Studying the Adsorption of Lead from aqueous Solution using Local Adsorbent Material Produced from Waste Tires by Pyrolysis

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ABSTRACT

In this research a local adsorbent was prepared from waste tires using two-step pyrolysis method. In the carbonization process, nitrogen gas flow rate was 0.2L/min at carbonization temperature of 500ºC for 1h. The char products were then preceded to the activation process at 850°C under carbon dioxide (CO_2) activation flow rate of 0.6L/min for 3h. The activation method produced local adsorbent material with a surface area and total pore volume as high as 118.59m^2/g and 0.1467cm^3/g, respectively. The produced local adsorbent (activated carbon) was used for adsorption of lead from aqueous solution. The continuous fixed bed column experiments were conducted. The adsorption capacity performance of prepared activated carbons in this work was investigated. The results in this study indicated that the produced activated carbon from waste tires was an attractive adsorbent for removal of lead from aqueous solutions. The optimum values of bed height, flow rate, initial concentration and particle size were found to be 0.04m, flow rate 1L/h, initial concentration 0.5mg/L and particle diameter 0.5mm, respectively.

Key words: pyrolysis, waste tires, activation, carbonization.

دراسة امتزاز عنصر الرصاص من المحلول المائي باستخدام مادة مازة محلية ناتجة من التحلل الفيزيائي للاطارات المستهلكة

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الخلاصة

في هذا البحث تم انتاج مادة مازة محلية تمتلك خصائص الامتزاز المشابهة للفحم المنشط باستعمال الاطارات المستعملة محليا كمادة خام بعملية التحلل الفيزيائي و تدوير هذه الاطارات المستعملة الى منتج مفيد . وهذه المادة تحضر بالتحلل الفيزيائي وعلى مرحلتين. في عملية الكربنة كان معدل جريان غاز النتروجين (0,2 لتر/دقيقة) وبدرجة حرارة (500 درجة سليزية). الفحم الناتج تم تنشيطه الى (850 درجة سليزية) وبتصريف (0.6 لتر/دقيقه) من غاز ثاني اوكسيد الكاربون. تم انتاج المادة بمساحة سطحية قدرها (118.95 م^2/غم) وبحجم المسام الكلي (0.1467سم^3/غم). وهذه المادة المازة المحلية استخدمت لامتزاز الرصاص من المحلول المائي. تم اجراء التجارب باسلوب النظام المستمر.حيث تم دراسة تأثير كل من معدل الجريان و التركيز و ارتفاع الحشوة و حجم الحبيبات على مخططات الازالة. تم تثبيت الظروف المثلى لكل تجربة وكالاتي: أرتفاع الحشوة (4سم)، معدل الجريان (1لتر/ساعة)، التركيز(0.5مغم /لتر) و حجم الحبيبات (0,5ملم).

الكلمات الرئيسية : التحلل الفيزيائي،الاطارت المستهلكة، التفعيل، الكربنة.

1. INTRODUCTION

Due to the continuous increase in the production and usage of automobiles, the number of waste tires will increase considerably. It was estimated that approximately (1.5×10^9) of waste tires are discarded worldwide every year, **Murillo, et al., 2005, and Banar, et al., 2012.** For example, the total number of waste tires in Iraq, and according to the mayoralty of Baghdad statistics an approximately of (4830 ton/yr) of waste tires are discarded. As a result, the large amount of waste tires were thrown, dumped in the landfills, stockpiled, they have become a serious source of environmental pollution, **Akyildiz, 2011.** In this way the sstockpiling of whole tires creates two significant hazards: mosquitoes and fires. The dumping of the used tires in the landfills is considered as one of the alternative procedure for dispose of the used tires. The land filling of whole tires consume a large volume of landfill space because the tires are relatively incompressible and 75% of the space a tire occupies is void, **Clark et al., 1993.** In fact, due to the high cost of legal disposal for tires, illegal dumping may increase. The disposal of tires is also becoming more expensive, while this trend is likely to continue, as landfill space becomes scarcer, **Mui et al., 2004.** The restrictions on disposal of tires in landfills are related more to the physical characteristics of tires and the space of the whole tires occupy in landfills than to concerns regarding contaminants, **Jang et al, 1998.**

In the recent years, the majority of discarded tires in the U.S. are being recycled or reused in some way and are not being discarded in landfills, **Jang et al, 1998.** Several attempts have been made to recycle and reuse the waste tires by turning it to some useful products that can be added (to/or) used directly as a raw materials in some industries, for example, by using them as dock bumpers, playground equipment, etc. However, from environmental and economic points of view, a much better solution is to convert such waste tires to valuable products that enhance the recycling and reusing techniques as global environmental strategies. Tire rubber consists primarily of styrene-butadiene rubber and carbon black as shown in **Table 1**. The carbon black acts as filler and a performance additive to increase strength and toughness. Various oils and additives are included in the tire rubber mixture to improve tire wear, softness, and performance, **Williams and Besler, 1995.**

The one possible way of recycling waste tires is pyrolysis. Pyrolysis is a thermo-chemical decomposition of organic material at elevated temperatures in the absence of oxygen or within inert environment. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. The word is coined from the Greek-derived elements *pyro* "fire" and *lysis* "separating, "**Helleur et al., 2001**. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content and char. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization, **Napoli et al., 1997.**

In the pyrolysis process, the organic volatile matter of tires (around 60 wt %) is decomposed to low molecular weight products, liquids or gases, which can be used as fuels or chemicals source. The non-volatile carbon black and the inorganic components (around 40 wt %) remain as solid residues and can be recycled and reused. However, for minimizing emissions the conditions of the pyrolysis process must be optimized, **Juma et al., 2006.** Tire pyrolysis (thermal decomposition in an oxygen free or inert) is currently receiving renewed attention. Recycling of tires by pyrolysis offers an environmentally attractive method, **Akyildiz, 2011.** This solid char may be used as reinforcement in the rubber industry, as activated carbon after carbonization and activation process or as smokeless fuel. **Table2** refers to the composition of waste tires resulted from the pyrolysis process at (900ºC). The pyrolysis process passing though different phases from the starting point till the end. **Table 3** represents the principle phases of the pyrolysis process as a function of temperature**.** Furthermore, pyrolysis of waste tires will be more attractive to produce a new materials as Basel convention which prohibits the marketing of waste tires, or dumping it in the landfill and as Iraq was lately signed Basel convention and be a member in this treaty that make Iraq to be obligate to follow all the instructions and legislations regarding the environmentally accepted methodologies for treating and disposing of the waste tires.

As the production of adsorbent from waste tires changes (hard-to-dispose) waste changes to (pollution-cleaning adsorbents), it is thought to be a very effective method to reduce environmental pollution, **Ariyadejwanich et al., 2003.**

The activated carbon (adsorbent) obtained from pyrolysis can be used in adsorption process as a secondary and advanced treatment technique in environmental engineering. It is used in practice for removal of various pollutants such as soluble organics, dyes, pesticides, lignin, methylene blue adsorption, an indicator for discoloration efficiency in wastewater treatment, the adsorption of phenol, and an indicator for the adsorption of organic phenolic compounds. From wastewaters and for removal of color and taste and odor-producing substances from natural waters that are to be used as potable water supplies, **Ariyadejwanich et al., 2003.** Thus, the production of local adsorbent material from waste tire rubber can provide a two-fold environmental and economic benefit: A recycling path is created for waste vehicles tires and new adsorbents are produced for commercial use in wastewater treatment.

2. MATERIALS AND METHOD

2.1 Materials

2.1.1 Waste tires

Waste tires were used in the present work representing a mixture of used truck tires, containing no steel or synthetic cord. Before being treated, the waste tires were shredded using an electrical drill (BOSCH 305) adopted with crushing disk and sieved to a size of 0.5mm by using (RETSCH sieves number 35) as shown in **Fig.1**

2.1.2 Lead Nitrate Solution ($Pb(NO_3)_2.2H_2O$)

A solution of lead nitrate prepared by using ($Pb(NO_3)_2.2H_2O$) salt. A 2.3g of this salt was dissolved in (40L) of distilled water with lead concentration of (10mg/L) and the concentration was measured by using atomic absorption (SENS AA DUAL) in the environmental engineering lab/ Environmental Department/Baghdad university. The prepared solution was kept at room temperature. The salt was bought from local market with the following specifications as shown in **table (4).**

2.2 Methods of analysis

2.2.1 Surface area, pore size and volume

Surface area is one of the key indicators attributed to the adsorptive properties of porous materials. Pores in different sizes are important to the adsorbent. The presence of micro- and mesopores in local adsorbent material enhance the adsorption of large adsorbates such as heavy metals molecules. The surface area and pore size of the produced activated carbon were measured using (SURFACE AREA ANALYSER/THERMO USA MR 9600).

2.2.2 Microscopic investigation

A microscope investigation was made for the produced adsorbent material by using (AA 3000 Scanning Probe Microscope) in the Nano- Technology center/ University of Technology.

3. EXPERIMENTAL PROCEDURE

The sieved waste tires particles filled in the refractory furnace of type (BARNSTEAD/ THERMOLYNE FURNACE 62700, 1.5KW) that was provided with a digital (EUROTHERM) controller in order to control the temperature. The furnace can reach a maximum temperature of 1000ºC and provided with a fan in order to evacuate air from it. Two pressurized cylinders of carbon dioxide gas and nitrogen gas (that purchased from local market) adopted with flow regulator adaptor (YAMAWITE 35) in order to control the flow of the gas to the furnace chamber to ensure the inert environment during the carbonization and activation phases. The pyrolysis process passes through two stages carbonization and activation. The two consequence processes were applied to produce the local adsorbent material.

3.1 carbonization process

A sieved sample to 0.5mm particle size was weighed using (SARTORIUS scale 7100) and put in the furnace. The sample was heated at a rate of 5^oC/min in the presence of high purity nitrogen gas to 500^oC typically $400\text{-}700^oC$, **Mui, et al., 2004** in an inert atmosphere with a gas flow of 0.2L/min controlled by a volumetric flow meter in a typical run, where it was maintained for (1h).

3.2 Physical activation process

Physical activation was performed by using carbon dioxide gas as oxidizing agent. The activation temperature is usually set to be 850^{o}C for 3h (according to the previous researches the activation temperature may range from 800-900^{o}C, **Mui et al., 2004** to maintain a sufficiently high reaction rate. The carbon dioxide gas was introduced during the whole process at a rate of 0.6 L/min.

3.3 Column system (continuous system)

Sixteen different column systems were carried out at various bed heights (0.01, 0.02, 0.03 and 0.04), particle size (0.5, 1 and 1.6 mm), initial concentration (0.5, 0.75, 5, 10 mg/L), flow rate (1, 5, 10 and 20 L/h), pH (5, 7, 9, and 11). All these experiments followed the same procedure.

3.3.1 Equipment

A schematic representation of the experimental equipment is shown in **Fig. 2.** A plastic column of height 0.5 m and diameter 0.1m was used. The produced activated carbon was placed in the column, to ensure a good distribution of the solution of (lead nitrate) from the above a plastic mesh were used and to support the activated carbon in the column another manual fabricated plastic screen were used to prevent any losses of carbon granules from the bed. A cylindrical glass container was used with the volume of 0.05 m^3 as storage for the solution and feeder to the column. The lead nitrate solution was pumped by means of a pump (MARQUS of 550 watt) from the feed container to the top of the bed.

4. RESULTS AND DISCUSSION

In this study, the major goal was to produce local adsorbent material from waste tires by pyrolysis process, the carbonization temperature was 500ºC, nitrogen gas flow rate was 0.2L/min while the activation process temperature and carbon dioxide gas flow was 850ºC and 0.6 L/min respectively and the physical characteristics of the produced activated carbon was measured. **Table 5** represents the results for this step.

4.1 Microscopic analysis

The microscopic analysis micrographs provide information on the structure in the produced local adsorbent material for analysis during the activation process. **Fig. 3,4 and 5** show the expansion in the microscopic structure of the pores.
The surface of the produced material is resulted from the presence of the bonds of hydrocarbons in the raw material without any cracks. This would account for its poor or negligible surface area. The framework development was so rapid, resulting extra

cavities and leads to crack formation. Due to this well-developed pores, the produced material possessed high surface area. The micrograph magnifies the internal cavities, which are now clearly visible. The rate of activation (the formation of pores in the process) will be influenced by the formation of oxides on the surface (small white particles which are scattered on the surface of the produced local adsorbent material), **Banar, 2012** as shown in **Fig. 6.**

4.2Column experiments (continuous process)

4.2.1 Effect of bed height (H)

The effect of varying the bed height (0.01, 0.02, 0.03, 0.04 m) was studied by fixing the initial concentration of lead solution 10mg/L, constant flow rate 20L/h and particle size 0.5mm. The experimental breakthrough curves are presented in **Fig .7.** From this figure, it can be observed that as the bed height increases, the breakpoint increases. This shows that at smaller bed height the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height. Smaller bed heights corresponds to lesser amount of adsorbent, consequently, a smaller capacity for the bed to adsorb adsorbate from solution. As the flow rate is kept constant, then increasing the bed heights will increase the contact time of the solute with the bed. The effect of bed height on the adsorption capacity of produced activated carbon was shown in **Fig .8** by plotting capacity versus bed height. This figure showed that increasing the bed height will increase the capacity, due to the fact that additional spaces on activated carbon sites will be available for the solution molecules to be adsorbed on these unoccupied sites; furthermore, increasing the bed height will give a sufficient contact time for these molecules to be adsorbed onto produced activated carbon bed.

4.2.2 Effect of flow rate

The effect of varying the flow rate (1, 5, 10 and 20 L/h) were studied by fixing the bed height at 0.04m, particle size 0.5mm and initial concentration 10 mg/L. The experimental breakthrough curves were presented in **Fig.9** as C_e/C_o versus time. This figure shows that as the flow rate increases, the breakthrough curve become steeper. The breakpoint decreases due to the residence time of pollutant in the column, which is not long for adsorption equilibrium to be reached at high flow rate. Therefore, at high flow rate the adsorbate solution leaves the column before equilibrium completely occurs due to the reduction in the contact time.

Increasing the flow rate will cause a reduction in thickness of the surface film, which is considered as a resistance for the mass transfer in turn that will increase the mass transfer rate. In addition, an additional mixing is caused because of increasing flow rate that will ease the penetration and the passage of the adsorbate molecules though the particles and occupying a site(s) onto the adsorbent.

4.2.3 Effect of initial concentration (C_o)

The effect of varying the solute initial concentration and the breakpoint curves were plotted, maintaining the bed height at 0.04m, flow rate at 1 L/h and varying the initial concentration (0.5, 0.75, 5, 10 mg/L) and particle size 0.5 mm. The results were presented in **Fig.10** The above breakthrough curves shows that any increase in the initial concentration made the breakthrough curve much steeper. This is due to increasing the driving force for mass transfer with increasing the concentration of solute in solution. In addition to that the higher initial concentration yielded a higher driving force along the pores thus the equilibrium was attained faster for higher adsorbate concentration. As the breakpoint was inversely related to the initial concentration, the time required to reach saturation decreases with increasing the inlet solute concentration.

4.2.4 Effect of the particle size

Effect of the activated carbon particle size (0.5, 1, 1.6mm) on the breakthrough curve were plotted by keeping the other parameters constant flow rate (1L/h), initial concentration (0.5mg/L) and bed height of (0.04m). These curves are presented in **Fig.11.** The breakthrough curves show that the time required for reaching the breakpoint increases as the particle size decreases. This is because when the particle size decreases, the surface area available for adsorption will increase, therefore the time for saturation will increase. As the particle size increases, the thickness of stagnant film around the particle increase, and the total length of the path inside the pore increases. Under these conditions, the overall kinetics of the process is low, because the time for a molecule of adsorbate to reach the adsorption site is more, as the diffusion path along the pores is large. The effect of the particle size on the capacity of produced activated carbon was shown in **Fig.12.** It is noticeable that increasing the particle size will decrease the capacity of produced activated carbon. This may attributed to the following; for small particles of produced activated carbon, the microspores are believed to be more readily accessible by the solution molecules and the transport is mainly due to film diffusion which is more effective than inter-particle diffusion. As the particle size increases, the transport due to inter-particle diffusion will be more dominant and, as it is a slow and not very effective process, the capacity will decrease as the particle size increases.

5. CONCLUSIONS

The local adsorbent material with medium porosities can be produced from pyrolysis of waste tires at 500ºC, followed by physical activation at 850 ºC. The surface areas and pore volume of the produced material were found to be (118.59 m^2/g) and (0.1467 cm^3/g) respectively.

In continuous process, the break point in the breakthrough curves in the system was related to: Flow rate, initial concentration, and bed height and particle size. The breakpoint time decrease with the followings:
a. Increasing the flow rate.
b. Decreasing the bed height.
c. Increasing particle size.
d .Increasing the initial concentration.
The adsorption capacity of the produced adsorbent was investigated. The adsorption capacity was increased with decreasing particle size, and related directly with the bed height.

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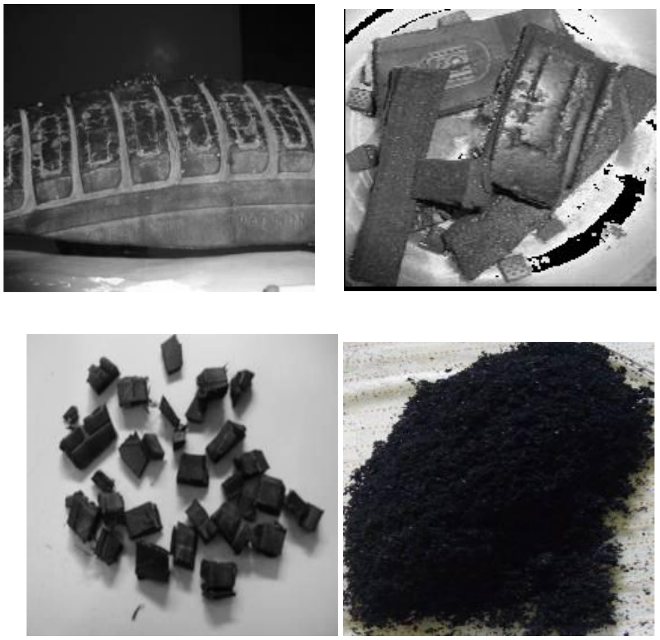

Figure1. Steps of shedding and grinding waste tires.

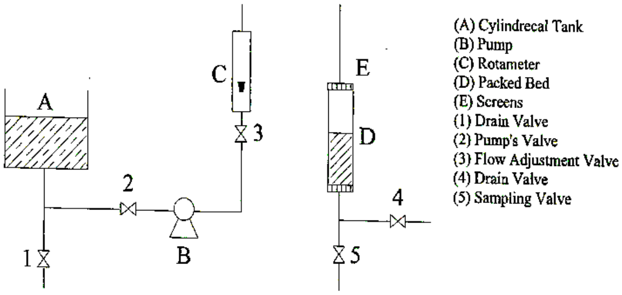

Figure2. Schematic representation of the experimental apparatus**.**

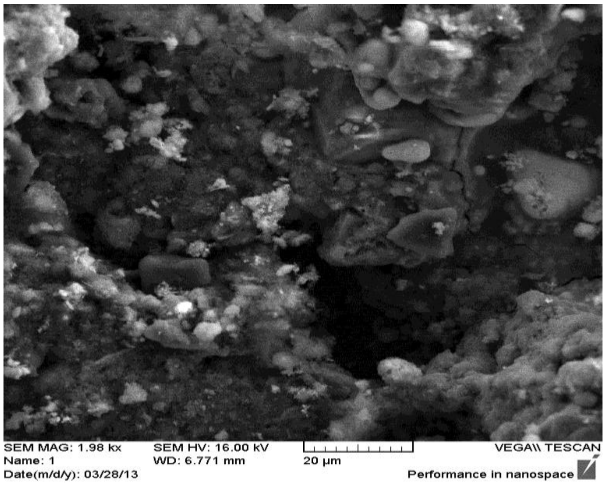

Figure3. The microscopic structure of the produced local adsorbent material at magnification power (1.98 kx).

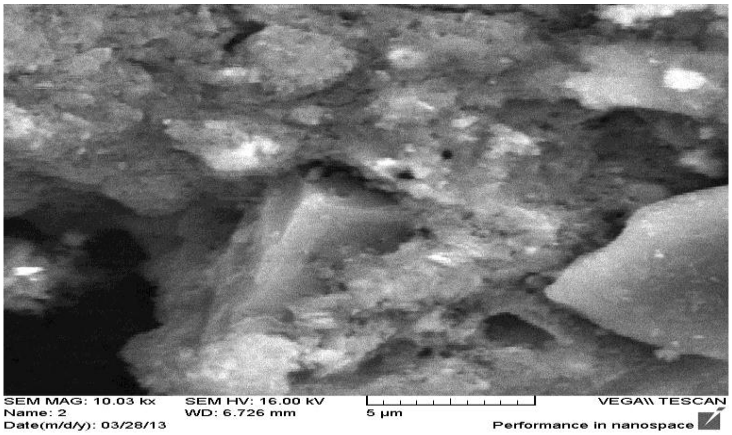

Figure4. The microscopic structure of the produced local adsorbent material at magnification power (10.03kx)

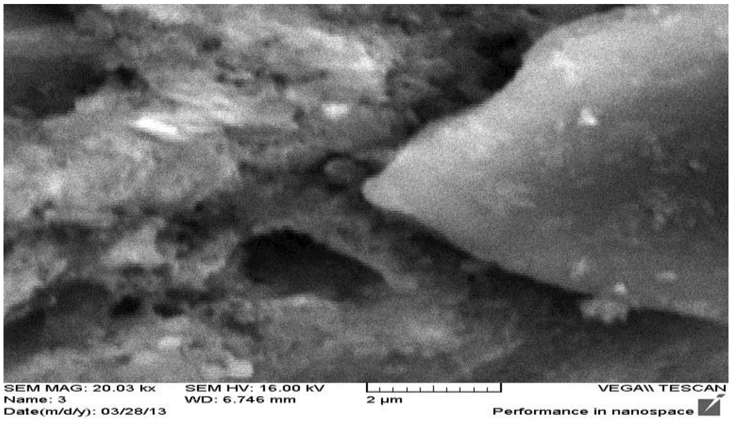

Figure 5. The microscopic structure of the produced local adsorbent material at magnification power (20.03 kx).

Figure6. Formation of white scattered particles on the surface.

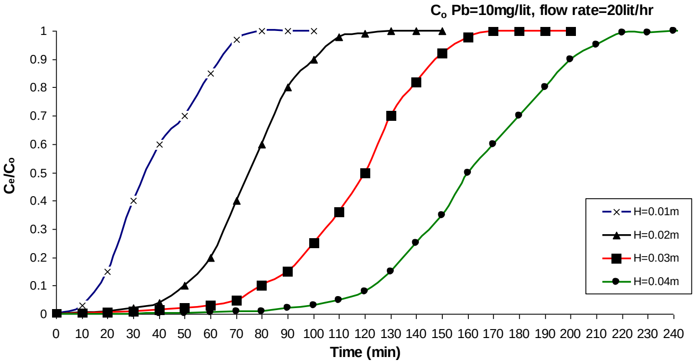

Figure7. Experimental breakthough curves for adsorption of Pb onto the produced activated carbon at different bed heights.

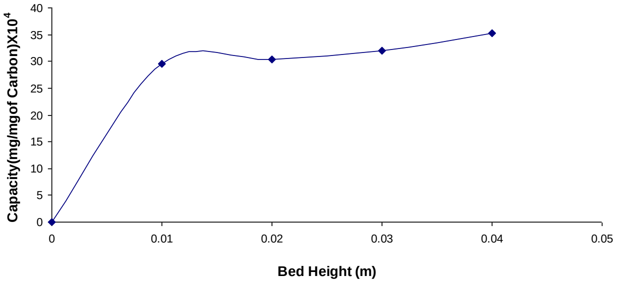

Figure8. Effect of bed heights on the capacity of the produced activated carbon.

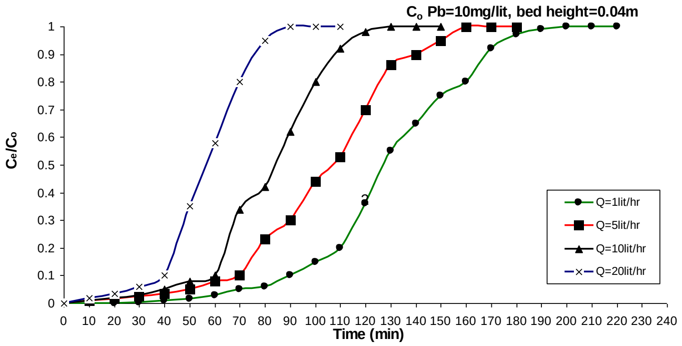

Figure9. Experimental breakthough curves for adsorption of pb onto the produced activated carbon at different flow rates.

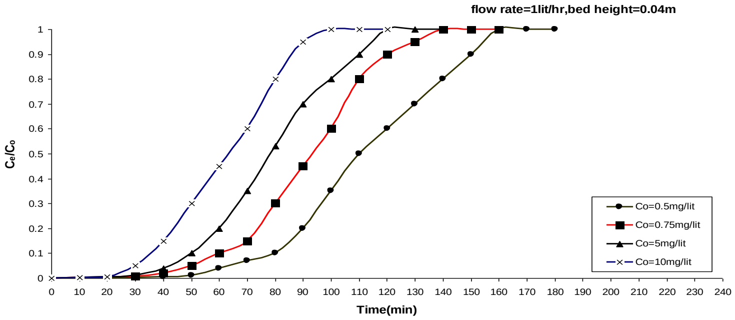

Figure10. Experimental breakthough curves for adsorption of Pb onto the produced activated carbon at different initial concentrations.

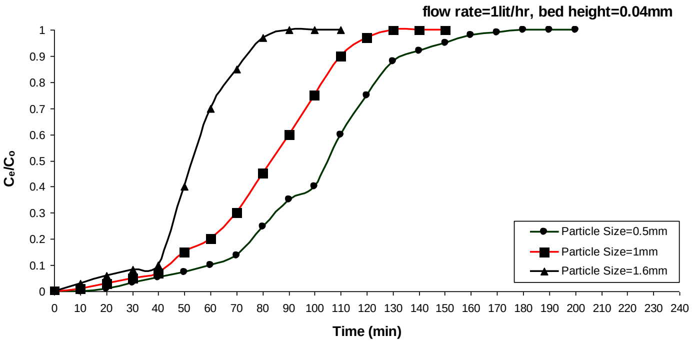

Figure11. Experimental breakthough curves for adsorption of Pb onto the produced activated carbon at different particle size.

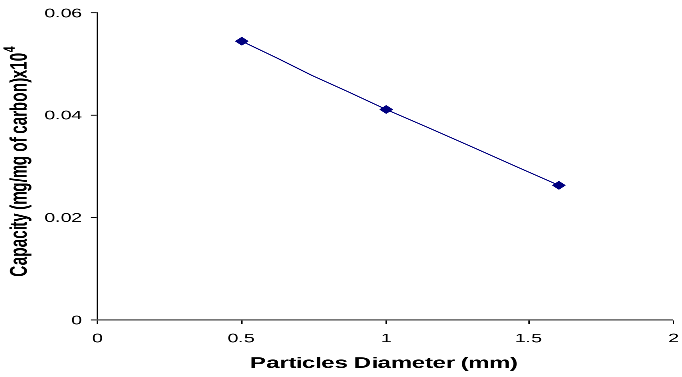

Figure12. Effect of the particle sizes on the capacity of the produced activated carbon

Table 1. Composition of tire rubbers

Component	Weight Percent[%]
Styrene-butadiene rubber (SBR)	62.1
carbon black	31.0
extender oil	1.9
zinc oxide	1.9
stearic acid	1.2
sulfur	1.1
accelerators	0.7

Table2. Composition of waste tires at pyrolysis process at (900 ºC).

Elemental analysis (wt.%)	**Waste tire**		
	Cunliffe and Williams, 1998	**Rodriguez et al., 2001**	**Murillo et al., 2005**
Carbon	86.4	88.64	83.92
Hydrogen	8.0	8.26	6.83
Nitrogen	0.5	0.43	0.78
Sulphur	1.7	1.43	0.92
impurities	3.4	1.24	7.55
Proximate analysis (wt. %)			
Moisture	1.3	0.94	0.79
Ash	7.1	3.83	4.16
Volatiles	62.2	64.09	64.97
Fixed carbon	29.4	31.14	30.08

Table3. The principle phases of pyrolysis process.

Temperature(ºC)	**Phases of pyrolysis process**
20-100	Mainly a dry phase meant for water removal and vapor formation.
100-150	Starting of thermal degradation reaction.
200-500	De-polymerization, H_2S separation, formation of olefin, paraffin, hydrocarbon and permanent gas.
500-600	Decomposition of long chain hydrocarbon into H_2, CO_2, CH_4 and olefin.
> 600	Mainly aromatic radical reactions with the formation of aromatic compounds take place.

Table4. The specification of lead nitrate.

Salt used to prepare the metal ionic solution	$Pb(NO_3)_2.H_2O$
Purity	98.5%
SolubiLy of the salt (mole/ L)	1.57
Hydrated cation radius (ºA)	2.61
Manufacturing company	BDH