiO2, and the impact of cationic surfactant were evaluated as well. Results show that the nano-TiO2 increased the rutting resistance of asphalt in high-temperature. Also, this research conducted photo-catalytic degradation test of NO2 for asphalt mixture with 5% nano-TiO2 content. The analysis shows that there are reversible reaction between NO2 and N2O4, and results indicated that the asphalt mixture has exhibited NO2 degradation effects[20]. Titanium dioxide (TiO2) is a photocatalyst which can accelerate the oxidation of nitrogen oxides (NOx) and other pollutants under ultraviolet (UV) radiation. The composition of the TiO2-cement mortar was optimized in terms of its mechanical properties. The long-term NOx degradation efficiency, abrasion resistance, and skid resistance of the spreading material were measured after it was subjected to 300 min polishing by the advanced Aachen Polishing Machine (APM). It was concluded that durable NOx degradation efficiency can be achieved by the developed method and the method is feasible for practical implementation[21]. In the present research, the rheological and mechanical characteristics of hot mix asphalt (HMA) as well as Nano TiO_2/SiO_2 binders, and whether they can work as photocatalytic substance when used in a Hot mix asphalt. For this purpose, different percentage of Nano composite materials in the form of powder is applied to the bitumen and tests were done to measure the rheological properties of bitumen samples. To evaluate bitumen resistance to fatigue, the fatigue test was also used on the specimens.

3. Experimental Procedure

3.1 Materials

The following table (Table 3) shows the crushed lime aggregates used in this research. The aggregates were graded according to AASHTO type IV scale standard. Nano powders composite was blended with a 60/70 penetration grade HMA asphalt binder (AC-10) whose properties of these virgin binders are shown in Table 4.

Table 3. Gradation of aggregates used in the present study.

Sieve(mm)	**19**	**12.5**	**4.75**	**2.36**	**0.3**	**0.075**
Lower–upper limits	100	90 – 100	44-74	28-58	5-21	2-10
Passing (%)	100	95	59	43	13	6

Table 4. The physical properties of the bitumen used in this study.

Property	Test method	Quantity	Specification limit
Penetration at 25 ^{o} C, 100g, 5 s (deci-mm)	ASTM D-5	66	60-70
Softening Point, ring and ball (^{o} C)	ASTM D36	51	49-56
Flash Point, Cleveland open cup (^{o} C)	ASTM D-92	262	Min 232
Ductility at 25 ^{o} C at 5 $^{cm}/_{min}$ (cm)	ASTM D-113	111	Min 100
Loss on heating, (%)	ASTM D-6	0.06	Max 0.8

Based on sol-gel method, Nano TiO2 powder is mixed with the asphalt binder, which is in emulsified state. Nano silica has found many uses in various applications

such as catalyst carriers, additives, rubber agents, plastics fiber and as a viscous agent in graphite materials. High stability, extremely large surface area, excellent adsorption, high dispersion capacity, and extreme pureness. These characteristics make the substance a good candidate for use a modifier to be added for asphalt mixture [22]. Table 5 shows Nano silica chemical and physical characteristics. In Figure (1), the SEM image of Nano silica. The image is magnified by 3000 times.

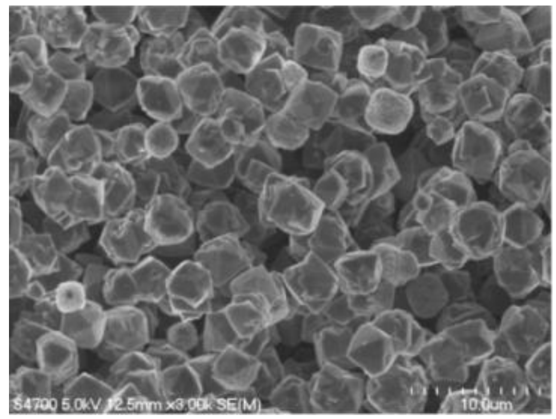


Fig.1. SEM image of Nano silica at 3,000× magnification.

Nano silica powder with the average diameter of 25 nm was used in the present research. Table 6 demonstrates the properties of the utilized Nano silica particles.

Table5. Chemical composition and physical properties of Nano silica.

Item	SiO_2 (%)	Ti (ppm)	Ca (ppm)	Na (ppm)	Fe (ppm)
Nano silica	≥99%	<120	<20	<50	<200

Table6. The physical properties of Nano silica.

Diameter (nm)	Surface volume ratio (m^2/g)	Density (g/cm^3)	Melting point(^{o}C)
20-30	130-600	2.1	1,600

Titanium dioxide (TiO2) is naturally occurred oxide of titanium. Rutile is the most abundant form of the TiO2 in nature, followed by anatase and brookite. Nano TiO2 consists of 80% anatase and 20% rutile, with a specific surface area of 50 and an average dimension of 21 nm. Nano titanium dioxide has five times larger surface area and four times lower opacity compared to normal TiO2. The substance has a large specific surface area (SSA) while having a tiny diameter of below 100 nm, which makes it an ideal nanoparticle. Tables (7) and (8) show the physical and chemical characteristics of Nano TiO2. These properties are used in the current study.

Figure (2) is a 3000x magnified image of Nano TiO2, and in Figure (3) physical specifications of the material are described.

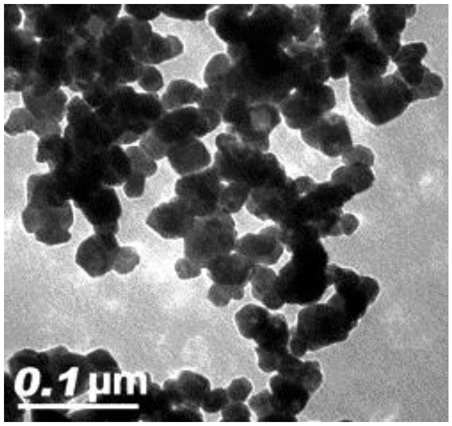


Fig. 2. SEM image of Nano Titanium at 3,000× magnification.

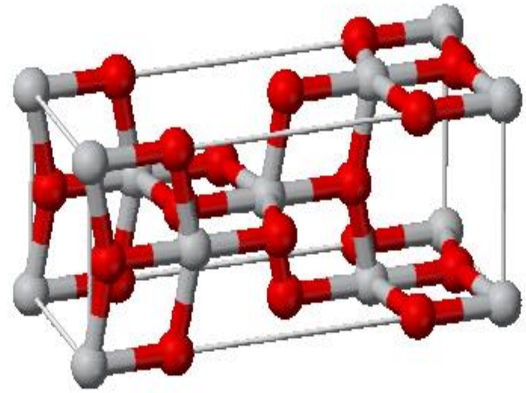


Fig. 3. Image of Molecular Structure Nano Titanium.

Table7. Chemical composition of Nano Titanium.

Item	TiO_2 (%)	Al (ppm)	Mg (ppm)	Si (ppm)	Ca (ppm)	S (ppm)	Nb (ppm)
Nano Titanium	≥99%	≤17	≤65	≤120	≤75	≤130	≤80

Table8. The physical properties of Nano Titanium.

Diameter (nm)	Surface volume ratio (m^2/g)	Density (g/cm ^{3})	Loss of ignition (%)
20	10-45	3.9	8.24

3.2. Preparation of Samples

In order to synthesize Nano TiO_2, a mixture of titanium isopropoxide (precursor), HCl, ethanol and de-ionized water was prepared and stirred for half an hour in pH of 1.5. Then, 10 cc of distilled water was added to the blend and mixed for 2 hours. Eventually, the compound was left at room temperature to dry and the resulting powder was exposed to 120 degree centigrade temperature for 60 minutes. Silicic acid is used to make silica powder. The particles were mixed and blended with THF for 1 hour. Titania gel was gradually mixed to the silica powder. The resulting compound was blended for 3 hours and was left to dry out at room temperature. The final product was then exposed at 120 degree centigrade for 60 minutes. Four asphalt binder samples were made, each containing different levels of nano materials. Table (9) shows the levels of Nano Sio2 added to the virgin binder. In Table (10), the steps in preparing specimen and the experiments carried out are given. A high shear mixer (4000 rpm) was used to mix the Nano TiO2 with bitumen at around 155°C for 15 minutes. To ensure the consistency of the modified bitumen , the samples were taken from different parts of the container and the results were the same.

Table9. Different combinations percentages of Nano additives in bitumen

Type of Combinations	TiO_2 (%)	SiO_2 (%)
Type A	1.25	0.5
Type B	2.5	1
Type C	5	2
Type D	6.25	2.5

Table10. Program for specimen preparation and testing.

Parameter	Levels
Percentages of Nano Powders in bitumen	A , B, C, D
ITF Test Temperatures	(5,25,40) °C
Type of Gradations	Topeka
ITF Stress levels	250 ,400 (KPa)

The surface was coated at a rate 0.25 Kg/m2. For this purpose, Nano TiO2/SiO2 was mixed and kept at a suspension liquid state in 2% concentration (v/v) and was sprayed as a coating. All specimens were sprayed in cross hatch pattern for field study. Prior to conducting the fatigue test on asphalt specimen, Marshal test (standard no. ASTM-D1559) [24] was done in order to find the optimum amounts of bitumen in each percentage of TiO2/SiO2 in the samples. It is worth mentioning that the type A-D Nano additives were chosen in this test.

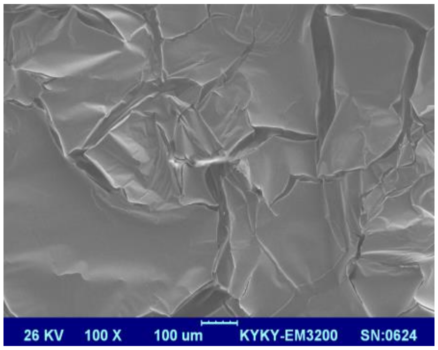
3.3. Scanning Electron Microscopy (SEM) Analysis Results

In Figure (4), an electron microscopy image of untreated bitumen is shown, while Figure(5) illustrates the Nano particle treated bitumen. From the Figure (5b), it is evident that there is a high tendency for Nano particle aggregation through creating an irregular network of particles. To resolve this issue and get the best results, the Nanoparticles have to be completely disperesed into the binder. The blending method could successfully combine Nano particles into bitumen, and a matrix of Nanoparticles and bitumen was achieved. An improve in adhesion between bitumen and aggregates was achieved due to the increased surface area of the treated bitumen using Nanoparticles. This is shown in Figure (5). A small amount of aggretation took place for some nanoparticles, however, most of nanoparticles were cmpletely scattered in the mixture (Figure 5c). According to Table 9, the amount of nano used in SEM images in Type C contains 5% nano titanium and 2% nano silica, which is also mentioned in the text.

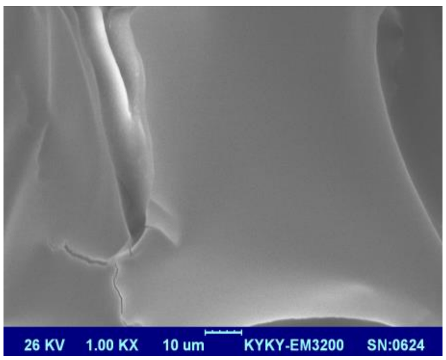
4. Laboratory Tests

4.1. Mechanical Tests

In order to measure the resiliency of asphalt specimen in terms of permanent deformation, a number of tests are often used. These include the dynamic creep, the wheel-tracking test, Marshall Test, repeated axial load test (RLA) (BS DD 185), and the static creep test [25]. In this study, to measure the fatigue resistance and cracking of the asphalt samples, the Nottingham Asphalt Test (NAT) was used. For evaluating the rheological characteristics of the bitumen samples, asphalt binder tests were done in the first studies.



(a)



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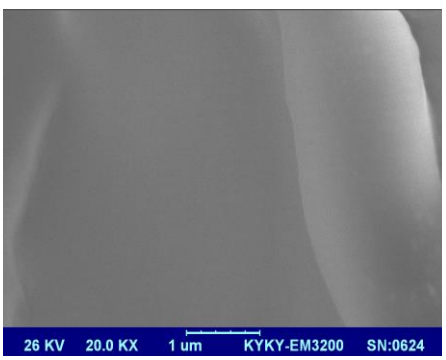
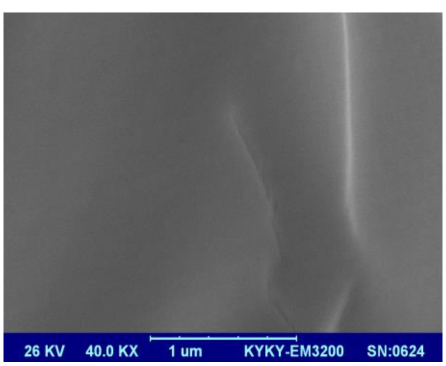
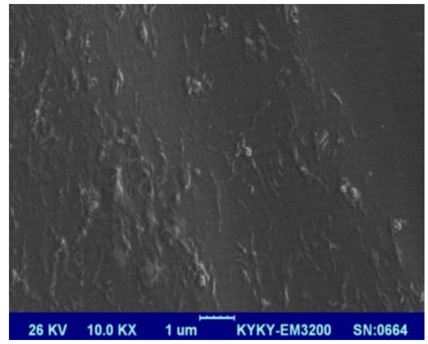


(c)

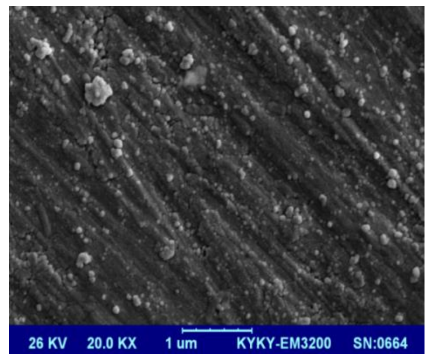


(d)

Fig. 4. SEM images of conventional asphalt binder, (a) 100× magnification; (b) 1,000× magnification; (c) 20,000× magnification; (d) 40,000× magnification.



(a)



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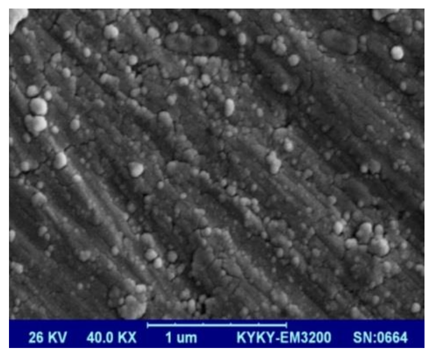

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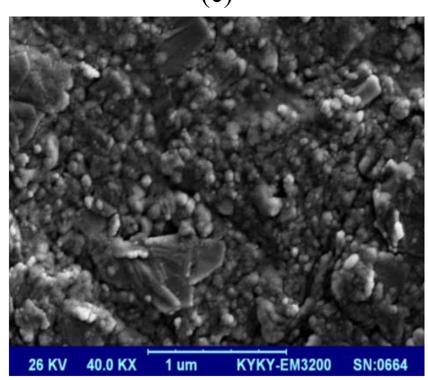

(d)

Fig.5. SEM images of modified asphalt binder with Nano TiO2/SiO2, (a) 10,000× magnification; (b) 20,000× magnification; (c) 40,000× magnification; (d) 40,000× magnification (other view).

In order to find the optimum levels of Nano particles, both untreated and modified bitumen samples (at different nanoparticle levels) were put to following tests: rheological, rotational viscosity (RV) (ASTM-D4402) and dynamic shear rheometer (DSR). The DSR (AASHTO T315) is used for evaluating the rheological response of the binders at high temperatures. In this study, a Brookfield rotational viscometer is used to determine the differences in the viscosity of untreated and modified asphalt binders when the mixture is in production or construction phase. The test is conducted at 120°C, 135 °C and 160°C and in accordance with ASTM-D4402 standard. An RV test is used to make sure that the mixture has enough fluidity at the time of pumping and mixing. In order to measure the fatigue cracking resistance of the specimen at different Nano TiO_2/SiO_2 levels, the ITF test was conducted. To find the fatigue life of the samples, an indirect tensile test of the ITF test was used. The specimens were prepared according to ASTM D1559 standard [24] and had the dimension of 100mm in diameter and 63.5 mm in thickness. Loading with constant strain is a means of fatigue life test. Another method is loading with constant stress. In the constant strain test, the stress is decreased as the number of loading stress increases. In constant stress test, the strain increases by increasing loading pulses [26]. A given tensile strain has to be kept steadily for every level of stress in order to establish an equation between the tensile strain and the number of cycles [27]. In this research, the stress levels of 250 and 400 kPa and temperatures of 5, 25 and 40 °C were applied for fatigue life stress. In table (8), the steps of preparing samples are provided. The equation between cycles until failure and tensile strain is established for all levels of Nano particles in the specimen. Analysis of regression was used to find the equation, as shown in Eq. (1). As can be seen, the equation is consistent with the model predicted by Wohler [27].

$$\varepsilon_t = aN_f^b \qquad \text{Eq. (2)}$$

4.2. Environmental Test

In order to reduce pollution from traffic and overcome them in the nearest position to their source of production, nanoscale photo-catalyst materials are used in the structure of emulsion asphalt binder, which can be applied as coating of pavement. In this study, nano titanium dioxide photocatalyst has been able to act as an additive to reduce the above-mentioned pollutants because of unique properties such as chemical reaction with harmful gases and their decomposition into harmless and washable materials. Also, nano silicon oxide produces high absorption rates in combination with nano titanium dioxide due to properties such as high affinity and improves the ability of photocatalyst to carry out chemical reactions. Nano-titanium dioxide, in the presence of sunlight, causes the reaction and speeds up the oxidation of harmful gases and, consequently, converts nitrogen dioxide gas into harmless and washable nitrate with water, which can be easily washed with water. The photocatalyst in the presence of nano silicon oxide has also been able to oxidize volatile organic compounds (VOCs) and convert them to water, carbon dioxide and chloride.

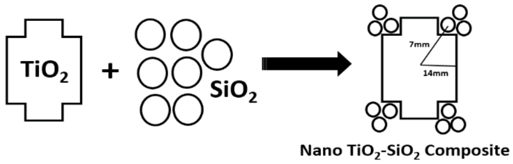

Fig. 6. Formation of nano composites 4-dimensional structure.

The effect of the resulting asphalt on reducing environmental pollutants including absorbing and decomposing NOx through photo catalysis phenomenon was explored in this research. For this purpose, a laboratory system, which enables the researchers to measure the photocatalytic efficiency was used. The setup is in accordance with the JIS TR Z 0018 "Photocatalytic materials – air purification test procedure", which a standard used in Japan. The system includes a source of pollutant, zero air source, a calibration device, a device for humidification, a photoreactor, as well as a chemiluminescent NOx analyzer. The system is depicted in Figure 7. Both air humidity and light level can be adjusted by the system to control and create various environmental conditions. The pollutant particles are let onto the photo-reactor (photocatalytic measurement device) through an air jet stream. The zero air generator provides the airflow, where the humidifier adds different level of humidity to create the required humidity.

Fig. 7. NOx analyser and photoreactor.

In photoreactor, the right conditions for light and air conditions can be replicated. To simulate sunlight for inducing photocatalytic activity, a fluorescent light source connected to the photocatalytic instrument is used. In order to determine the amount of absorbed pollutant, the level of pollutant was measured in the inlet and outlet of the photoreactor. In this research, a chemiluminescent NOx analyzer (Thermo 42i) was sued to evaluate the effectiveness of the device in removing NOx. We let an airflow containing 450 ppb NOx to move on the surface of the asphalt samples. Relative humidity was maintained at 20% and the experiment was done at room temperature. Calibration of Thermo 420i was done through gas phase titration. This procedure was performed in accordance with the EPA instructions. In this process, a quick phase reaction according to the equation below takes place where NO and O interact to produce NO2:

$$NO + \dot{O}_3 \rightarrow NO_2 + \dot{O}_2 \qquad \text{Eq. (3)}$$

The above-mentioned calibration reactor uses this rule to provide known levels of NO an NO2 applied to the NOx analyzer. To ensure linearity and conversion efficiency of ozone, the calibration of NOx analyzer was done in five NO levels and four levels of ozone. To keep the monitoring device within the predefined accuracy limits, it was calibrated from 0 to 500 ppm. This is the conventional range suitable for environmental air measurement purposes.

As well as, in order to validate and evaluate the percentage of reducing environmental pollutants by asphalt pavements made with nano materials, samples made under field testing were also exposed to pollutants and evaluated by a spectrophotometer. The device is model DR5000 made by the HACH factory, which is used in ambient conditions at temperatures of 10 to 40 degrees Celsius, humidity of less than 80 percent, and indirect light to measure the amount of nitrate, phosphate and sulfate. The Genesis model spectrophotometer device is also used to measure the amount of nitrite (Figure 8).

Fig. 8. NO2 analyser content in water.

5. Results and Discussion

5.1. Mechanical Tests

For theological measurement, rotational viscosity (RV) test and classical test were done on untreated bitumen and the bitumen treated with different levels of Nano additives. The data achieved of these tests are provided in Table (11). As is evident from the Figures, all levels of Nano additives positively affect the rheological characteristics of bitumen. At room temperature (25°C), the bitumen under study had a high stiffness, due to the stiffness of the Nano additives. In addition, the Nano treated bitumen showed little sensitivity to large fluctuation in temperature. In comparison with the untreated bitumen, it may also have higher resilience to plastic deformation or rutting. According to the results of the study, another benefit of bitumen containing Nano additive is the improvement of the softening point through lowered temperature sensitivity of the treated bitumen. Rotational viscosity test was used to evaluate the flow resistance of the fluid.

Table11. Basic properties of Nano modified bitumen binders.

Property	Conventional Bitumen	Modified Bitumen Type A	Modified Bitumen Type B	Modified Bitumen Type C	Modified Bitumen Type D
Penetration at 25 °C (d-mm)	66	64.2	61.7	59.1	60.5
Softening Point (°C)	51	55.3	59.2	61.1	56.5
Ductility at 25 °C at 5 cm/min (cm)	111	92	82	78	81
Penetration index	-0.356	0.39	0.99	1.71	0.64

Asphalt samples were tested at 120°C, 135°C and 160°C by Brookfield Viscometer. Figure. (9) shows the plot achieved from rotational viscosity device. As is evident from the plot, the softening property of the specimens is improved, so that Nano particles increased the viscosity by about 250% on average at temperatures ranging from 120°C to 160°C. As a result, it is safe to say that at the highest environmental temperatures, modified binders show higher stiffness.

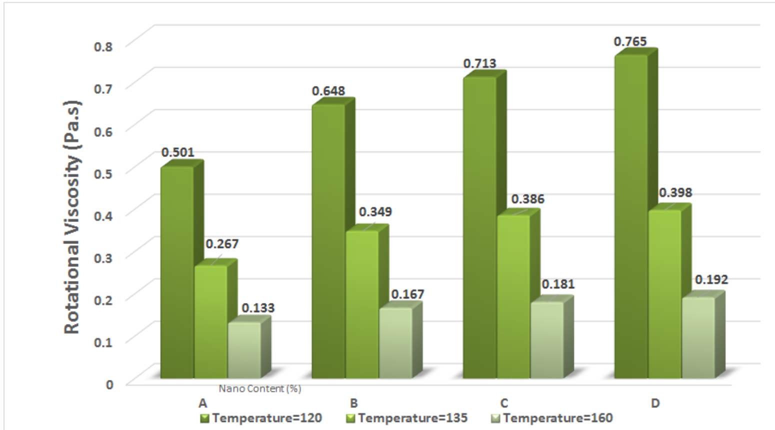

Fig. 9. Rotational Viscosity test results on conventional and modified asphalt binder.

A DSR temperature sweep test was done while the strain was kept steady. A frequency of 10 rad/s was retained during the test. According to the outcome of the test, in comparison with the untreated asphalt, the complex modulus was enhanced while the phase angle was decreased. At temperatures between 64 to 82°C, the value of master curves slope (G*) dropped from untreated asphalt to treated asphalt. By increasing temperature, the phase angle of all specimen including modified and unmodified samples increased. As it can be seen from Figure (10) and Figure (11), the treated asphalt samples had more desirable elastic and viscous properties compared to the untreated asphalt.

Figure (12) shows the amounts of tensile strain in specimen containing different levels of Nano TiO2/SiO2 at cyclic loading conditions. Figure 10 and 11 also reveals that as the loading cycles increase, the gap between treated and untreated samples increases. In samples containing Nano additives, higher tensile strain was measured. The additives decreased both the growth rate of the micro-cracks and the cracks caused by the creep. Higher tensile strength was resulted due to existence of Nano TiO2/SiO2 in samples. Consequently, crack and micro-crack formation was decreased by modifiers. In addition, the number of cycles to failure was significantly reduced with different levels of Nano TiO2/SiO2. In Figure. (12), the model of fatigue behavior based on Eq. (2) for samples with different level of TiO2/SiO2 and their correlation coefficients are provided. The improvement in fatigue life is directly proportional to the level of Nano additives added to the specimen.

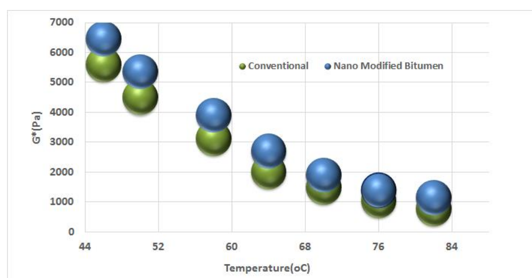

Fig. 10. Complex Modulus Versus Temperature

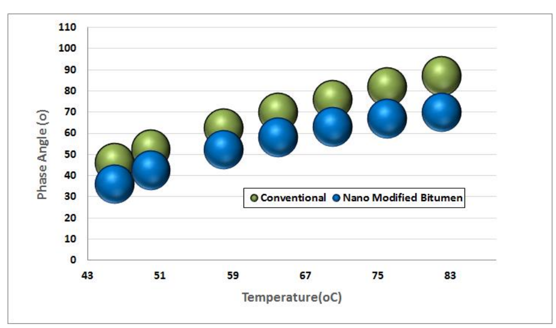

Fig. 11. Phase Angle Versus Temperature.

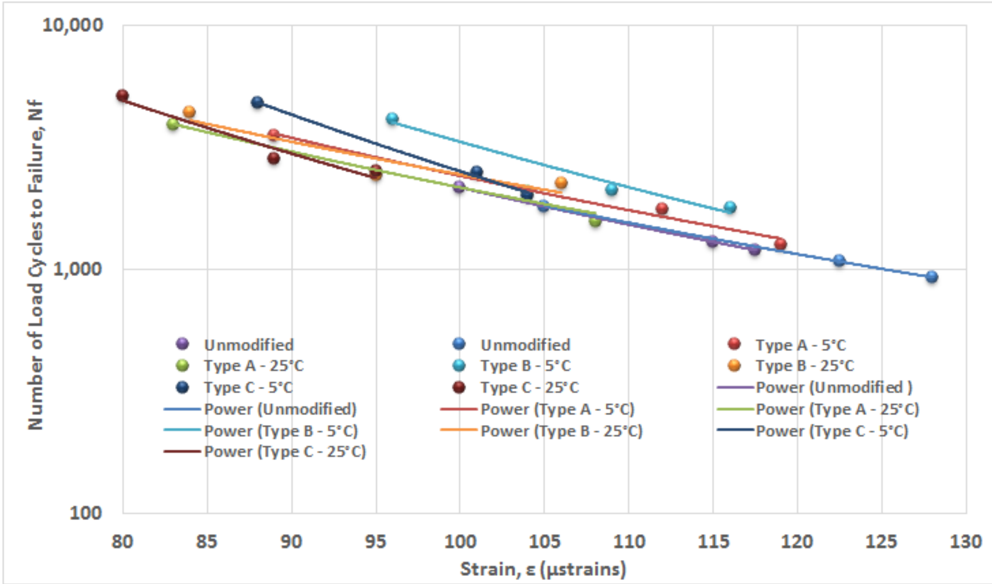

Fig. 12. Strain versus number of loading.

5.1. Environmental Result

The aim of performing the environmental tests is to determine the effect of the application of nanomaterials in asphalt pavement in reducing the amount of chemical and non-chemical pollutants in the air. The equations related to photocatalyst chemical reactions used in the surface layer of pollution absorbent as well as the formulation related to nitrogen oxide absorption and volatile organic compounds (VOCs) are listed below. Initially, nano silica oxide reacts with nano-titanium dioxide with the help of sol-gel method and forms a tetrahedral (four-dimensional) structure. This will increase the available surface area of photocatalyst. As a result, the addition of SiO2 affects the photocatalytic activity of TiO2 and causes the acceleration in the process by increasing water absorption and hydroxyl groups. As previously stated, TiO2 reacts in the presence of sunlight and creates Superoxide and hydroxyl radicals (OH.), whose function is oxidation and consequently reduction in the amount of environmental pollutants such as nitrogen oxide and volatile organic compounds (VOCs). A state of oxidation of nitrogen oxide and volatile organic compounds with hydroxyl radicals (OH) through the mediation of TiO2 photocatalyst are done by the following equations:

$$NO + \dot{OH} \xrightarrow{TiO_2} NO_2 + \dot{H}$$

$$NO_2 + \dot{OH} \xrightarrow{TiO_2} NO_3 + \dot{H} \qquad \text{Eq. (4)}$$

$$VOC + O_2 + \dot{OH} \xrightarrow{TiO_2} CO_2 + H_2O$$

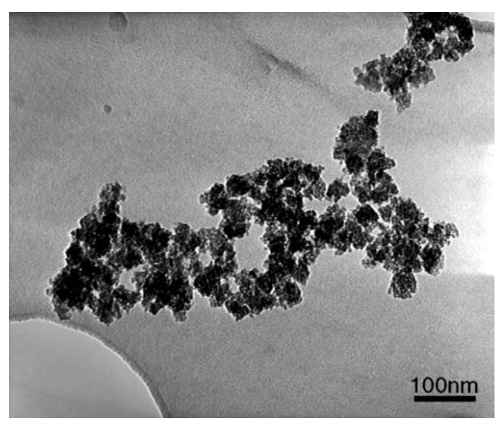

Fig. 13. SEM images of Tetrahedral structure of TiO2 and SiO2.

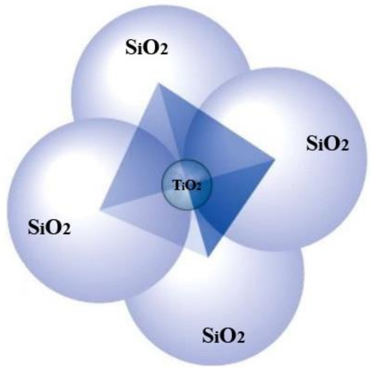

Fig. 14. Tetrahedral structure of TiO2 and SiO2.

Table (12) indicates that NOx is greatly decreased, showing the beneficial effect of mixing Nano modifiers to the binder. To make sure that the equilibrium is fully achieved, the UV light was turned on two hours after the test was to begin.

The equilibrium was achieved at 430 ppb in inlet as measured at the inlet when the light was off. A sharp decrease in the NO concentration was measured in the outlet flow and NO2 was observed due to the oxidation of NO. Throughout the photocatalytic test, a slight increase in the level of NOx was seen. The light turned off and the gas supply shut down after five hours from the experiment. This let the desorption to proceed. Under laboratory conditions, the NO reduction efficiency was 83% due to the use of TiO2/SiO2 photocatalyst, and the average reduction for NOx was calculated as 63%.

The preliminary results obtained from experimental tests on conventional asphalt samples and asphalt samples of absorbent coatings show that we observed 60% absorption of pollutants, especially nitrogen oxide (NO) even after 3 to 5 days when the samples were exposed to contamination.After making asphalt samples with dimensions of 25 x 35 cm with modified emulsion asphalt binder via photocatalyst materials on a nanoscale, the samples were placed in a glass chamber on which direct light of UV was applied. Then, the asphalt pavement surface was contaminated during different days by putting the vehicle exhaust and a gasoline container inside the test chamber, and, the simulation was carried out as in real mode. Then, Contamination Monitoring Test were conducted as follows after 8 days when the samples were exposed to pollutants. First, after removing the samples from the glass container, the pure water prepared from the

laboratory of water and sewage was poured to 50 ml on the asphalt sample and, after

about 10 to 15 minutes (that the nitrates in the coating surface are dissolved in water), the water is collected and transferred to the laboratory immediately. The contaminated water in the laboratory initially passed through a filter to remove its opacity and then, the amount of nitrate and nitrite in the water was determined with the aid of a spectrophotometer. Finally, the amount of nitrates was converted into nitrogen oxide-absorbed gas with the help of chemical equations and the following relations. The steps of performing the test are shown in Figures 15 to 18.

Table 12. Average NO_X reduction and NO reduction for Nano incorporated into binder mixes.

Sample	NO_X Reduction %	NO Reduction %
Type A	7.1%	8.78%
Type B	8.9%	9.6%
Type C	10.6%	11.91%
Type D	11.71%	12.1%

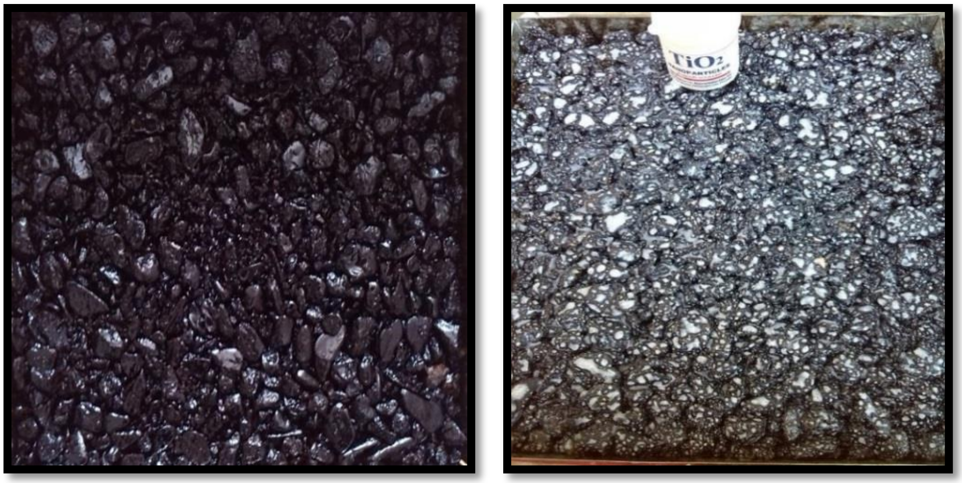

Fig. 15. Image of asphalt sample containing contamination absorbent coating with modified emulsion asphalt binder.

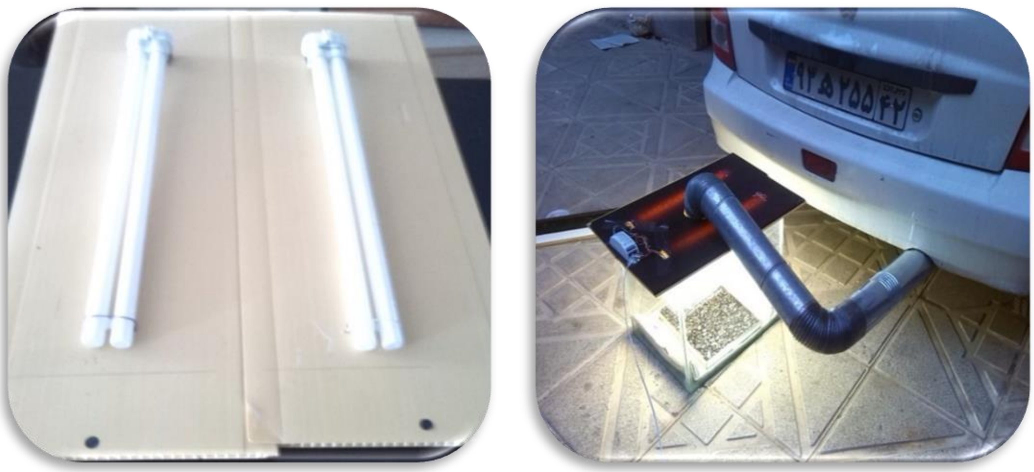

Fig. 16. Simulation of vehicle exhaust fumes at emission stage of pollutants on asphalt samples and UV light used.

Fig. 17. Contaminated water samples accumulated from the surface of asphalt pavement.

The focus of nitrates on six different samples, including modified and simple samples was measured. Measurements were performed during 8 consecutive days. Accumulation of nitrates at the pavement surface was measured by dissolving them in pure water. To collect the nitrates of surface pavement, 40 ml of pure water prepared from the laboratory was poured onto the surface of the pavement, and it was collected via a syringe after 10 minutes and immediately transferred to the laboratory. Increasing the amount of nitrate and nitrite in the water indicates a reduction in the amount of nitrogen oxide available in the air and its absorption by pavement.

Fig. 18. Use of electrolyzed water to absorb environmental contaminants at the pavement surface.

The amount of nitrate and nitrite in the water of samples accumulated was measured using a spectrophotometer. With the help of this device, amount of nitrate and nitrite in the water was obtained in terms of milligrams per liter (ppm), and the amount of nitrate and nitrite accumulated at the pavement surface was converted to the amount of oxidized pollutants in the atmosphere in terms of ppm V with the help of direct relation and the molar equation given in oxidation of nitrogen oxide as well as the amount of nitrate deposited in the surface of the pavement.

Figures 19 and 20 show the amount of nitrate dissolved in water and the absorption rate of nitrogen oxide emissions in the air according to the results obtained from the contamination monitoring test on the modified samples by the nitrate and nitrite analyzer (Spectrophotometer) of the Water and Sewerage Laboratory. Figures 21 and 22 show the accumulation of nitrates and the absorption rate of nitrogen oxide emissions measured during a period of 8 days. It is clearly observed in Figure that the photocatalytic reduction of nitrogen oxide occurs in modified samples. Photocatalytic oxidation activities are very active during the first day, which is followed by reducing the absorption of pollutants in the next days.

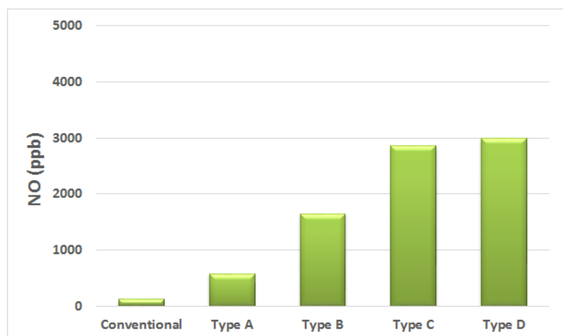

Fig. 20. The amount of nitrogen oxide absorbed in the contamination monitoring test for simple and modified samples.

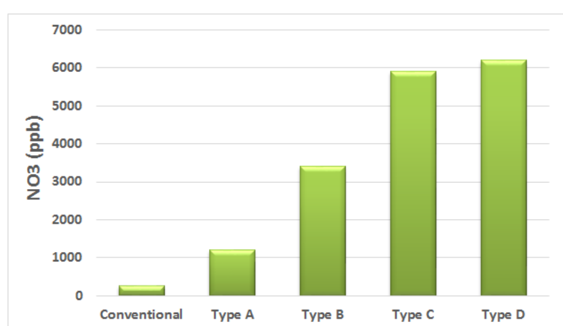

Fig. 19. The amount of nitrate dissolved in water in the contamination monitoring test for simple and modified samples.

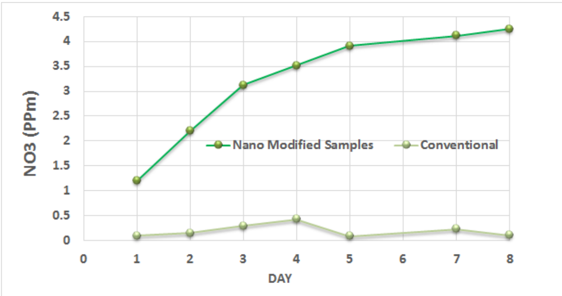

Fig. 22. Absorption rate of nitrogen oxide emission in the contamination monitoring test in terms of time.

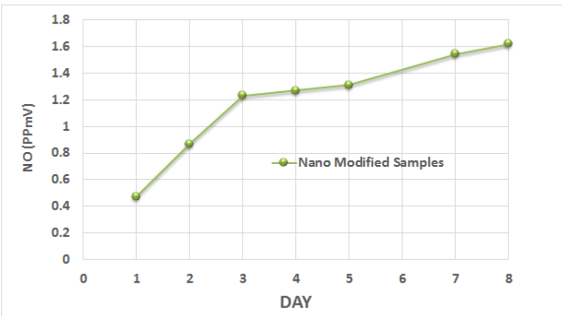

Fig. 21. Accumulation of nitrates measured in the contamination monitoring test for simple and modified samples in terms of time.

As can be seen in the graphs, the absorption rate of pollutants enhances by increasing the percentage of nano materials compounds, so that the simple sample is free of absorption and the sample with C type percentage is determined as optimal mode, since then, there is no significant increase in the absorption rate of pollutants with an increase in the percentage of nanoparticles. The nano composite has a large surface area of between 274.1 and 421.1 square meter per gram and lead to decreasing in pollution.

According to the graphs, it is clear that the photocatalytic reduction of nitrogen oxide occurs in modified samples. Photocatalytic oxidation activities are very active during the first day, which is followed by reducing the absorption of pollutants in the next days.

6. Conclusion

In this research, the advantage of adding Nano TiO2/SiO2 to the asphalt binder in the process of producing warm mix asphalt (HMA) is studied. Four levels of additives containing crystal form of anatase-based titanium dioxide and SiO2 in the form of powder was mixed to an ordinary asphalt binder (A to D samples). The resulting mixtures were evaluated for basic rheological and sharp tests as well as fatigue tests. In constructing HMA, a solution of titanium dioxide (as water base) was sprayed in the form of a thin layer over the surface and TiO2/SiO2 was mixed to the asphalt binder. Concerning the results of the tests, the following outcomes can be deduced:

- When the Nano additives was mixed to the asphalt binder, the resulting product had little effect on NOx reduction, probably because only a little amount of TiO2 was available on the surface.

- When the Nano additive was sprayed over the surface, the efficiency of the surface to remove NOx pollutants in the air varied between 41 to 63%.

- According to the results of the rheological tests, Nano particles change the physical characteristics of ordinary binder.

The current study showed that modifying binders largely affect the fatigue performance of HMA mixtures. The study also established a strong correlation between fatigue resistance improvements in HMA samples and more viscosity (higher binder stiffness). This was more evident at higher temperatures.

The sensitivity of Nano modified specimen was higher than that of ordinary samples.

Therefore, in comparison with the untreated samples, the treated specimen has more resilience against plastic deformation.

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