

**Generation of Activated Carbon on the Surface of Used
Vehicle Tires through Pyrolysis Treatment**

By

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Generation of Activated Carbon on the Surface of Used Vehicle Tires through Pyrolysis Treatment

ABSTRACT

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This study investigated the generation of activated carbon (AC) on the surface of used vehicle tires through pyrolysis treatment. Granular activated carbon (GAC) is a useful remediation tool, which in recent years has been used to remediate contaminated sediments. The generation of AC on the surface of used tires would be beneficial for sediment remediation as this form of AC could easily be removed from the sediment once saturated eliminating any chance of leaching. Pyrolysis conditions were held isothermally ranging from 20 to 50 min with ten min intervals. The ranges of temperatures investigated in this study were 250 to 290° C and 330 to 360° C. AC generation was quantified using American Standard Test Method Designation D4607-94. The control samples had an average iodine number of 151 mg/g \pm 21.7 %. Pyrolysis conditions that generated the greatest iodine number were 340° C held isothermally for 20 min, which produced an iodine number for the solid sample of 669 mg/g \pm 22.2 %. The powdered sample with parallel pyrolysis condition generated an iodine number of 577 mg/g \pm 2.44 %. No observable pattern was seen between generation of AC and holding temperature and time. Commercially sold GAC has a range of iodine numbers from 800 - 1,200 mg/g. The American Water Works Association (AWWA) has a minimum of 500 mg/g requirement for AC. This

being said, while samples generated iodine numbers lower than those of commercially sold GAC it is still applicable for remediation as it meets the AWWA requirements.

TABLE OF CONTENTS

ACKNOWLEDGMENT	III
ABSTRACT.....	IV
LIST OF TABLES	VII
LIST OF FIGURES	VIII
INTRODUCTION.....	1
MATERIALS AND METHODOLOGY	5
MATERIALS AND EQUIPMENT.....	5
PYROLYSIS TREATMENT	6
IODINE NUMBER	6
RESULTS AND DISCUSSION	7
PYROLYSIS TREATMENT	7
IODINE NUMBER	8
<i>INTACT TIRE SAMPLES</i>	<i>10</i>
<i>POWDERED TIRE SAMPLES</i>	<i>11</i>
SUMMARY OF CONCLUSIONS	14
FUTURE STUDIES	15
REFERENCES.....	17

LIST OF TABLES

Table 1. Holding temperatures and times with corresponding sample numbers.	19
Table 2. Iodine numbers for Samples A and B, average iodine numbers, and percent differences for solid samples.	20
Table 3. Maximum average iodine number and percent of overall maximum iodine number for solid samples.	21
Table 4. Iodine numbers for Samples A and B, average iodine numbers, and percent differences for powdered samples.	22
Table 5. Maximum average iodine number and percent of overall maximum iodine number for powdered samples.	23

LIST OF FIGURES

Figure 1: Conceptual model of in situ GAC treatment sorbing contaminants which desorb from contaminated sediment.....	24
Figure 2: Conceptual model of in situ sediment remediation with structured activated carbon...	25
Figure 3: Experimental setup for pyrolysis treatment.....	26
Figure 4: Tire sample after simulation of procedure performed in Mui et al. (2010).....	27
Figure 5: Tow-Master tire sample processed at 250° C and held isothermally for 20 min.....	28
Figure 6: Visual alterations of Sample 44 before and after pyrolysis treatment.	29
Figure 7: Load Star tire sample processed at 360° C and held isothermally for 40 min.....	30
Figure 8: Average iodine numbers for Samples 1-4. Error Bars are based on percent differences from Table 2.....	31
Figure 9: Average iodine numbers for Samples 5-8. Error Bars are based on percent differences from Table 2.....	32
Figure 10: Average iodine numbers for Samples 9-12. Error Bars are based on percent differences from Table 2.	33
Figure 11: Average iodine numbers for Samples 13-16. Error Bars are based on percent differences from Table 2.	34
Figure 12: Average iodine numbers for Samples 17-20. Error Bars are based on percent differences from Table 2.....	35
Figure 13: Average iodine numbers for Samples 33-36. Error Bars are based on percent differences from Table 2.	36
Figure 14: Average iodine numbers for Samples 37-40. Error Bars are based on percent differences from Table 2.	37
Figure 15: Average iodine numbers for Samples 41-44. Error Bars are based on percent differences from Table 2.	38
Figure 16: Average iodine numbers for Samples 45 and 46. Error Bars are based on percent differences from Table 2.	39

Figure 17: Average iodine numbers for powdered Samples 37-40. Error Bars are based on percent differences from Table 4.	40
Figure 18: Average iodine numbers for powdered Samples 41-44. Error Bars are based on percent differences from Table 4.	41
Figure 19: Average iodine numbers for powdered Samples 45 and 46. Error Bars are based on percent differences from Table 4.	42
Figure 20: Relationship between iodine number and holding temperature for Samples 1-20.....	43
Figure 21: Relationship between iodine number and holding temperature for Samples 33-46....	44
Figure 22: Relationship between iodine number and holding temperature for powdered Samples 33-46.	45
Figure 23: Comparison of iodine numbers for intact and powdered tire samples.	46

DEDICATION

This thesis is dedicated to both of my parents who encouraged me to get a college degree before
I even knew what college was.

INTRODUCTION

An estimated 290 million scrap tires were generated in 2003 and 275 million more have been previously improperly disposed of in the United States (U.S. EPA, 2012). Vehicle tires are scrapped when they are no longer road worthy (i.e. unsafe to drive on, punctured, etc.). This is problematic due to their engineered durability which makes tires highly resistant to decomposition. The large number of vehicle tires being discarded every year is a significant threat to the environment; however processes that use them as building blocks for new remediation techniques would provide a beneficial use.

Used tires are not considered a hazardous waste by the Environmental Protection Agency, but the products produced (i.e. oil, gases, and heavy metals) through burning used tires are classified as hazardous (U.S. EPA, 2012). Scrap tire piles can spontaneously combust; though infrequent, these fires pose a problem because they can burn uncontrollably for months producing acrid black smoke (Riddle, 2009). Due to the infrequency of spontaneous tire fires, the health and environmental concerns associated with these fires are minimal. The major health and environmental concern associated with scrap tire piles is they provide breeding grounds for rodents and mosquitoes, which are known to carry diseases that are harmful to humans and household pets (U.S. EPA, 2012). The most effective way to reduce mosquito and rodent growth is to eliminate their potential habitats such as scrap tire piles.

By the end of 2003 approximately 80% of newly generated used vehicle tires were recycled as ground rubber and other products (U.S. EPA, 2012). Waste vehicle tires were also used in nontraditional asphalt, as fuel, exported, and various other pathways. By finding additional innovative uses for waste tires the amount and size of scrap tire piles can be reduced even more dramatically.

Pyrolysis is the process of exposing an organic compound to very high temperatures in the absence of oxygen resulting in its decomposition; it is an irreversible process (Bronstein et al., 1987). Pyrolysis specific to generating activated carbon uses a carbon source that is heated in the absence of oxygen to break the cross linkages between the carbon bonds. The broken cross linkages provide sites for sorption of contaminants. Pyrolysis may provide an additional pathway by which discarded tires can be reused.

Pyrolysis has been used to convert waste tires to granular activated carbon (GAC), but the process has not been studied with the objective of preserving the structure of the tire while still incorporating activated carbon on the surface of the tire (Gupta et al., 2011; Mui et al., 2010). If activated carbon can be generated at the tire surface it would provide a basis for sediment remediation. Tires converted to activated carbon could be placed in contaminated sediments. Similar to the dynamics described by Luthy et al. (2004), the activated carbon tires would adsorb contaminants after they desorbed from the sediments.

Anthropogenic sources have contaminated extensive amounts of sediment not limited to marine sediments (i.e. lake and river sediments). Sediment contamination in the United States is nationwide (National Research Council, 2007). The prevalence of sediment contamination is problematic as it impacts aquatic life, wild life, and human health either directly or through bioaccumulation (National Research Council, 1989). The most common sediment contaminants are pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and chlorinated hydrocarbons (Technology Innovation and Field Services Division, 2013). Of these PAHs are a Class A carcinogen; Class A carcinogens are known to cause cancer in humans (Watts, 1998). Though not known to cause cancer in humans, the most prevalent group of hydrophobic organic contaminant of concern in sediments are PCBs, which are a Class B2

carcinogen. (Cho et al., 2009; National Research Council, 2007). This class designation indicates that there is no evidence of human carcinogenicity, however there is evidence that PCBs cause cancer in animals.

The widespread sediment contamination has brought attention to developing a technique that is capable of remediating sediments. Bioremediation, soil vapor extraction, and zero-valent iron degrade a narrow range of contaminants and are generally incapable of treating sorbed contaminants and dense nonaqueous phase liquids (DNAPLs) due to mass transfer limitations (Watts and Teel, 2006). These remediation techniques would therefore be ineffective for sediment remediation. In-situ chemical oxidation (ISCO) would be effective for rapid cleanup and destruction of sorbed contaminants and DNAPLS; however this remediation technique is not always an economical option. Studies have been conducted using GAC to treat sediment contamination with encouraging results (Luthy et al., 2004; Tomaszewski et al., 2007)

Luthy et al. (2004) investigated the use of activated carbon as an in situ treatment for reducing the bioavailability of PCBs in marine sediment at Hunters Point in San Francisco Bay, California. They also investigated the bioaccumulation of PCBs in benthic organisms. They found that after 6 months of contact time with activated carbon the aqueous PCB concentration was reduced by 86% relative to their control. Similar results were observed in the reduction of bioaccumulation of PCBs in benthic organisms. They concluded that the PCBs are less bioavailable due to its strong binding to the activated carbon.

A similar study was conducted in Richmond, California in which activated carbon was mixed with marine sediments contaminated with dichlorodiphenyltrichloroethane (DDT) (Tomaszewski et al., 2007). The area was dredged 6 years prior to the study. Dredging proved to be less effective than desired as residual DDT concentrations were above the maximum

contaminant levels (MCLs). Tomaszewski et al. (2007) proposed the addition of activated carbon to the sediment to further treat residual DDT contamination. Their study found the addition of ACRS activated carbon to the sediment reduced the aqueous phase concentration of DDT by 83%. The results of Tomaszewski et al. (2007) demonstrate the effectiveness of utilizing activated carbon as a means of in situ stabilization of DDT in marine sediments as a more permanent and effective solution than dredging.

The concept of desorption of contaminants from sediment particles and sorption to activated carbon particles is illustrated in Figure 1. The contaminants in the aqueous phase are adsorbed by the available GAC and desorption of contaminants from sediment particles to the aqueous phase occurs to achieve equilibrium. The newly desorbed contaminants are now available for sorption to GAC that still has attachment sites.

Due to the high efficiency of activated carbon to remove contaminants and a trend in our society to recycle, alternative base materials are being used. Alternative base materials used to generate activated carbon include coconut, almond, and pecan shells; waste newspaper, and food processing waste to reduce the cost of activated carbon generation (Zhonghua and Srinivasan, 199; Dias et al., 2007; Dall'Orso et al., 1998; Mahapatra et al., 2012). Activated carbon generated from these base materials have proved to be effective in removing contaminants in addition to reducing the amount of waste our society creates.

Commercial grade activated carbon has a range of iodine numbers from 800 – 1,200 mg/g (Y-Carbon, 2013). Determination of the iodine number is a common tool used to quantify the sorptive capacity of activated carbon. It is a measure of the amount of iodine adsorbed by 1 g of activated carbon. The adsorption of iodine is used as an indicator of the porosity of activated carbon as the iodine is adsorbed in the pores of the activated carbon. While the iodine number

does not directly correlate to the ability of the activated carbon to adsorb various other contaminants it provides a quantifiable gauge by which activated carbon can be rated.

This study investigated the generation of activated carbon on the surface of used vehicle tires. Though conversion of used vehicle tires to activated carbon is not a new concept, preserving the structure of the tire and generating activated carbon on the surface of the tire has not previously been studied. Compared to the dynamics of the Luthy et al. (2004) and Tomaszewski et al. (2007) this study proposes treating contaminated sediments with whole tires (Figure 2). The primary objective of this study was to investigate the effect of temperature and holding time on the generation of activated carbon on used tire surfaces. The secondary objective was to examine the sorptive capacity of activated carbon on the tire surfaces using an iodometric titration.

MATERIALS AND METHODOLOGY

MATERIALS AND EQUIPMENT

Four Load Star K550 trailer tires and a single Tow-Mast trailer tire were obtained from Les Schwab Tires. All tires were bias ply without steel radial reinforcement. An Isotemp Basic Muffle Furnace (Fisher Scientific) was used for the pyrolysis treatment. Compressed nitrogen gas was acquired from A-L Compressed Gases, Inc. Sodium hydroxide pellets, hydrochloric acid (HCl) (37.7%), and soluble potato starch were purchased from J.T. Baker Laboratory. Sodium thiosulfate penta-hydrate (99.5%) and iodine solution (1.0 N) were obtained from Sigma Aldrich.

PYROLYSIS TREATMENT

The tread of the tires was cut into 5 cm by 5 cm squares. The cut tire samples were rinsed with deionized water to remove any road debris, dust, etc. The tire samples were then allowed to dry for 12 hours prior to undergoing pyrolysis treatment.

A schematic of the experimental setup used for the pyrolysis treatment is shown in Figure 3. The temperature muffle furnace was heated to 100° C prior to placing the samples in the furnace. Once equilibrium was achieved, the samples were placed in the muffle furnace, the temperature was held constant at 100° C, and the chamber was flooded with nitrogen for 30 min to eliminate any oxygen present in the system. After flooding the chamber with nitrogen, the temperature of the muffle furnace was adjusted to the desired holding temperature ranging from 250 to 360° C with holding times ranging from 20 to 50 min (Table 1).

After the samples had been held at the designated temperature and time, the samples were cooled in the muffle furnace to 150° C with continued nitrogen flow. The samples were rapidly cooled after the system reached 150° C until reaching 110° C to reduce nitrogen consumption. All pyrolysis reactions were performed at atmospheric pressure.

IODINE NUMBER

After the samples had undergone the pyrolysis treatment, iodine numbers were determined for the activated carbon produced on the tire surfaces by performing an iodometric titration. Iodometric titrations were performed in duplicate for each sample. To perform the titration an aliquot of tire (1 - 5 grams) was removed from the 5 cm by 5 cm tire sample. The aliquot of sample was heated in an oven for approximately 2 hrs at 150° C to remove any residual

moisture then stored in a desiccator until the sample had returned to room temperature (ASTM International, 2011).

The iodometric titration was performed for both powdered and solid samples. The powdered samples were prepared using a mortar and pestle to create a powder of which 60% by weight passed through a 325- mesh screen and 95% by weight passed through 100-mesh screen in accordance with the ASTM standard procedure. The powdered samples were also heated for 2 hrs at 150° C and placed in a desiccator until the iodine number was measured.

After cooling to room temperature, the 1-5 g of the sample was placed in a 125 ml Erlenmeyer flask. The samples were heated to a gentle boil with 10 ml of 5% HCl for 30 seconds to remove any sulfur which could interfere with obtaining an accurate iodine number. After boiling, the samples were allowed to cool to room temperature followed by the addition of 40 ml of 0.1 N iodine solution. The sample was then shaken for 4 min and passed through a 45 µm membrane filter. The filtrate was collected and 10 ml was placed in a 125 ml Erlenmeyer flask and titrated with 0.1 N sodium thiosulfate until a clear endpoint was achieved (ASTM International, 2011).

RESULTS AND DISCUSSION

PYROLYSIS TREATMENT

Two sets of pyrolysis treatments were conducted: one with the Tow-Master tire and one with the Load Star tire. Results for these tests were significantly different. The initial pyrolysis treatment using the Tow-Master tire was modeled after the production of activated carbon by Mui et al. (2010). This process held the sample isothermally for 2 hrs at 500° C with continued nitrogen flow. The sample was then cooled to 200° C in the presence of nitrogen. This procedure

proved ineffective for generation of activated carbon on the surface of the tire sample due to tire disintegration (Figure 4). It was determined that Tow-Master tire samples did not maintain their structure at temperatures exceeding 250° C (Figure 5).

Samples prepared from the Load Star tires did not show any visible signs of alteration when exposed to the pyrolysis conditions used for the Tow-Master tire samples. Additional testing was performed with the Load Star tire samples to determine a range of temperatures for the pyrolysis treatment. Load Star samples were processed from 250° C to 290° C in an attempt to determine the maximum temperature these samples could withstand as it was not yet known these samples would perform so differently than the Tow-Master samples. Once temperatures of 290° C were achieved, with no visible signs of tire structure deteriorations, a higher range of temperatures was investigated: this range was 330° C to 360° C (Figure 6). The maximum temperature was discovered when a sample was held isothermally at 360° C for 40 min during pyrolysis treatment; this sample disintegrated (Figure 7). Therefore, the maximum temperature for Load Star sample pyrolysis was 360° C.

IODINE NUMBER

Load Star samples that maintained their structure through pyrolysis treatment were analyzed using an iodometric titration to determine the iodine number which is used as an indicator of the adsorptive capacity (ASTM International, 2011). Though the iodine numbers gauge the adsorptive capacity of activated carbon it does not correspond to how effectively the sample will adsorb other constituents (ASTM International, 2011).

Following the iodometric titration, Equation 1 was used to determine the concentration of iodine in the filtrate (C). Equation 2 was then used to find the iodine number (X/M) specific to

the sample. Prior to using Equation 2 the dilution factor (DF) was calculated. The volume of iodine used (I) was 40 ml and the volume of HCl was 10 ml (H). The volume of filtrate (F) used for the titration was 10 ml resulting in a DF of 5.

$$S(N_1) = F(C) \quad (1)$$

Where: S = sodium thiosulfate used to reach titration endpoint (ml)

N_1 = sodium thiosulfate concentration (N)

F = filtrate volume (ml)

C = residual iodine solution concentration (N)

$$\frac{X}{M} = \frac{[A - (DF)(B)(S)]}{M} \quad (2)$$

Where: X/M = iodine adsorbed per gram of carbon (mg/g)

A = (N_2) (12693)

N_2 = iodine concentration (N)

DF = dilution factor

$$DF = \frac{I+H}{F}$$

I = iodine volume (ml)

H = 5% HCl used (ml)

F = filtrate volume (ml)

B = (N_1) (126.93)

N_1 = sodium thiosulfate concentration (N)

S = sodium thiosulfate use to reach titration endpoint (ml)

M = carbon used (g)

INTACT TIRE SAMPLES

Iodine numbers, average iodine numbers, and percent difference for each sample are listed in Table 2. The large percent differences listed in Table 2 indicate that the samples were not homogenous. Average iodine numbers for intact tire samples are shown in Figures 8 – 16. The average maximum iodine number for each pyrolysis temperature and percent of the overall maximum iodine number are listed in Table 3. The predominant pyrolysis holding times, corresponding to maximum iodine numbers, for intact samples were 30 and 40 min.

A similar trend in iodine numbers is seen in Figure 8 and Figure 9 . Iodine numbers at these temperatures increased from 20 to 40 min and peaked at a holding time of 40 min. Iodine numbers for holding times of 50 min were lower than those at 40 min. Nevertheless, they were still larger than iodine numbers for 20 and 30 min holding times.

A similar trend is also seen in Figure 10 and Figure 11. The iodine number was greatest at 30 min holding times instead of 40 min. The iodine number for Sample 10 from Figure 10 is $264 \text{ mg/g} \pm 11.0 \%$. The peak iodine number from Figure 11 is $452 \text{ mg/m} \pm 3.18 \%$ for Sample 14.

Samples 17 – 20 shown in Figure 12 were the only samples that followed the hypothesis that increasing holding time would create a larger iodine number. Sample 20 with a holding time of 50 min had an iodine number of $609 \text{ mg/g} \pm 17.3 \%$, which is much larger than iodine numbers produced at lower holding times. An exponential equation was fit to the data which has an R^2 value of 0.95.

The same trend shown in Figure 8 and Figure 9 is seen in Figure 13, which has a peak iodine number of $506 \text{ mg/g} \pm 35.3 \%$. The iodine number for Sample 36, while smaller than the iodine number of Sample 35, is larger than iodine number for Sample 33 and 34. This trend was also seen in Figure 8 and Figure 9.

Sample 37 has an iodine number of $669 \text{ mg/g} \pm 22.2 \%$, the largest for samples processed at this holding temperature as seen in Figure 14. Unlike trends seen in Figure 8, Figure 9, and Figure 13 the sample that was held isothermally for 40 min produced the lowest iodine number.

A peak iodine number of $446 \text{ mg/g} \pm 1.59 \%$ was achieved at a holding time of 30 min seen in Figure 15 similar to Figure 10 and Figure 11. Unlike Figure 10 and Figure 11 however, the iodine number peaks again at a 50 min holding time. Sample 44 has an iodine number of $408 \text{ mg/g} \pm 29.9 \%$. Though this second peak did not produce an iodine number as high as that produce by Sample 42 it is still a trend that had not been seen at previous holding temperatures.

Iodine numbers for samples held isothermally for 20 and 30 min are shown in Figure 16 as samples held for 40 and 50 min did not maintain their structure. Sample 45 had an iodine number of $567 \text{ mg/g} \pm 9.64 \%$, while Sample 46 had an iodine number of $342 \text{ mg/g} \pm 11.6 \%$. This trend appears similar to that seen in Figure 14 which also had a peak iodine number occurring at the lowest holding time.

Pyrolysis conditions for all intact samples and their corresponding average iodine numbers are shown in Figure 20 and Figure 21. It is apparent from these figures that there is not a general trend between pyrolysis treatment conditions and generation of activated carbon. The maximum iodine numbers for each holding temperature and corresponding pyrolysis conditions are listed in Table 3. Additionally, listed in Table 3 is a comparison of maximum iodine numbers for each holding temperature.

POWDERED TIRE SAMPLES

Iodine numbers, average iodine numbers, and percent difference in which samples were ground to a powder consistent with the ASTM standard test method are shown in Table 4.

Table 4 represents Samples 36- 46 as Samples 33-35 could not be ground enough to create a powder; i.e., the samples had large portions of rubber which were resistant to crumbling. An attempt to convert Samples 1-20 to powder was not made because these samples were exposed to lower ranges of heat and still maintained their characteristic durability. Average iodine numbers for powdered samples are shown in Figures 17 - 19. The average maximum iodine number for each pyrolysis temperature and a percent of the overall maximum iodine number is shown in Table 5. The predominant pyrolysis holding time, corresponding to maximum iodine numbers, was 50 min.

A peak iodine number of $605 \text{ mg/g} \pm 1.44 \%$ occurred at a holding time of 50 min shown in Figure 17. There is an additional smaller peak of $581 \text{ mg/g} \pm 3.99 \%$ for the sample held isothermally for 20 min. In comparison to iodine numbers for samples that underwent pyrolysis treatment at the same holding temperature, shown in Figure 14, there is not a similar pattern. Additionally, larger iodine numbers were recorded for solid samples.

For Samples 41-44 the largest iodine number occurred for the 50 min holding time. The peak iodine number was $596 \text{ mg/g} \pm 1.17 \%$. Unlike what was seen for Samples 37-40 the powdered sample produced the largest iodine number. There was however not an overall similar trend of iodine numbers.

A peak iodine number of $596 \text{ mg/g} \pm 0.02 \%$ for Sample 46 is shown in Figure 19. Sample 45 has a very similar iodine number of $584 \text{ mg/g} \pm 2.05 \%$. This is not similar to the iodine number recorded for the solid sample seen in Figure 16, which has a 225 mg/g difference. Additionally, the iodine number for Sample 46 is lower than the iodine number for Sample 45 when titrations were performed with solid samples.

Pyrolysis conditions for all powdered samples and their corresponding average iodine numbers are shown in Figure 22. Similar to Figure 20 and Figure 21 there is not a general trend between pyrolysis treatment conditions and generation of activated carbon. The maximum iodine numbers for each holding temperature and corresponding pyrolysis conditions are listed in Table 5. Additionally, listed in Table 5 is a comparison of maximum iodine numbers for each holding temperatures.

A comparison of iodine numbers for intact tire samples and powdered tire samples is shown in Figure 23. The powdered samples have consistently higher iodine numbers than intact samples. The two exceptions are Sample 37 and Sample 45. Sample 37 is the only sample that the intact tire sample has a larger iodine number than the powdered sample. The intact tire sample for Sample 45 has a slightly lower iodine number than the powdered sample but the difference is negligible in comparison to difference for all other samples. The powdered samples show less variation in iodine number than intact samples. This is potentially due to the heterogeneous consistency of the intact samples caused by the point injection of nitrogen for the pyrolysis experimental set up.

Iodine numbers consistent with this study were obtained in a similar study that used waste vehicle tires for the generation of activated carbon. The range of iodine numbers achieved in that study were 405- 965 mg/g (Aweed 2008). Aweed (2008), while trying to generate activated carbon, used a different activation technique. Instead of using pyrolysis treatment Aweed (2008) activated the material with mineral hydroxide. This is confirmation that the iodine numbers determined in this study are valid.

SUMMARY OF CONCLUSIONS

Tire segments (5 cm by 5 cm squares) were evaluated for surface conversion through pyrolysis treatment to activated carbon as a basis for in situ sorption of contaminated sediments using entire tires. Iodine numbers were determined to quantify the sorptive capacity of generated activated carbon. Iodine numbers for intact tire samples ranged from 162 to 669 mg/g. Iodine numbers for powdered samples ranged from 573 to 605 mg/g. Retail GAC iodine numbers range from 800-1,200 mg/g and the highest achieved iodine number of this study was $669 \pm 22.2 \%$ (Y-Carbon, 2013). The American Water Works Association requires a minimum iodine number of 500 mg/g for activated carbon (U.S. EPA, 2013). These criteria were met by certain samples in this study.

There is no trend observed between pyrolysis holding time and iodine number. Pyrolysis holding times of 30 and 40 min were the most effective for production of maximum iodine numbers for intact tire samples, while 50 min holding times provided maximum iodine numbers for powdered sample. The maximum iodine number achieved in the pyrolysis of intact tire samples was $669.18 \text{ mg/g} \pm 22.17 \%$ with pyrolysis conditions of 350°C held isothermally for 20 min. The parallel powdered sample produced an iodine number of $577 \text{ mg/g} \pm 2.44 \%$. Therefore, the most effective pyrolysis condition was 350°C held for 20 min. The second largest iodine number was $605 \pm 1.44 \%$, which was held isothermally at 340°C for 50 min. In contrast the parallel intact tire sample had an iodine number of $356 \pm 1.02 \%$. Though the relationships between the effect holding temperature and time have on the sorptive capacity of the sample is unclear, it was evident that the pyrolysis of intact tire samples was generating an adsorptive surface as the control sample had an average iodine number of 151 mg/g.

Activated carbon generated on intact tires is a new remediation technique that has potential for sediment remediation. This type of remediation is beneficial compared to techniques currently available because it is economical, it recycles waste material, and once saturated, unlike GAC sediment remediation, the material can be removed from the site, thus eliminating potential leaching over time.

FUTURE STUDIES

Future studies of activated carbon generation on intact tires should investigate:

- holding temperatures ranging from 340 to 360° C as these samples maintained structure and were successfully ground into powder suggesting that much of the rubber forming the tire was converted through pyrolysis treatment.
- the differences between non-steel radial reinforced tires and steel radial reinforced tires as the steel structure could enhance the tires ability to maintain its structure when the tire undergoes pyrolysis treatment.
- the various composition of the rubber used to create tires and how different rubber compositions affect pyrolysis treatment.
- the effect pyrolysis has on the side walls of the tires as this study focused on the tread of the tires.
- the effect various pressures have on the activated carbon production through pyrolysis as all tests for this study were performed at atmospheric pressure.
- the ability of the generated activated carbon to sorb contaminants in a mesocosm.

Additionally, due to high percent differences for solid testing a revision to the existing pyrolysis treatment experimental setup should be considered if the subject is further investigated. An apparatus which can distribute the nitrogen evenly throughout the muffle furnace as opposed to a point source which was used in this study should be used.

REFERENCES

- ASTM International. *D4607-94 Standard Test Method for Determination of iodine Number of Activated Carbon*. West Conshohocken: ASTM Int'l, 2011.
- Aweed, Khalid A. "Preparation of Activated Carbon from Wastes Tires by Minerals Hydroxide." *Tikrit Journal of Pure Science*, 2008.
- Bronstein, Arthur J., Thomas J. Creswell, Eric A. Hamp, Raven I. McDavid Jr., and Virginia McDavid. *The Random House Dictionary of the English Language*. New York: Random House, Inc., 1987.
- Cho, Yeo-Myoung, et al. "Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment." *Environmental Science and Technology*, 2009: 3815-3823.
- Dall'Orso, M., G. San Miguel, G. D. Fowler, and C. J. Sollars. "Scrap tyres-alternative uses and disposal options." *RS-Milano*, 1998: 250-259.
- Dias, Joana M., Maria C.M. Alvim-Ferraz, Mauual F. Almeida, Jose Rivera-Utrilla, and Manuel Sanchez-Polo. "Waste materials for activated carbon preparation and its use." *Journal of Environmental Management*, 2007: 833-846.
- Gupta, V. K., Bina Gupta, Shilpi Agarwal, and Arunima Nayak. "A Comparative Investigation on Adsorption Performances of Mesoporous Activated Carbon Prepared from Waste Rubber Tire and Activated Carbon for a Hazardous Azo Dye- Acid Blue 113." *Journal of Hazardous Materials*, 2011: 891-901.
- Luthy, Richard G., et al. *In Situ Stabilization of Persistent Organic Contaminants in Marine Sediments*. Department of Defense Strategic Environmental Research and Development Program, 2004.
- Mahapatra, Kalyani, D. S. Ramteke, and L. J. Paliwal. "Production of activated carbon from sludge of food processing industry under." *Journal of Analytical and Applied Pyrolysis*, 2012: 79-86.
- Mui, Edward L.K., W. H. Cheung, Marjorie Valix, and Gordon McKay. "Mesoporous activated carbon from waste tyre rubber for dye removal from effluents ." *Microporous and Mesoporous Materials*, 2010: 287-294.
- National Research Council. *Contaminated Marine Sediments: Assessment and Remediation*. Washington D.C.: National Academy of Sciences, 1989.
- . *Sediment Dredging at Superfund Megsites: Assessing the Effectiveness*. Washington D.C.: The National Academies Press, 2007.

- Riddle, Margaret. *Historic Link*. December 8, 2009.
http://www.historylink.org/index.cfm?DisplayPage=output.cfm&file_id=9233 (accessed January 22, 2013).
- Roy, Christian, Blaise Labrecque, and Bruno de Caumia. "Recycling of scrap tires to oil and carbon black by vacuum pyrolysis." *Resources, Conservation and Recycling*, 1990: 203-213.
- Technology Innovation and Field Services Division. *Contaminated Sites - Clean-up Information*. January 18, 2013. <http://www.clu-in.org/contaminantfocus/default.focus/sec/Sediments/cat/Overview/> (accessed January 23, 2013).
- Tomaszewski, Jeanne E., David Werner, and Richard G. Luthy. "Activated Carbon Amendment as a Treatment for Residual DDT in Sediment from a Superfund Site in San Francisco Bay, Richmond, California, USA." *Environmental Toxicology and Chemistry*, 2007: 2143-2150.
- U.S. EPA. *Drinking Water Treatability Database- Granular Activated Carbon*. January 24, 2013.
<http://iaspub.epa.gov/tdb/pages/treatment/treatmentOverview.do?treatmentProcessId=2074826383> (accessed January 24, 2013).
- . *United States Environmental Protection Agency*. November 14, 2012.
<http://www.epa.gov/osw/conserva/materials/tires/index.htm> (accessed November 16, 2012).
- Watts, R., and A. Teel. "Treatment of Contaminated Soils and Groundwater using ISCO." *Practical Periodical of Hazardous, Toxic, and Radioactive Waste Management*, 2006: 2-9.
- Watts, Richard J. *Hazardous Wastes: Sources, Pathways, Receptors*. New York: John Wiley & Sons, Inc., 1998.
- Y-Carbon. *Y-Carbon*. 2013. http://www.y-carbon.us/Iodine_number_according_to_ASTM_4607_p/idn-01.htm (accessed January 24, 2013).
- Zhonghua, Hu, and M. P. Srinivasan. "Preparation of high-surface-area activated carbons from coconut shell." *Microporous and Mesoporous Materials*, 1999: 11-18.

Table 1. Holding temperatures and times with corresponding sample numbers.

Sample No.	Holding Temperature (°C)	Holding Time (minutes)
1	250	20
2	250	30
3	250	40
4	250	50
5	260	20
6	260	30
7	260	40
8	260	50
9	270	20
10	270	30
11	270	40
12	270	50
13	280	20
14	280	30
15	280	40
16	280	50
17	290	20
18	290	30
19	290	40
20	290	50
33	20	330
34	30	330
35	40	330
36	50	330
37	20	340
38	30	340
39	40	340
40	50	340
41	20	350
42	30	350
43	40	350
44	50	350
45	20	360
46	30	360
47	40	360
48	50	360

Table 2. Iodine numbers for Samples A and B, average iodine numbers, and percent differences for solid samples.

Sample No.	(X/M) _A	(X/M) _B	Avg. X/M	Percent Difference
Control	135	168	151	21.7
1	154	170	162	9.81
2	175	212	193	19.3
3	251	273	262	8.55
4	206	220	213	6.18
5	150	150	150	0.27
6	185	186	186	0.93
7	261	248	254	5.04
8	232	210	221	9.75
9	140	167	153	17.2
10	250	279	264	11.0
11	188	172	180	8.78
12	172	173	172	0.37
13	334	349	342	4.38
14	459	445	452	3.18
15	489	361	425	30.1
16	332	317	324	4.61
17	240	276	258	14.2
18	311	280	295	10.6
19	354	441	397	21.9
20	556	662	609	17.3
33	389	391	390	0.37
34	411	443	427	7.35
35	596	417	506	35.3
36	376	573	475	41.5
37	743	595	669	22.2
38	501	444	472	11.9
39	307	329	318	7.15
40	359	356	357	1.02
41	423	353	388	18.1
42	449	442	446	1.59
43	372	328	350	12.6
44	347	469	408	29.9
45	540	594	567	9.64
46	323	362	342	11.6

Table 3. Maximum average iodine number and percent of overall maximum iodine number for solid samples.

Temperature (°C)	Time (min.)	Iodine Number (mg/g)	Percent of Maximum
250	40	262	39.1
260	40	254	38.0
270	30	264	39.5
280	30	452	67.6
290	50	609	91.0
330	40	506	75.7
340	20	669	100
350	30	446	66.6
360	20	567	84.7

Table 4. Iodine numbers for Samples A and B, average iodine numbers, and percent differences for powdered samples.

Sample No.	(X/M) _A	(X/M) _B	Avg. X/M	Percent Difference
36	572	573	572	0.03
37	584	570	577	2.44
38	569	593	581	3.99
39	542	563	553	3.66
40	610	601	605	1.44
41	587	587	587	0.09
42	584	581	583	0.61
43	581	584	582	0.56
44	592	599	596	1.17
45	578	590	584	2.05
46	596	596	596	0.02

Table 5. Maximum average iodine number and percent of overall maximum iodine number for powdered samples.

Temperature (°C)	Time (min.)	Iodine Number (mg/g)	Percent of Maximum
330	50	572	94.6
340	50	605	100
350	50	596	98.4
360	30	596	98.4

* Samples for 360° C turned to ash after holding times of 30 minutes.

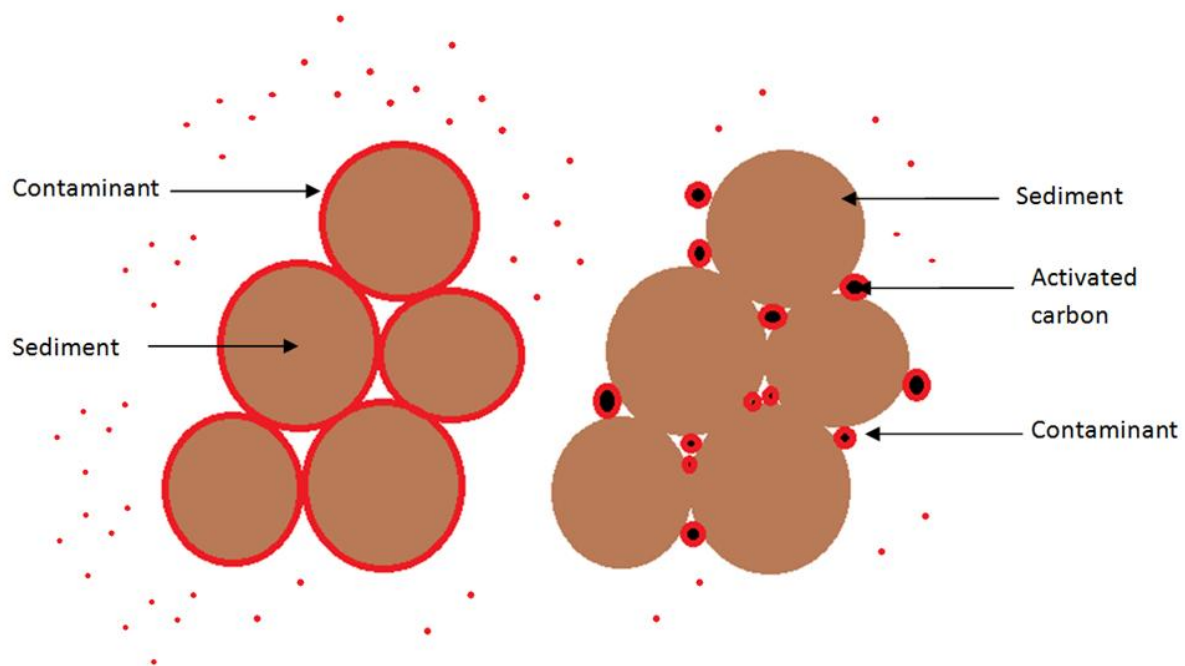


Figure 1: Conceptual model of in situ GAC treatment sorbing contaminants which desorb from contaminated sediment.

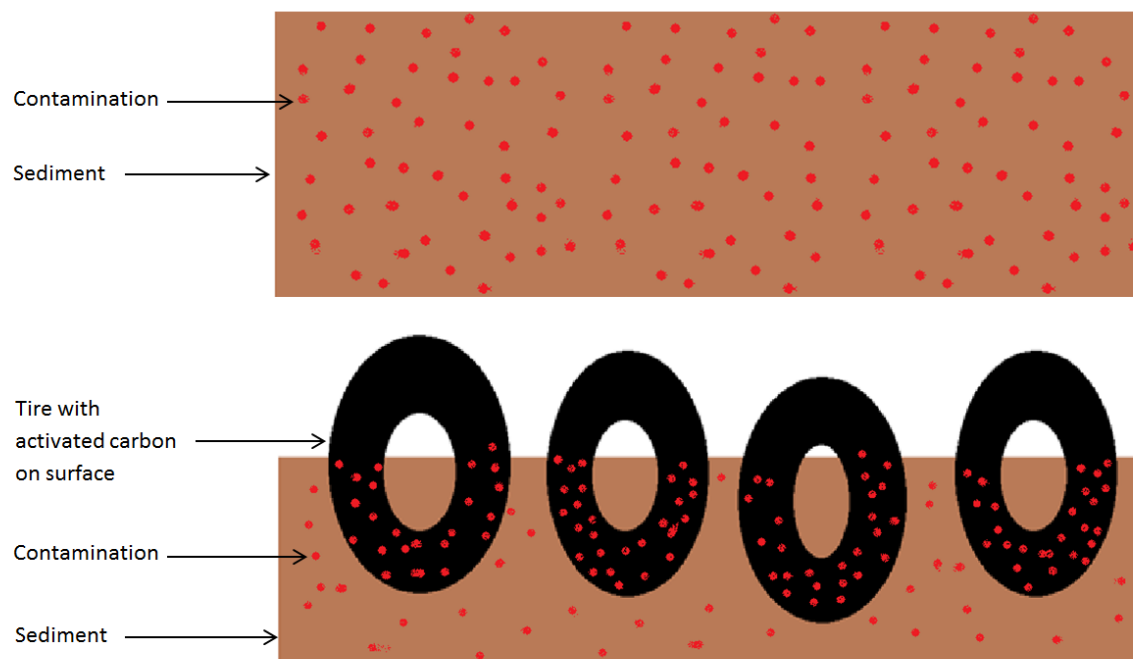


Figure 2: Conceptual model of in situ sediment remediation with structured activated carbon.

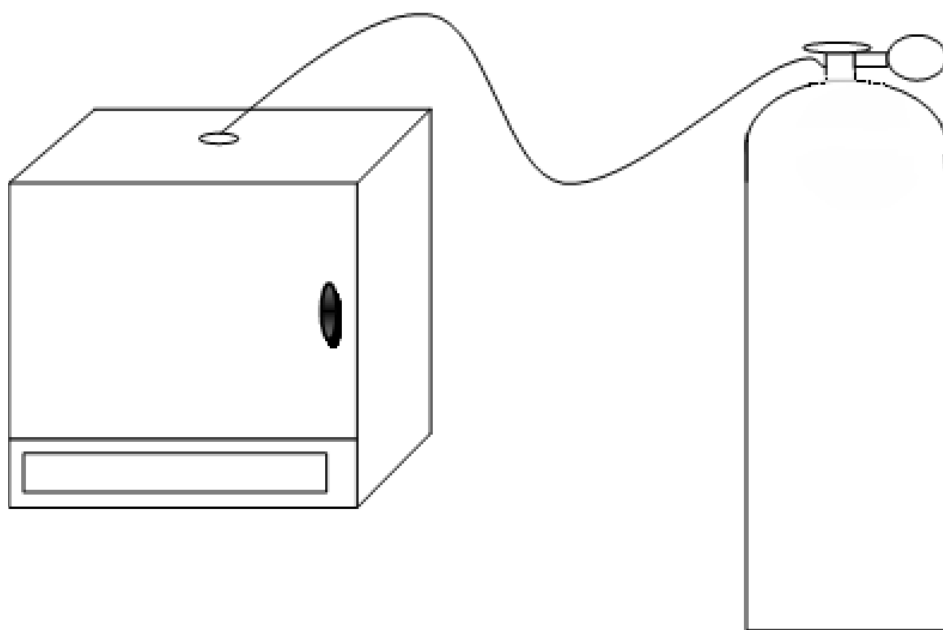


Figure 3: Experimental setup for pyrolysis treatment.

Compressed nitrogen gas injected into the muffle furnace to reduce/eliminate oxygen from the system.



Figure 4: Tire sample after simulation of procedure performed in Mui et al. (2010).



Figure 5: Tow-Master tire sample processed at 250° C and held isothermally for 20 min.

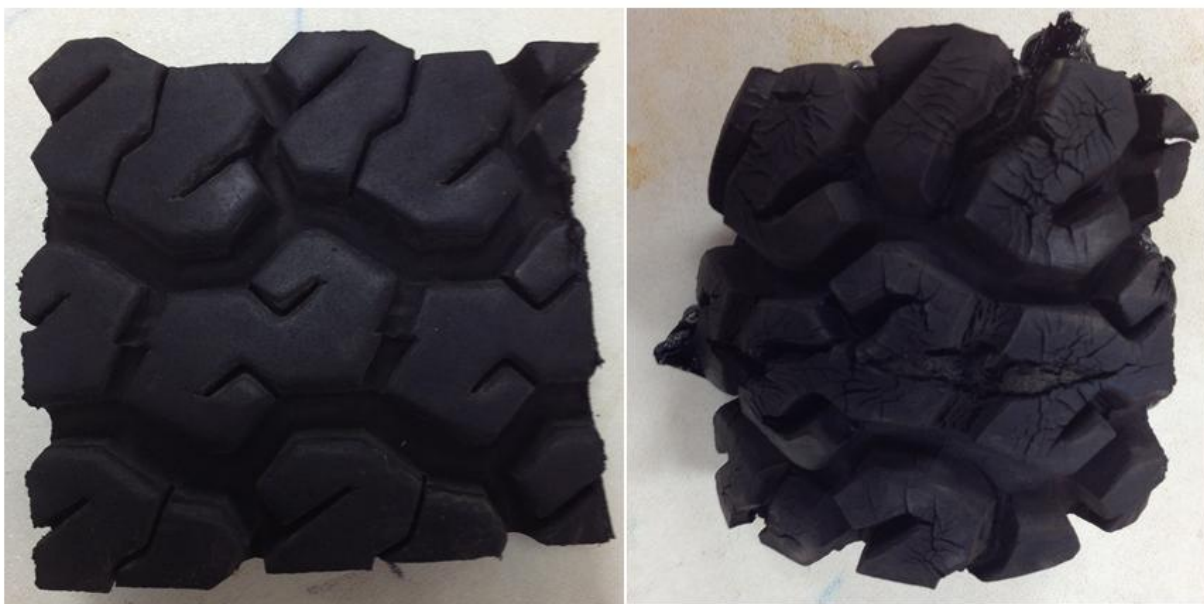


Figure 6: Visual alterations of Sample 44 before and after pyrolysis treatment.



Figure 7: Load Star tire sample processed at 360° C and held isothermally for 40 min.

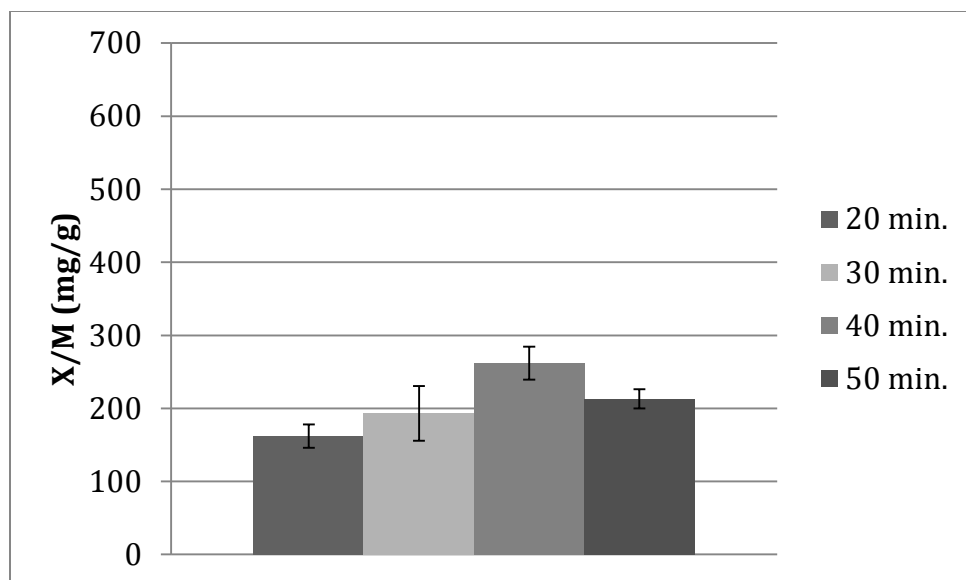


Figure 8: Average iodine numbers for Samples 1-4. Error Bars are based on percent differences from Table 2.

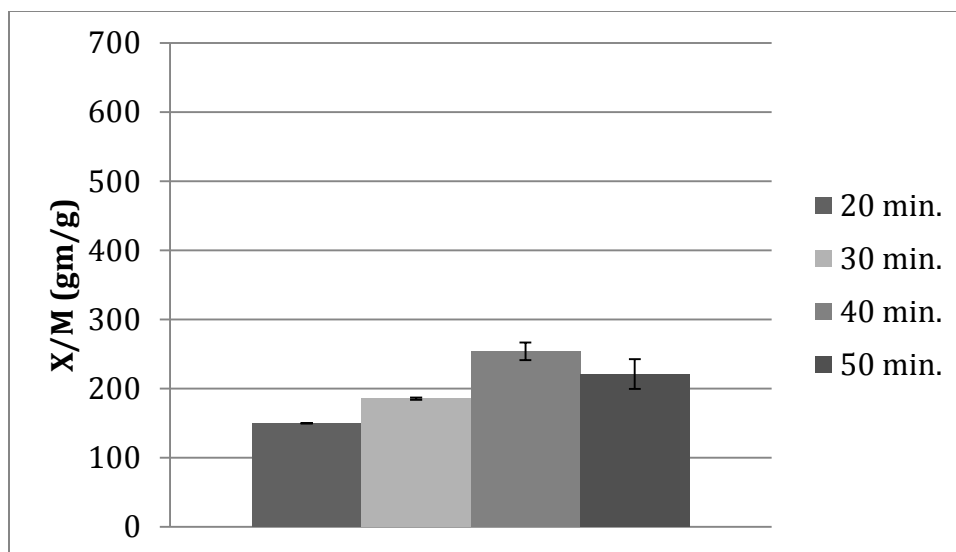


Figure 9: Average iodine numbers for Samples 5-8. Error Bars are based on percent differences from Table 2

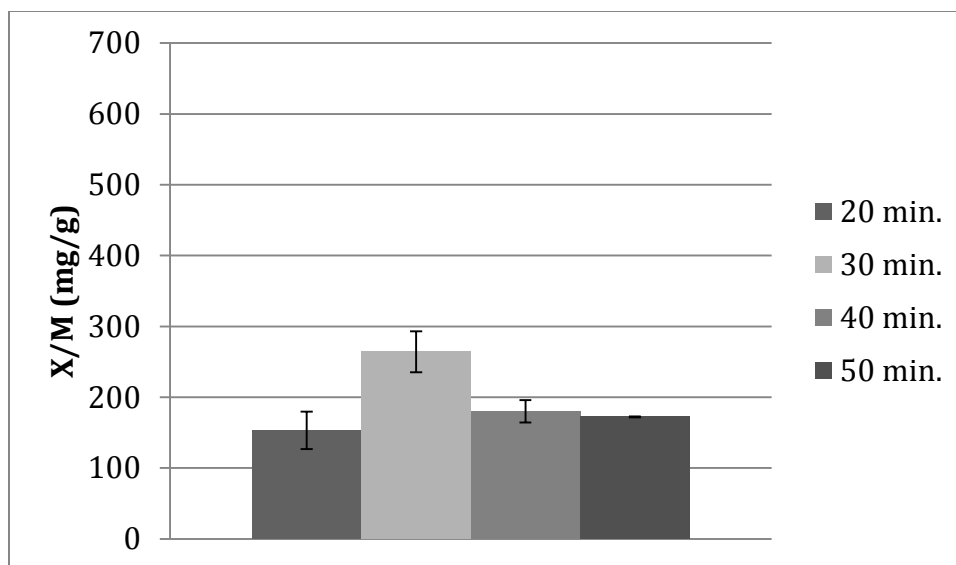


Figure 10: Average iodine numbers for Samples 9-12. Error Bars are based on percent differences from Table 2.

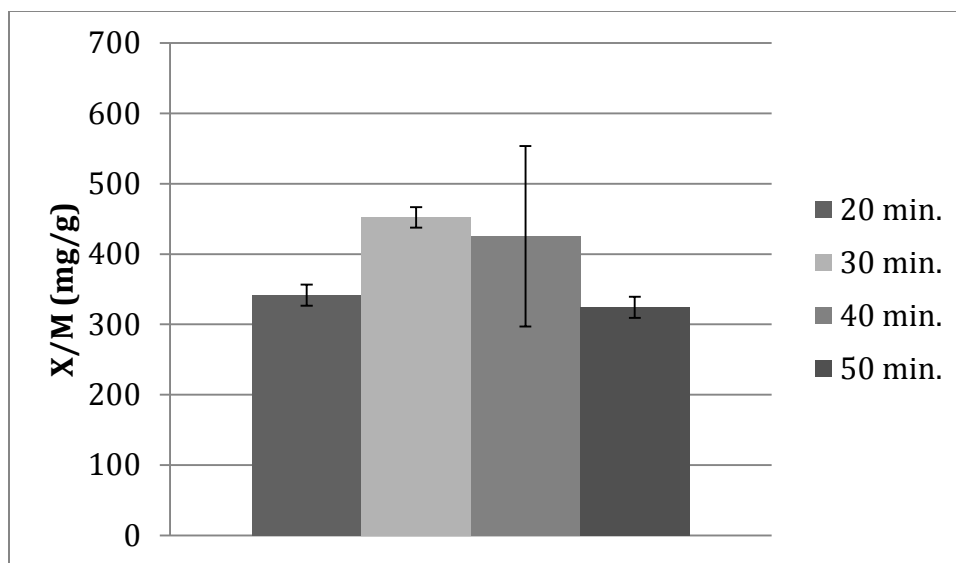


Figure 11: Average iodine numbers for Samples 13-16. Error Bars are based on percent differences from Table 2.

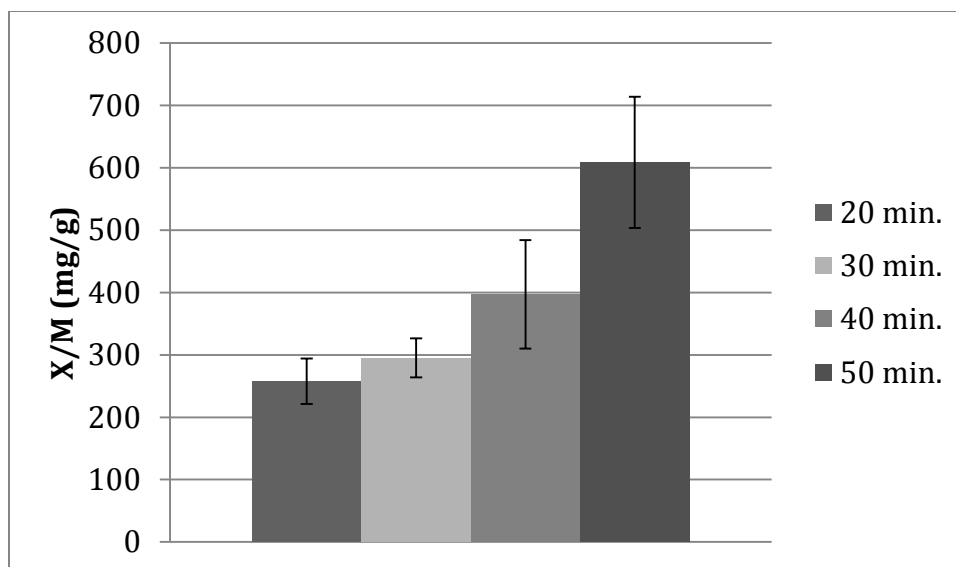


Figure 12: Average iodine numbers for Samples 17-20. Error Bars are based on percent differences from Table 2

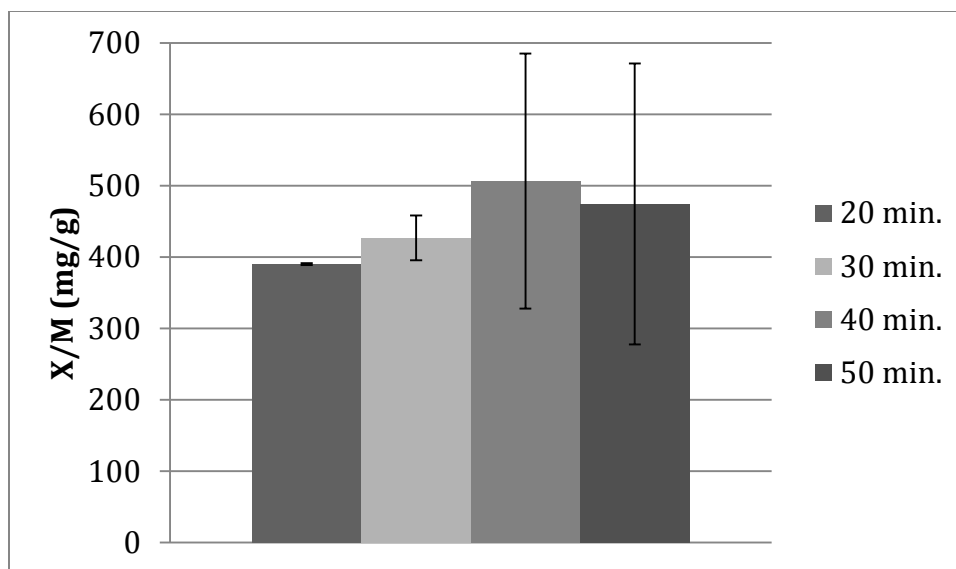


Figure 13: Average iodine numbers for Samples 33-36. Error Bars are based on percent differences from Table 2.

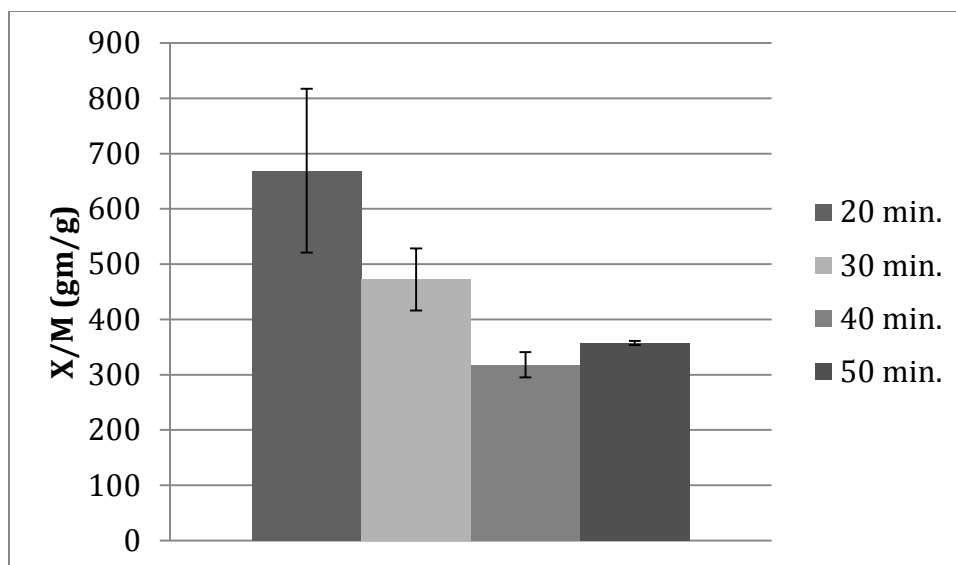


Figure 14: Average iodine numbers for Samples 37-40. Error Bars are based on percent differences from Table 2.

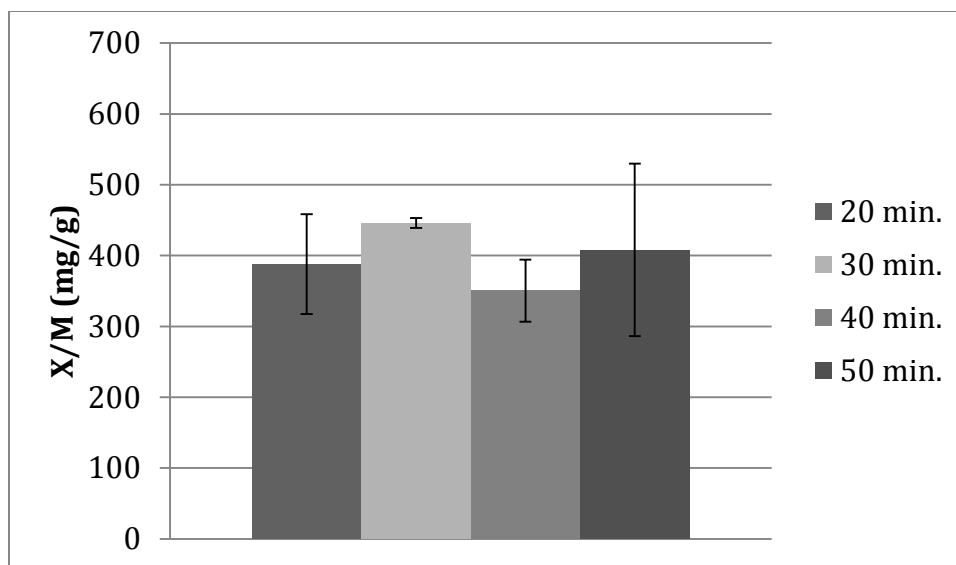


Figure 15: Average iodine numbers for Samples 41-44. Error Bars are based on percent differences from Table 2.

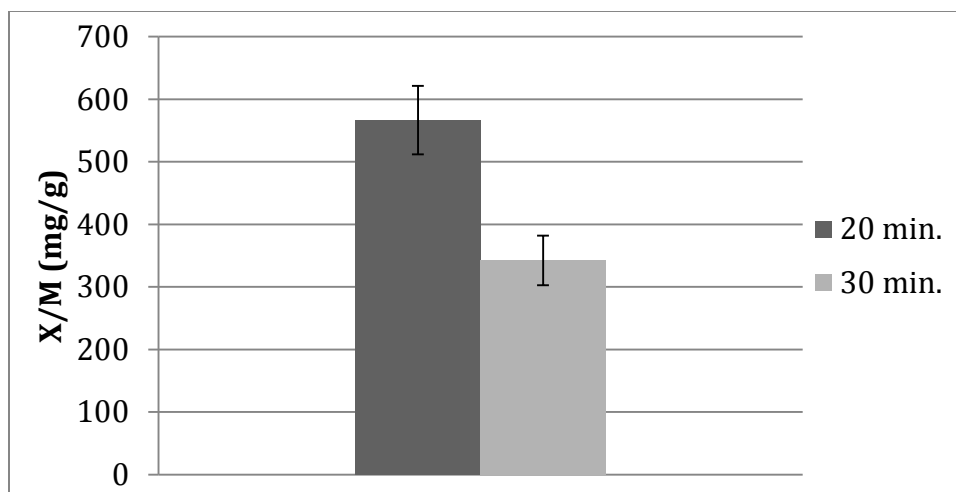


Figure 16: Average iodine numbers for Samples 45 and 46. Error Bars are based on percent differences from Table 2.

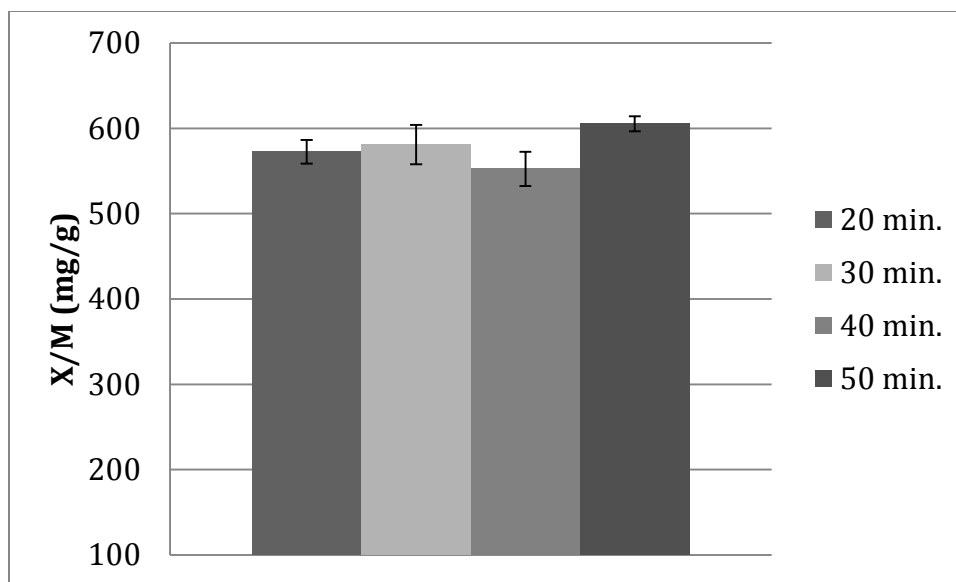


Figure 17: Average iodine numbers for powdered Samples 37-40. Error Bars are based on percent differences from Table 4.

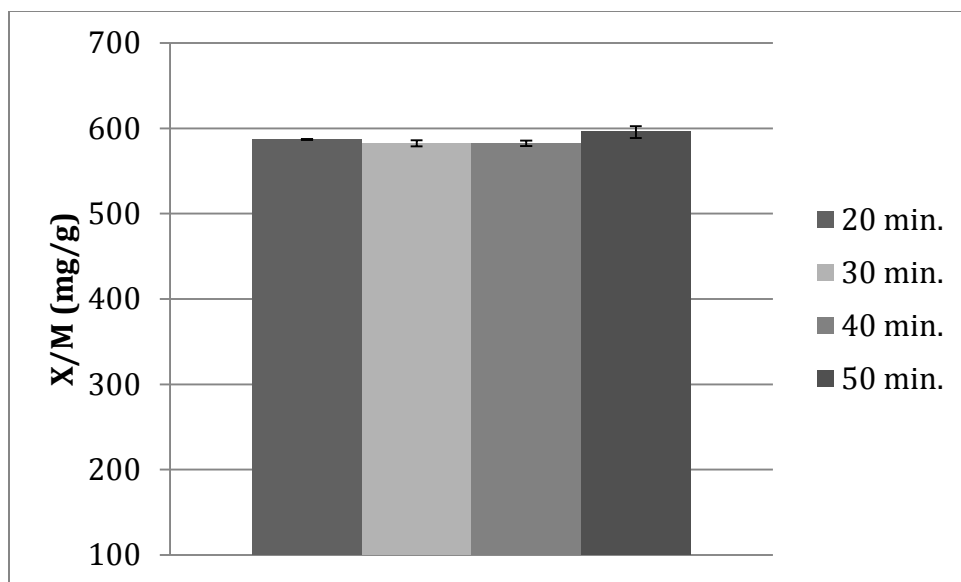


Figure 18: Average iodine numbers for powdered Samples 41-44. Error Bars are based on percent differences from Table 4.

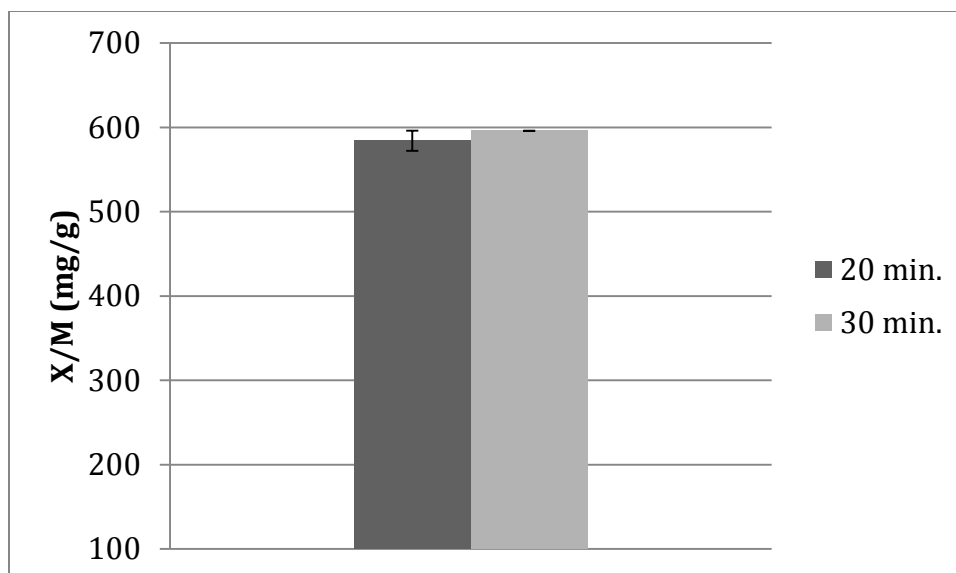


Figure 19: Average iodine numbers for powdered Samples 45 and 46. Error Bars are based on percent differences from Table 4.

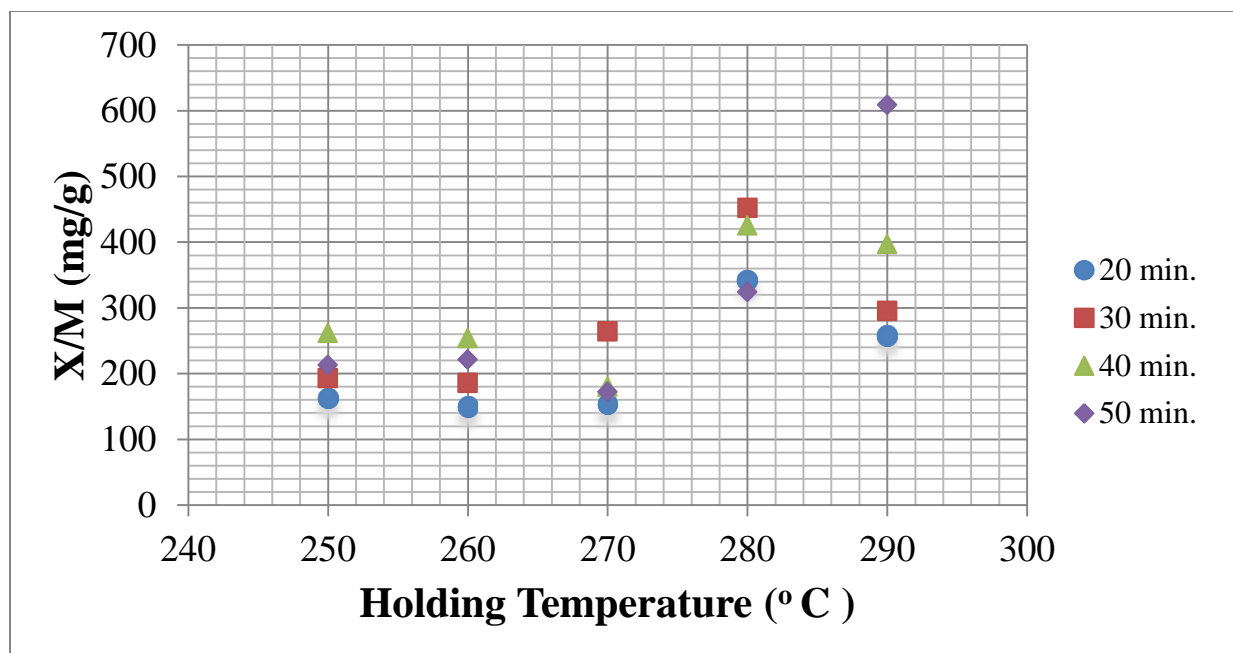


Figure 20: Relationship between iodine number and holding temperature for Samples 1-20.

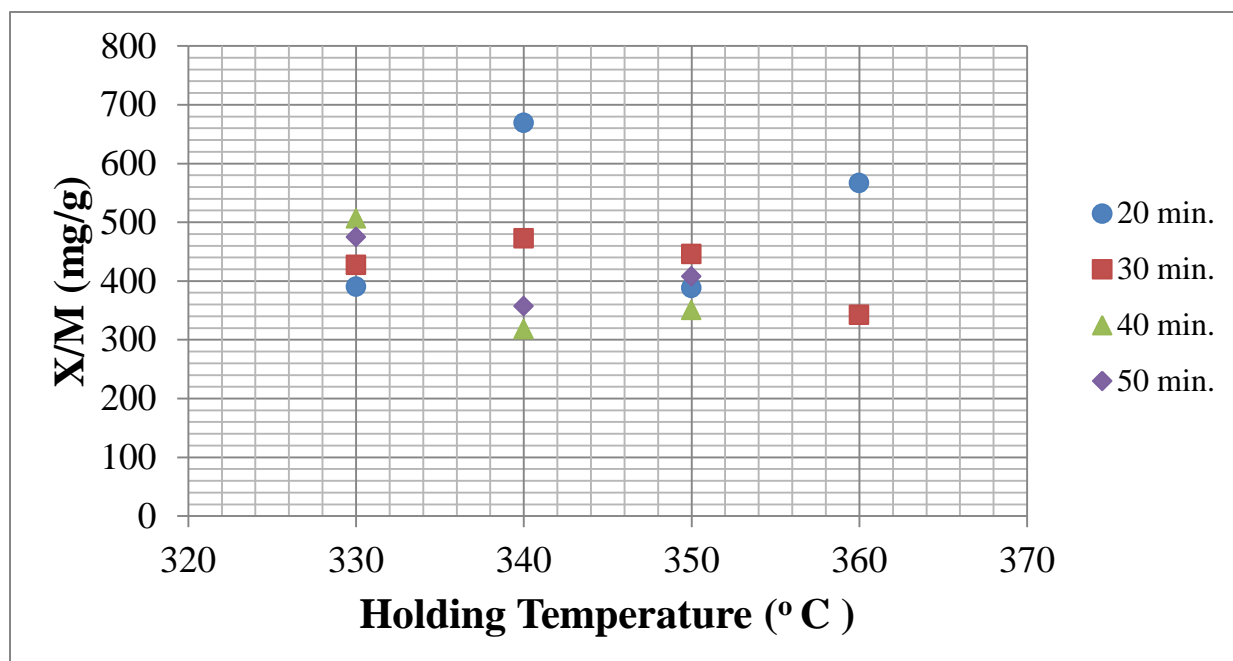


Figure 21: Relationship between iodine number and holding temperature for Samples 33-46.

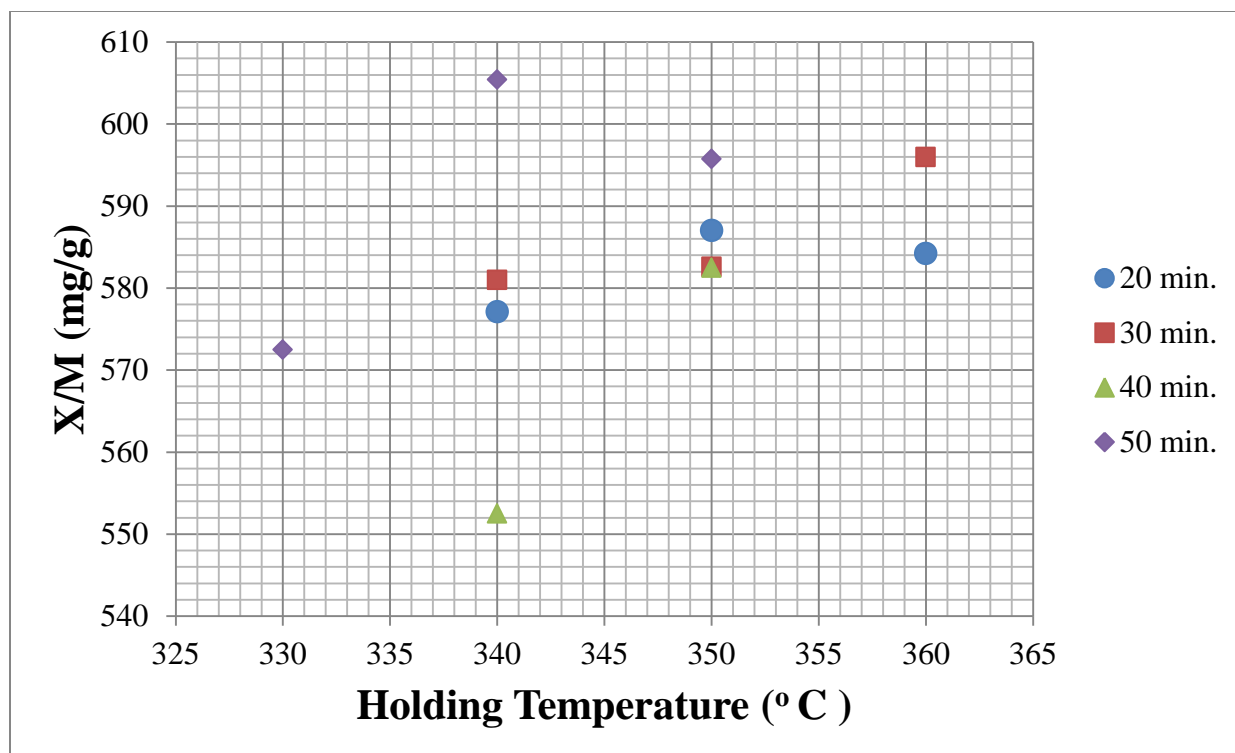


Figure 22: Relationship between iodine number and holding temperature for powdered Samples 33-46.

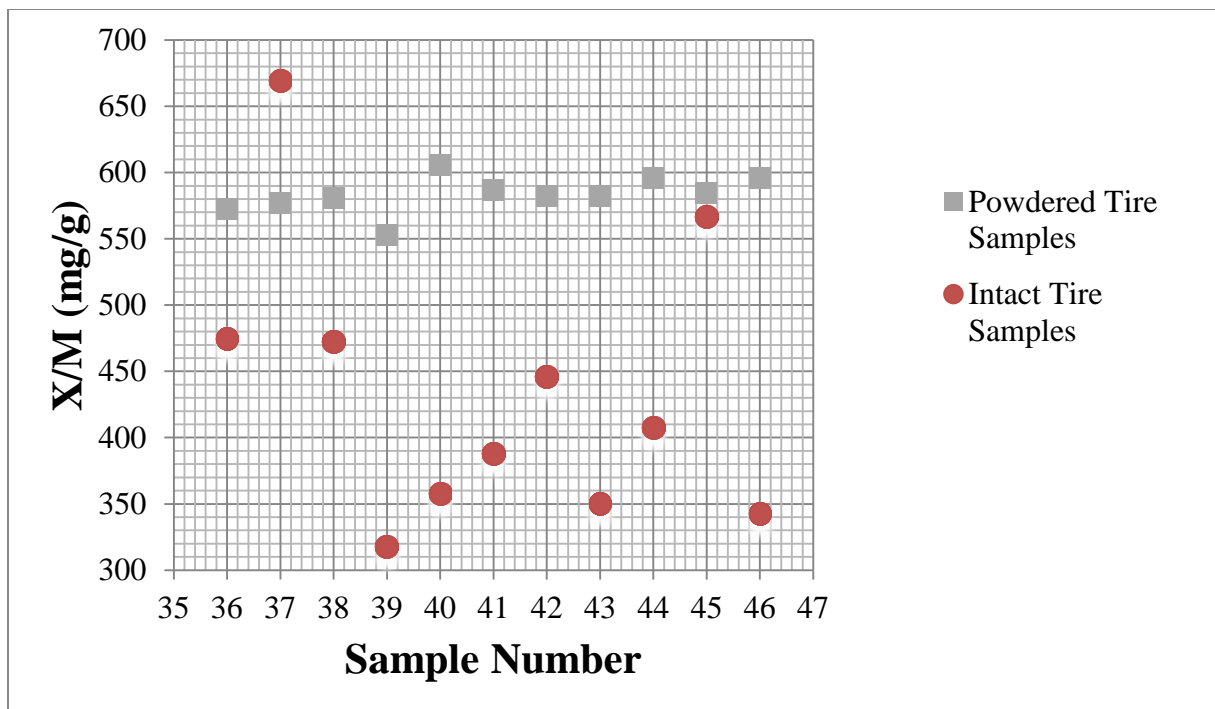


Figure 23: Comparison of iodine numbers for intact and powdered tire samples.