



The adsorption of Cr(VI) and organic matter by new generation pyrolysis char

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ARTICLE INFO

Article history:

Received 24 July 2020
 Received in revised form 6 January 2021
 Accepted 6 January 2021
 Available online 30 March 2021

Keywords:

Char, adsorbent, waste tire, pyrolysis

ABSTRACT

Waste vehicle tires (WT) and high density polyethylene (HDPE) were pyrolyzed at 300, 500 and 700°C by slow pyrolysis. Solid product (pyrolysis char) were collected and pyrolysis char was used as adsorbent for COD and Cr(VI) removal. The char samples were characterized by BET, EDS, SEM and XRD analysis. Based on the BET, SEM and XRD results of the char samples, WT 700 can be used as adsorbents for Cr (VI) and organic material adsorptions. Cr(VI) and COD removal efficiency of char adsorbent were investigated. In the adsorption experiments, char was used as 0.1-0.5 g/100 mL doses and at 50°C and 80°C adsorption temperatures. The effects of adsorption temperature and char dosage on the adsorption efficiency were investigated. The maximum Cr(VI) adsorption capacity of this new generation char was found to be 14.09 mg/g for 80°C adsorption temperatures. 0.5 g/100 mL adsorbent dose was better in COD and Cr (VI) removals. The correlation of PSD1 (pseudo first order kinetic model) was better than PSD2 (pseudo second order kinetic model) for all doses. The Temkin and Langmuir isotherms were better isotherm for COD and Cr(VI) removals, respectively. A new approach were present to evaluation of waste HDPE and waste tires with this study.

Doi: 10.24012/dumf.773523

Introduction

Vehicle tires are important production for automotive industry. Today, a significant amount of waste vehicle tires are produced in the world. Turkey generates 300000 tons of waste tires per year [1]. These waste tires can cause serious environmental as well as health problems because they are not biodegradable. Tyre manufacturing companies use different toxic chemical additives like styrene-butadiene and polybutadiene within tires depending on its intended use [2] Vehicle tires are produced rubber and various additive materials.

Rubber material contain styrene-butadiene (~65%), carbon black (~31%), zinc oxide (~3%), and sulphur (~2%) [3]. The storage of waste tires in landfills and the incineration of those tires is prohibited according to Regulation of End of Life Tires in Turkey [4]. Until the 1960's, the produced vehicle tires used to be processed mechanically since raw rubber was used in the vehicle tire production and these tires could have been used in vehicles. When the using of synthetic rubber was increased, the production costs and the need for mechanical recycling reduced.

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Introduction

Consequently, the rate of rubber recycling fell to only 2 % after 1995 [5]. Pyrolysis of waste tires is one of the recent technologies in using of pyrolysis oil and solid products as an alternative fuel and adsorbent material. In this process, the organic compounds of the waste tire are decomposed to oil (liquid) and gas products while the inorganic compounds like metal compounds remain practically unaltered, allowing their separation to be recovered. Pyrolysis process is a significant recycling method for waste vehicle tires, Formation of toxic compounds in the environment can be prevented by this process. The usefull products are obtained from this process as fuels and/or adsorbent.

In scientific literature, there are many studies on using of pyrolysis oil as fuel [6-9]. Hurdogan and his colleagues investigated using of pyrolysis oil in diesel engines as fuel. They were determined engine emissions and engine performance. As a result, waste tire oil can be used as fuel [6]. Murugan et al. researched a study of pyrolysis oil obtained from waste tires, as a fuel in diesel engine. The results of the study showed that it is possible to start the engine filled with 70% pyrolytic oil [6,7].

Adsorption has long been used as a wastewater treatment technique for the removal of some

pollutants at industrial scale [10]. Activated carbon (AC) has been known since the middle ages to be able to remove dissolved substances from liquids. Many factors affect the amount of adsorption; chemical properties of the adsorbate, activated carbon properties, and liquid phase characteristics such as pH and temperature [11]

There are studies in which waste tire pyrolysis char is used in wastewater treatment [12,13]. In these studies, organic matter and heavy metals were successfully removed with char [12,13,14]. Some of these studies were given in Table 1.

A number of scientific studies showed that waste tire chars display strong adsorption capabilities for substances such as organic chemicals, dyes, heavy metals in wastewater or aqueous solution (Table 1). Generally, char samples that obtained from high pyrolysis temperature were shown to have high adsorption efficiency [12,13]. In the study of Amri et al. (2009), char was used as adsorbent for the adsorption of phenol. The maximum adsorption capacity of Langmuir isotherm was obtained as 156.250 mg / g [12]. The kinetics of Cu^{+2} removal by oxygenated and unoxxygenated char adsorbent obtained from waste tires was modeled with different kinetic models.

Table 1. Some adsorption studies from literature

| Reference | Pyrolysis Process System | Pyrolysis Temperature | Specific Surface Area | Activation /Preprocessing (for char) | Adsorbed element/compound |
|--------------------|--------------------------------|-----------------------|--|--------------------------------------|-------------------------------|
| Amri et al., 2009 | Muffle furnace | 800°C | 273 m ² /g | + | Phenol |
| Mui et al., 2010 | Muffle furnace | 1023-1323 °K | 99 m ² /g -48 m ² /g | + | Dye |
| Quek et al., 2011 | Horizontal tubular reactor | 550°C | 73.3 m ² /g | + | Cu^{+2} |
| Lian et al., 2013 | Horizontal cylindrical furnace | 200°C-800°C | - | + | Cu^{+2} /Naphthalene |
| Gupta et al., 2014 | Muffle furnace | 500°C | 562 m ² /g | + | p-cresol |
| Wang et al., 2014 | Stainless tube | 450°C - 800°C | 114 m ² /g | - | Methylene blue |
| Li et al., 2015 | Fixed bed quartz reactor | 500°C - 700°C | 54.9 m ² /g -73.5 m ² /g | + | Elementel mercury |

The char samples were obtained as oxygenated and unoxxygenated. According to study results,

adsorption of char samples were determined to occur via three and two distinct stages for

oxygenated and unoxygenated chars, respectively [14]. In a study adsorption of methylene blue by activated tire char was investigated. Reserchers were found the second-order model as the best fit [11].

As seen in Table 1 and in other studies, tire char samples have mesoporous-microporous structure with high specific surface area of 55 m²/g to 562 m²/g. Furthermore, these char samples were obtained by activation or pre-processing for increasing their surface area. In the production of activated tire char, energy source and chemical materials are used. The non-activated tire chars may also be used for water and wastewater treatment.

Industrial wastewaters contain toxic heavy metals in which high amounts are remained in the natural environment [16]. Cr (VI) is an important heavy metal pollutant in surface water and groundwater. This metal is originated from wastewater discharge of industrial facilities such as the metal coating and processing, otomotive industry, dye production [17]. The toxicity of Cr (VI) is high. Therefore, wastewater containing Cr (VI) must be treated before discharging into biological systems. Forms in which this element is toxic are Cr (VI), chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻). It has a mutogenic and teratogenic effect especially for kramat creatures [18].

The best heavy metal treatment method must be cost effective and capable of decreasing the metal. Adsorption is the most economic method for heavy metal removal using different adsorbents [19-20]. Many studies on AC adsorption have been carried out for enhancement of the Cr(VI) adsorption performance [21-22]. Activated carbon is generally obtained from natural sources such as coal and wood. Therefore, studies are still being carried out to produce higher effective, low-cost and environment-friendly adsorbent materials. In the last years, adsorbents have been prepared from solid wastes such as waste plastics, waste tires, biomass wastes [23-24].

In the scope of this study, firstly the waste vehicle tires and HDPE wastes were pyrolyzed in fixed bed pyrolysis reactor and the structure of pyrolytic chars were analyzed by FTIR, EDS,

SEM and BET analysis. The non-activated char samples were used as adsorbent for adsorption of toxic Cr(VI) anions and organic matter from synthetic wastewater. The adsorption capacity of pyrolysis char and kinetic parameters were evaluated.

Experimental

Preparation of pyrolytic chars

Fixed bed pyrolysis system was preferred for the pyrolysis of waste tires. Pyrolysis temperatures are 300, 500 and 700°C. Heating rate is 5°C/min. The pyrolytic chars were passed through a 250 mesh sieve to obtain uniform powder before using as adsorbent. All the char samples were non-activated (used as they are generated).

Characterization of pyrolytic chars

Char samples that obtained from pyrolysis process were characterized by different analyses. The surface properties of char materials were examined using an BET (Brunauer-Emmett-Teller) analyzer. Functional groups of char samples were determined by FTIR analyzer. The surface topography and EDS (Energy-Dispersive X-Ray Spectroscopy) elemental composition of char samples were scanned by SEM (Scanning Electron Microscope). XRD analyses were carried out on ray diffractometer with ID detector and furnace (up to 600 0C annealing). The XRD patterns were determined in range of $2\theta = 10-90^\circ$.

Adsorption studies

In Cr (VI) and organic matter removal studies, 170 mg/L potassium dichromate (K₂Cr₂O₇) and 700 mg/L Sodium acetate (C₂H₃NaO₂) standard solutions were used, respectively. Concentrations of the Cr(VI) and organic matter were determined using Standart Methods [25]. Chars that obtained at 700°C pyrolysis temperature were evaluated as adsorbent. Adsorption studies were performed in batch system at 50°C and 80°C for 0.1 g/100 mL, 0.3 g/100 mL and 0.5 g/100 mL adsorbent doses in 120 minutes. After the adsorption process, homogeneous liquid was seperated for COD

(Chemical Oxygen Demand) and Cr (VI) analyses.

Kinetic models of adsorption studies

The pseudo-first order kinetic model (Eq.1) and pseudo-second order (Eq.2) kinetic models were performed for the kinetic calculations of the adsorption study.

$$\log(qe - qt) = \log qe - \frac{k_1 t}{2.303} \quad (1)$$

where q_e : amounts of removed Cr (VI) or organic matter (mg/g), q_t : amounts of removed Cr (VI) or organic matter (mg/g) at any time, k_1 : rate constant (min^{-1})

$$\frac{t}{qt} = \frac{1}{k_2} \cdot qe_2 + \frac{t}{qe} \quad (2)$$

where k_2 : rate constant (min^{-1})

Adsorption isotherms

The adsorption capacities were calculated according to Eq.3.

$$q = \frac{V(C_0 - C_e)}{m} \quad (3)$$

where V : volume of sample (L), m : amount of adsorbent (g), C_0 : initial Cr(VI) concentrations (mg/L) and C_e : the and equilibrium Cr(VI) concentrations (mg/L)

Different theoretical models could be applied to experimental data for find a model which describes equilibrium data. Langmuir, Freundlich and Temkin isotherms have been generally used to describe the equilibrium determined between removed ions on the adsorbent (q_e) and ions in water (C_e) at equilibrium [26]. A monolayer adsorption onto a surface is explained by Langmuir model. This model is represented by Eq.4 [31]. The Freundlich isotherm (Eq. 5) is a multilayer adsorption isotherm. This isotherm supposes that the removed of ions occurs on a heterogeneous surface of adsorbent. According to Temkin isotherm, the heat of adsorption

would change linearly [27]. The Temkin isotherm assumes that taking into the account of between the adsorbent and adsorbate interactions by Eq.6 [28].

$$qe = \frac{q_{\max} \cdot b \cdot Ce}{(1 + b \cdot Ce)} \quad (4)$$

$$qe = k \cdot Ce^{1/n} \quad (5)$$

$$qe = B \cdot \ln A t + B \cdot \ln C e \quad (6)$$

where q_{\max} (mg/g): value of maximum adsorption capacity, b : rate constant of Langmuir adsorption, k and n : constants of Freundlich, A : equilibrium binding constant of Temkin isotherm (L/g), B : Constant (J/mol) (related to heat of sorption).

Results and discussion

Characterization of pyrolysis char

In the scope of the study, waste tire (WT) samples and waste HDPE and waste tire mixtures (for different mixture ratio) were pyrolysed at 300°C, 500°C and 700°C. Firstly, BET and FTIR analyses were performed for char characterization. FTIR spectras were given in Fig.1. These results were summarized in Table 2, together with pyrolysis yields. In waste tire pyrolysis, as the pyrolysis temperature increases the pyrolysis yield increases for each group. Furthermore, the pyrolytic char became more porous with the increase of specific surface area and specific porosity. Generally, the porosity increases and the specific surface area increases with the increase of decomposition. S_{BET} values were char samples (405-519 m^2/g) were higher than activated tire chars were obtained from other scientific studies [30].

HDPE wastes were shown significantly effective on co-pyrolysis with WT. In WT-HDPE co-pyrolysis, as HDPE ratio increased, pyrolysis yields increased. Also pyrolysis temperature and decomposition increased, carboxylic and lactonic acid groups were converted to phenolic groups for WT pyrolysis and WT-HDPE co-pyrolysis. The peaks observed in FTIR spectra of WT-HDPE char samples represented the aliphatic C-H groups

and aromatic C-C groups. Chars obtained from WT-HDPE co-pyrolysis were showed higher aromatic structure from WT pyrolysis char samples. When the temperature increased from 300°C to 700°C, specific surface area and specific pore volume of WT-HDPE chars increased by 4-6.5% and 4-5%, respectively. During depolymerization, a physical change become at the surface of the char samples. The complex functional groups (carboxylic and lactonic acid grups) decomposed to phenolic acid groups. As result, the large number of pores were generated in the char structure.

Because that char samples were found to be mesoporous and macroporous materials, they may show good adsorption properties. In WT-HDPE pyrolysis, highest pyrolysis yields were obtained at 700°C pyrolysis temperature for all ratios. WT chars (300°C,500°C,700°C) and WT-HDPE chars (700°C) were analysed by EDS, XRD and SEM. Table 3 shows the composition some pyrolytic chars. According to EDS results, C peak is the biggest peak at a binding energy of 285-290 eV. Another major elements are O (545-550 eV), S (591-597 eV), Zn (1020-1021 eV) and Si (624-628eV). In WT pyrolysis, when pyrolysis temperature increase from 300°C to 700°C, C elements content of WT chars increases from 79.53% to 85.89%, whereas the O contents increase from 11.94% to 21.57%. Intense deoxygenation and dehydrogenation reactions occur during depolymerization. Accordingly, the wedge becomes more aromatic at 700C [32].

Waste tyre pyrolysis char composition was mainly 78.9 wt.% of carbon, 6.9 wt.% of volatiles compounds and 13.7 wt.% of ashes. Thus, the waste tire char becomes a good source of activated carbon [24].

When HDPE ratio increased, these C elements ratio increased for WT-HDPE pyrolysis. These

result were supported by Table 2 and Fig.1. When HDPE ratio increased, phenolic, carboxylic acid groups and aliphatic groups were decomposed to aromatic C-C groups. C elements ratio increase as pyrolysis temperatures increase and pyrolysis yields increase (Table 2 and Fig.1). Besides this, it is notable the WT char samples has higher Zn and Si compared with WT-HDPE char samples. These elements are from additives of tire structure. When WT ratio was decreased phenolic and carboxylic acid, these other elements decreased. WT25+HDPE75 char samples has higher C and O ratios compared with its WT char samples. Consequently, according to pyrolysis yields (Table 2) and elemental composition (Table 3) results, WT-HDPE waste mixtures in co-pyrolysis showed higher elemental decomposition and higher aromatic structure as compared to WT samples pyrolysis. X-Ray diffraction (XRD) analyses results for char samples are shown in Fig. 2. In Fig.2(A), two peaks are observed at 22° and 46°, which related to the 002 and 10 bands (diffuse graphite bands). The peak is binded to the graphitic structures of crystallites of pyrolytic char and the two-dimensional band (at 46°) is added to atomic order (like graphite) within a single plane structure [33]. According to (Fig.2 (B)), the broad bands (at 22°) show that HDPE-WT char samples have a disordered structure. This disordered carbon structure occurs from aliphatic side chains and morphous carbon.

The intensity of the XRD spectra of all char samples became weaker as the pyrolysis temperature increased. As result, the peak of spectras became sharper and more symmetric.

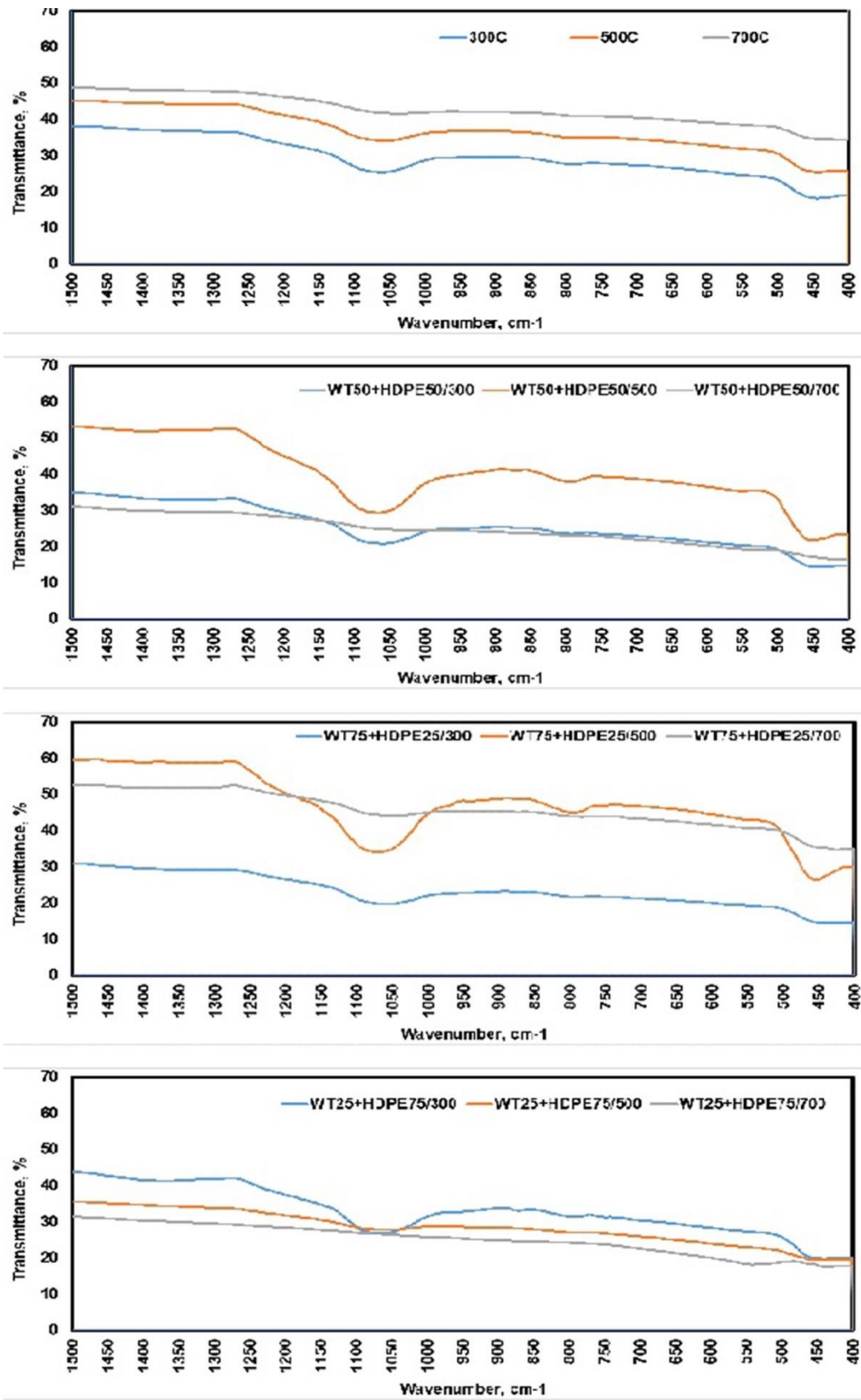


Figure 1. FTIR spectras of char samples

Table 2. Pyrolysis yields and different properties of char samples

| Char Name | Yield (%) | Different properties of char samples | | |
|-----------------|-----------|---|-------------------------------------|--|
| | | Specific Surface Area S_{BET} (m^2/g) | Specific Pore Volume V (cm^3/g) | Functional Groups (Determined from FTIR spectrums) |
| WT/300 | 59.18 | 424 | 0.108 | Phenolic groups, carboxylic groups, lactonic acid groups |
| WT/500 | 64.07 | 497 | 0.119 | Phenolic groups, carboxylic acid groups |
| WT/700 | 60.79 | 519 | 0.135 | Phenolic acid groups |
| WT25+HDPE75/300 | 86.23 | 411 | 0.123 | Phenolic acid groups, aliphatic C-H groups, aromatic C-C groups |
| WT25+HDPE75/500 | 89.45 | 405 | 0.123 | Phenolic acid groups, aliphatic C-H groups, aromatic C-C |
| WT25+HDPE75/700 | 90.06 | 428 | 0.129 | Phenolic acid groups, aliphatic C-H groups, aromatic C-C groups |
| WT50+HDPE50/300 | 76.50 | 442 | 0.103 | Phenolic groups, carboxylic acid groups, aliphatic C-H, aromatic C-C groups |
| WT50+HDPE50/500 | 79.10 | 423 | 0.110 | Phenolic groups, carboxylic acid groups, aliphatic C-H groups, aromatic C-C groups |
| WT50+HDPE50/700 | 83.56 | 417 | 0.109 | Phenolic acid groups, aliphatic C-H groups, aromatic C-C groups |
| WT75+HDPE25/300 | 70.82 | 431 | 0.128 | Phenolic groups, carboxylic groups, lactonic acid groups, aromatic C-C groups |
| WT75+HDPE25/500 | 71.64 | 445 | 0.130 | Phenolic groups, carboxylic groups, aliphatic C-H groups, aromatic C-C groups |
| WT75+HDPE25/700 | 75.43 | 459 | 0.133 | Phenolic groups, aliphatic C-H groups, aromatic C-C groups |

*[WT(X)+HDPE(Y)/(C) : X: WT ratio – Y: HDPE ratio – C:Pyrolysis temperature]

Table 3. Elemental composition of char samples

| Char Name | Elemental Composition (wt%) | | | | | | |
|-----------------|-----------------------------|-------|-------|------|------|------|------|
| | C | O | S | Zn | Cu | Ca | Si |
| WT/300 | 79.53 | 11.94 | 0.84 | 2.38 | 0.81 | 0.57 | 3.71 |
| WT/500 | 67.96 | 12.43 | 0.56 | 1.75 | 0.69 | 0.15 | 6.85 |
| WT/700 | 85.89 | 21.57 | 0.946 | 4.87 | - | 0.44 | 6.73 |
| WT25+HDPE75/700 | 88.72 | 4.5 | 1.84 | 3.06 | 0.25 | 1.01 | 0.25 |
| WT50+HDPE50/700 | 84.41 | 7.92 | 1.12 | 1.43 | 0.81 | 1.77 | 1.46 |
| WT75+HDPE25/700 | 72.25 | 15.80 | 0.20 | 0.58 | 0.54 | 0.27 | 0.73 |

Morphology of the chars obtained from pyrolysis of WT and WT-HDPE were given in Fig. 3. It is seen that there are developed pores over the surface of WT char samples. There are more pores on the surfaces of the WT char compared to WT-HDPE char, due to the aromatic structure of HDPE. It was apparent that at higher pyrolysis temperature, a larger

number of developed pores were observed for all samples.

Based on the BET, SEM and XRD results of the char samples, WT 700 can be used as adsorbents for Cr (VI) and organic material adsorptions, due to the importance of mesopore structure to many adsorption methods.

Adsorption kinetics results

COD and Cr(VI) removal efficiencies were given in Fig. 4 for all samples. The rate of change in COD and Cr(VI) removal showed a much faster increase for 50°C than for 80°C.

COD removal efficiencies were between 60-90% and 40-60% for 50°C and 80°C, respectively. Similarly, maximum Cr(VI) removal efficiencies were %80 and %70 for 50°C and 80°C adsorption temperatures. As the reason for these results, it can be say that when adsorption temperature increased, pore size of char decreased. Consequently, it can be say that adsorption efficiencies of COD and Cr (VI) decreased.

Because of the porous morphology of char samples, as the adsorbed COD and Cr(VI) increased, char surface area decreased and adsorption efficiencies decreased for all samples. In removal of COD and Cr (VI), 0.5 g/100 mL adsorbent dose were better than other doses. According to the adsorption results, COD and Cr (VI) adsorption was rapid in the first 20 minutes. Afterwards, the adsorption rate decreased for all doses and temperature values. While all samples showed a decreasing adsorption rate with increasing contact time, the adsorption capacity for the WT700 has increased significantly.

The parameters of the kinetic models are calculated and given in Table 4. Pseudo first order model parameters for all doses showed better results than pseudo second order model parameters. According to Pseudo first order model results, adsorption rate and surface adsorption are closely related. It is known that the adsorption capacity depends on the active pores on the surface of the char [34,35]. The adsorption rates increased with adsorbent dose, as shown by the increasing rate constants from Table 4. However, increasing rate of adsorption with increasing to 80°C adsorption temperature was not observed for all doses. The decreasing in adsorption could be due to the increasing of precipitation, which decreasing of the concentration of Cr (VI) and COD for 80°C. Another reason could be the increased external

resistance with higher temperature. This resistance occurs against to metal transport by the boundary layer. As result, lower rates of metal removal occurs for higher adsorption temperature[18]. The isotherm constants of the Langmuir, Freundlich and Temkin models were given in Table 5. According to R^2 values, the Temkin isotherm were better than Langmuir and Freundlich isotherm for COD removal. However, the data fit Langmuir isotherm better than other isotherm models for Cr (VI). Therefore, the these isotherms shows that the Cr(VI) was adsorbed in monolayers of WT700. According to Langmuir analysis, the maximum Cr(VI) adsorption capacity of WT700 was determined as 0.486 mg/g and 14.09 mg/g for 50°C and 80°C adsorption temperatures, respectively. These results show that the Cr (VI)adsorption is monolayer adsorption on homogeneous surfaces of WT700 rather than multilayer adsorption on heterogeneous surfaces of WT700.

Ecological and Economic Advantages of Study

Among the industrial adsorbents, activated carbon having high porosity is the most important of the adsorbents currently used for controlling environmental pollution. Commercially active carbons are obtained by activating carbon obtained from wood, lignite, charcoal, through various processes.

Energy and chemical gases are used in the activation of these adsorbents. Activation temperatures are between the 500-800°C. Commercial active carbon surface area is between 400-1600 m²/g. Natural resources are being destroyed in the production of activated carbon. In addition, activated carbon production cause high energy costs. Therefore, new of adsorbents generation from wastes can be preferred instead of these commercial activated carbons. Moreover, the activation process was not carried out in the production of these chars. By using only electrical energy, both waste tires have been removed and a new adsorbent

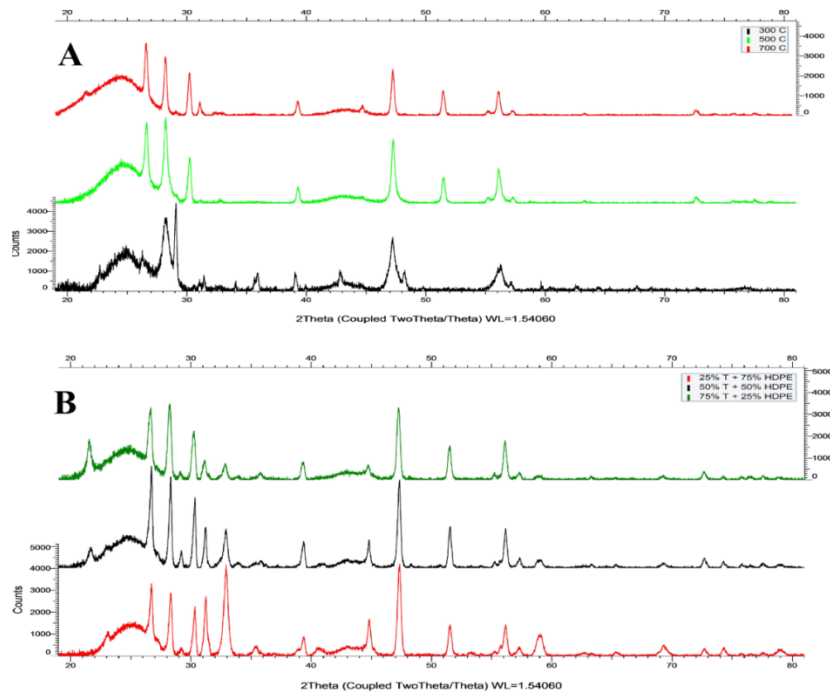


Figure 2. X-Ray diffraction (XRD) characterization for char samples

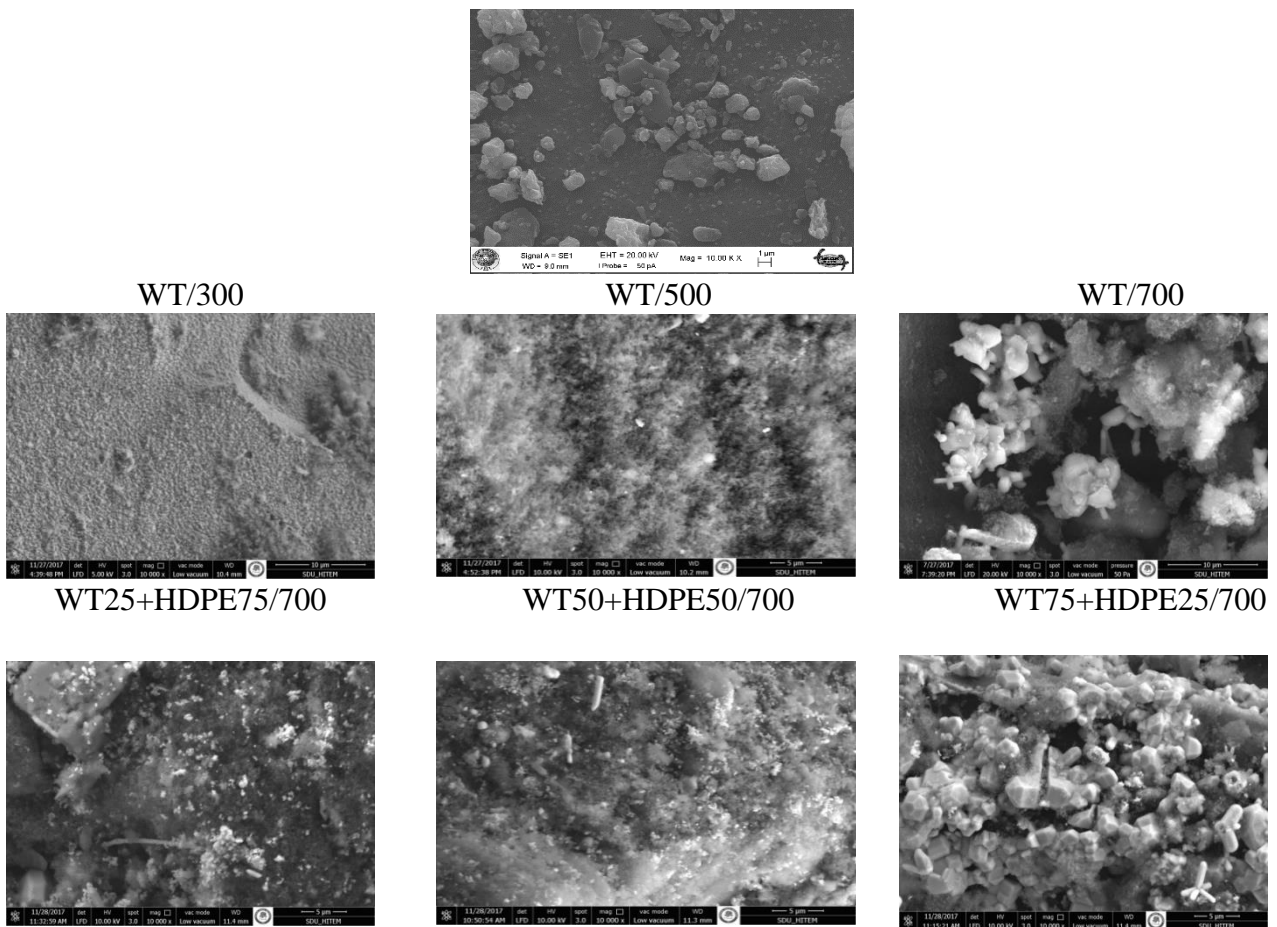


Figure 3. SEM images of WT and WT-HDPE char samples (X10000)

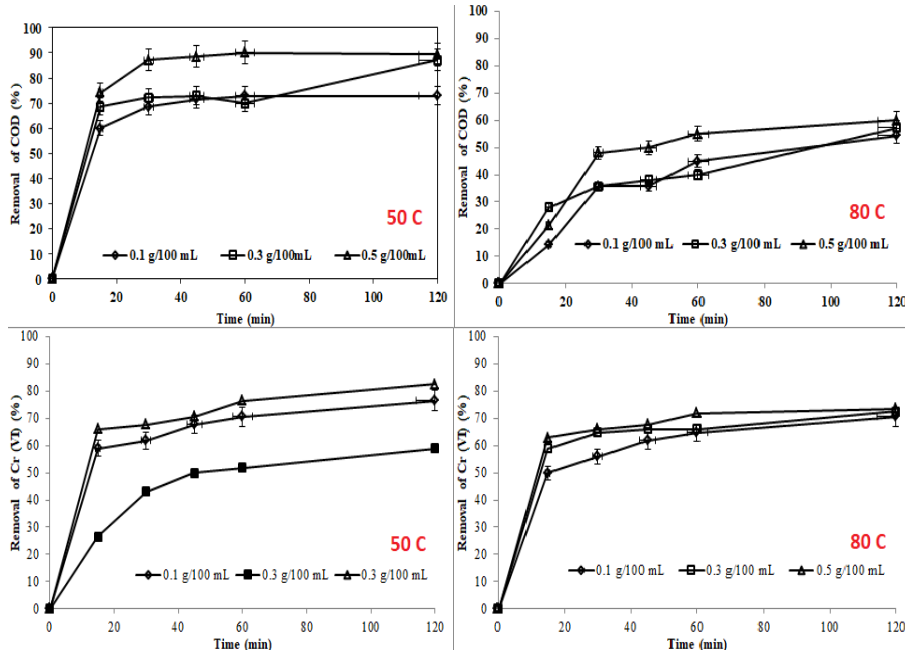


Figure 4. Adsorption efficiencies of COD and Cr (VI) with time

material has been obtained from these wastes. In addition, a natural resource has not been destroyed. A cost analysis has been carried out for application of this study in a medium-scale pyrolysis facility. In Table 6, costs were given for pyrolysis facility [36]. In Turkey, cost of commercial activated carbon is changed between the 890-1115 \$/tone. According to

Table 6, WT tire char cost is 540 \$/tone. The adsorbent obtained from waste tire pyrolysis are more economic than commercial activated carbon. This study provides environmental friendly and economic benefits in production of adsorbent.

Table 4. Kinetic parameters of kinetic models

| | Pseudo First Order | | | | Pseudo Second Order | | | |
|--------|--------------------|-------|--------|-------|---------------------|-------|--------|-------|
| | 50°C | | 80°C | | 50°C | | 80°C | |
| | 0.1 g/100 mL | | | | | | | |
| | k_1 | R^2 | k_1 | R^2 | k_2 | R^2 | k_2 | R^2 |
| COD | 0.0065 | 0.825 | 0.0078 | 0.995 | 0.0075 | 0.942 | 0.0081 | 0.924 |
| Cr(VI) | 0.0075 | 0.994 | 0.0063 | 0.991 | 0.0088 | 0.987 | 0.0075 | 0.988 |
| | 0.3 g/100 mL | | | | | | | |
| | k_1 | R^2 | k_1 | R^2 | k_2 | R^2 | k_2 | R^2 |
| COD | 0.0025 | 0.974 | 0.0033 | 0.991 | 0.0035 | 0.975 | 0.0045 | 0.977 |
| Cr(VI) | 0.0029 | 0.990 | 0.0047 | 0.997 | 0.0029 | 0.963 | 0.0061 | 0.954 |
| | 0.5 g/100 mL | | | | | | | |
| | k_1 | R^2 | k_1 | R^2 | k_2 | R^2 | k_2 | R^2 |
| COD | 0.0074 | 0.997 | 0.0045 | 0.998 | 0.0091 | 0.994 | 0.0081 | 0.988 |
| Cr(VI) | 0.0082 | 0.993 | 0.0059 | 0.994 | 0.0088 | 0.987 | 0.0075 | 0.990 |

Table 5. Isotherm constants in adsorption of COD and Cr(VI)

| Constants | 50 °C | | 80 °C | |
|-----------------------|--------|--------|--------|--------|
| | COD | Cr(VI) | COD | Cr(VI) |
| Langmuir | | | | |
| Q _m (mg/g) | 0.651 | 0.486 | 6.950 | 14.09 |
| K _L (L/mg) | 0.001 | 0.002 | 0.0142 | 0.274 |
| R ² | 0.661 | 0.993 | 0.9471 | 0.993 |
| Freundlich | | | | |
| K _F | 1.430 | 1.087 | 3.349 | 23.517 |
| 1/n | 0.542 | 0.241 | 0.622 | 15.055 |
| R ² | 0.974 | 0.989 | 0.966 | 0.988 |
| Temkin | | | | |
| B | 413.0 | 8.071 | 597.90 | 927.0 |
| A _t | 1657.0 | 0.101 | 3281.4 | 3512.9 |
| R ² | 0.999 | 0.976 | 0.998 | 0.931 |

Table 6. Costs for pyrolysis facility

| | |
|--|----------|
| Facility Capacity (tone/day) | 70-270 |
| Cost of Capital (\$) | 16-90 |
| Operating and maintenance cost (\$/7 year) | 80-150 |
| Facility Capacity (tone/7 year) | 178850 |
| Capital+Operating+Maintenance Cost (\$/7 year) | 96000000 |
| Unit Cost (\$/tone) | 540 |

Conclusions

Pyrolysis chars which are generated from waste tire were used as a recycled adsorbent material for the adsorption of Cr(VI) and organic materials from water in this study. When pyrolysis temperature increase from 300°C to 700°C, C elements content of WT chars increase. The according to BET analysis, the char produced from 700°C pyrolysis temperature (WT700) showed high specific surface. As result, these adsorbent successfully adsorbed Cr(VI) anions from water. The maximum Cr(VI) adsorption capacity of WT700 was found to be 14.09 mg/g for 80°C adsorption temperatures. 0.5 g/100 mL adsorbent dose was better in COD and Cr (VI) removals. The correlation of pseudo first order model was better than pseudo second order model for all doses. The Temkin and Langmuir isotherms were better isotherm for COD and Cr(VI) removals, respectively. The chars obtained from this study can adsorb Cr(VI) and organic matter. As result, WT700 adsorbent obtained from waste tire pyrolysis is non-activated. No other chemicals and energy were

used as in other production process of active carbon. These non-activated char were show good adsorbent properties. Successful results were obtained from adsorption experiments. This study might significantly provide the economic and environmental benefits in the production of adsorbent. Waste tires can also be studied for the removal of other pollutant parameters in the subsequent studies after this work. In this study, only WT was used in adsorption experiments. However, adsorption experiments of co-pyrolysis char can be performed for evaluation of waste HDPE in water treatment.

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