REMOVAL OF LEAD FROM WASTE OIL USING ULTRASOUND ASSISTED WITH RICE BRAN

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ABSTRACT

Heavy metal ion such as lead is toxic and represent as hazardous pollutants due to its persistent in the environment. In this study the rice bran was used for the sorption of lead from waste lubricant oil in the presence and absence of ultrasound. The main objective of this study is to get the optimum condition towards lead removal from waste oil in the presence and absence of ultrasound. The effect of temperature, particle size and adsorbent dosage on removal of lead was investigated. Temperatures of solutions and adsorbent dosage were varied from 40 - 90 ^{o}C and 1 – 6 g/100 mL, respectively while the particle size of rice bran were prepared in the range of 0 – 200, 400 -500 and 630 - 800 µm. From the result obtained, the optimal temperature of solution for highest adsorption of lead were 80 °C and 90 °C, respectively, in the presence and absence of ultrasound. Of the particle sizes studied, 0 – 200 µm of rice bran exhibited the highest adsorption capacities and in adsorbent dosage studies, the results indicated that the adsorption process reached equilibrium after 4 g/100 mL in presence and absence of ultrasound. The results of this study showed that higher lead adsorption was observed at higher temperature, smaller particle size and larger adsorbent dosage. In the presence of ultrasound the rice bran was a more efficient sorbent for lead sorption than its absence. The effect of ultrasound on the sorption process could be explained by the thermal and non-thermal properties of ultrasonic field. As conclusion, ultrasound was synergetic with rice bran as adsorbent when they were used together to extract heavy metals from waste oil.

ABSTRAK

Ion logam berat seperti plumbum adalah beracun dan merupakan bahan pencemar berbahaya kerana kewujudan yang berterusan di dalam persekitaran. Dalam kajian ini, sekam padi digunakan untuk menyerap plumbum dari sisa minyak pelincir pada kehadiran dan ketiadaan gelombang ultrasonik. Tujuan utama penyelidikan ini adalah untuk mendapatkan keadaan optimum penyerapan plumbum dari sisa minyak pada kehadiran dan ketiadaan gelombang ultrasonik. Pengaruh suhu, saiz zarah, dan kuantiti sekam padi terhadap kadar penyerapan plumbum diselidiki. Suhu sampel dan kuantiti sekam padi dikaji masing-masing pada 40-90 oC dan 1 - 6 g/100 mL manakala saiz zarah sekam padi dikaji pada julat 0 - 200, 400 -500 dan 630-800 µm. Dari keputusan yang diperolehi, suhu optimum penyerapan plumbum tertinggi adalah 80 ° C dan 90 ° C, masing-masing, pada kehadiran dan ketiadaan gelombang ultrasonik. Dari saiz zarah yang diselidiki, 0 - 200 µm menunjukkan kapasiti penyerapan tertinggi dan dalam kajian kuantiti sekam padi, hasil kajian menunjukkan bahawa kadar penyerapan mencapai keseimbangan pada 4 g/100 mL pada kehadiran dan ketiadaan gelombang ultrasonik. Keputusan kajian menunjukkan bahawa kadar penyerapan plumbum semakin tinggi pada suhu yang lebih tinggi, saiz zarah yang lebih kecil dan kuantiti sekam padi yang lebih banyak. Dengan kehadiran gelombang ultrasonik, keupayaan sekam padi dalam penyerapan plumbum lebih tinggi dari ketiadaannya. Pengaruh gelombang ultrasonik terhadap proses penyerapan dapat dijelaskan dengan sifat terma dan bukan-terma lapangan ultrasonik. Sebagai kesimpulan, kombinasi gelombang ultrasonik dan sekam padi sebagai penyerap adalah lebih efisien untuk mengekstrak logam berat dari sisa minyak berbanding ketiadaannya.

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LIST OF ABBREVIATIONS AND SYMBOLS

$	-	US Dollar
$^{\circ}C$	-	Degree Celsius
%	-	Percentage
Min	-	Minute
H	-	Hour
Ppm	-	Part per Million
kHz	-	Kilohertz
g	-	Gram
kg	-	Kilogram
m	-	Meter
µm	-	Micrometer
mgg^{-1}	-	Milligram per Gram
$mol\ g^{-1}$	-	Mole per Gram
$mg\ kg^{-1}$	-	Milligram per Kilogram
$m^2\ g^{-1}$	-	Meter Square per Gram
g/L	-	Gram per Litre
mL	-	Millilitre
g/mL	-	Gram per Millilitre
$mg\ L^{-1}$	-	Milligram per Litre
$mmol\ L^{-1}$	-	Millimole per Litre
Cu	-	Copper
Ni	-	Nickel
Pb	-	Lead
Zn	-	Zinc
Cd(II)	-	Cadmium Ion
Cr (VI)	-	Chromium Ion
Pb(II)	-	Lead Ion

AAS	-	Atomic Absorption Spectrometer
*D*P	-	Diameter Particle
FTIR	-	Fourier Transform Infrared Spectroscopy
KOH	-	Potassium Hydroxide
MBAC	-	M. baccifera activated charcoal
MBRC	-	M. baccifera raw charcoal
US	-	Ultrasound
WB	-	Wheat Bran

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Toxic wastes such as waste lubricant oils are often discharged into the environment due to high consumption for transportation. According to the international regulations, waste lubricants are considered as hazardous substances. The worldwide annual consumption of lubricants is reaching 40 million tons. One large part of waste oils is used motor oils which contain mainly paraffinic, naphthenic and aromatic hydrocarbons, additives, degradation products and metals. Among the metal impurities, lead is actually the major one. With a content of 1000 ppm of lead, the use of these waste oils cause problem. The major part of the collected waste oils is burned or dumped on the ground. Only a small part is treated, generally for recycling in fresh oil production. As dumping waste oils causes a dramatic pollution of the water reserves, and furthermore burning waste oils containing lead is dangerous, it is then important to decrease their lead content, especially in countries where the automobile park is rather old, like in southern and eastern Europe, Asia, Africa and Latin America (A. Fontana et al., 1996).

Heavy metal ions such as lead, cadmium, mercury, chromium, nickel, zinc and copper are non-biodegradable, carcinogenic and can be toxic. Among all, lead is the most important because of its high toxicity. Lead leads the list of environmental threats because, even at extremely low concentration, lead has been shown to cause brain damage in children (M. Ahmedna., 2004). Lead also is a cumulative poison, which can accumulates mainly in bones, brain, kidney and muscles. Lead poisoning in human causes severe damage to kidney, nervous and reproductive systems, liver and brain (T.K. Naiyaa et al., 2009). According to the ranking of metal interested priorities referred by Volesky, lead is one of the most interesting heavy metal for removal and/or recovery considering the combination of environmental risk and reserve depletion (B. Volesky, 2001).

Various methods exist for the removal of lead ions from solution, such as filtration, chemical precipitation, ion exchange, sorption by activated carbon and others. From the viewpoint of economics, these methods are not generally acceptable and different groups have recently focused the research on the use of low cost sorbents such as bagasse sugar (V.K. Gupta et al., 2003), hematite (D.B. Singh et al., 1998), perlite (T. Mathialagan et al., 2002), starch xanthate (R.E. Wing et al., 1975), sawdust of pinus sylvestris (C.V. Taty-Costodes et al., 2003) and discarded automobile tires (A.S. Gunakera et al., 2000). Cost is an important parameter for comparing the sorbent materials. Hence, the usage of indigenous biodegradable resources for treating hazardous waste would be less expensive. Rice bran contains functional groups associated with proteins, polysaccharides and cellulose as major constituents. Metal uptake is believed to occur through a sorption process involving the functional groups mentioned above. The cost of this biomaterial is negligible compared with the cost of activated carbon or ion-exchange resins which are in the range of approximately $2.0–4.0 kg (Y. Bulut and Z. Baysal, 2005).

In this study, rice bran which frequently causing disposal problem has been used as an interesting and cheap medium for the sorption of lead from waste oil. This was done in the presence and absence of treatment ultrasound. Ultrasound through its mechanical waves is known to have an effect on the sorption process. Ultrasonic waves strongly affect mass transfer between two phases. It is well understood that ultrasonic waves have a greater efficiency for interface mixing than conventional agitation. This behaviour could be the reason for the enhancement of the sorption kinetic process.

1.2 Problem Satement

Nowadays, constant efforts are being made to develop improved and innovative methods of waste oil treatment. While developing new methods, economic feasibility and user friendly concepts are given much importance. Various processes for the removal of metals are available but the most commonly used process give high cost. Keeping this in view, considerable attention has been given to develop low cost adsorbents for removal of the different heavy metals when the concentration is not very high.

In nature, there are so many materials which possess the properties of ion exchange and adsorption. Some materials are already in use even for commercial purposes. Some of the examples are zeolite, apatite, bentonite, etc. Activated carbon is the most widely used adsorbent (S.A. Wasay et al., 1999) only because of its more surface area. The cost of activated carbon is high which leads to limited uses particularly in developing countries. Hence in search of materials having similar properties, the attention has been diverted towards the agricultural and forestry products such as rice bran.

However, all the researches that have been carried out are only considering the adsorption process alone in heavy metal removal. On the other hand, this research is focusing on ultrasonic process assisted with rice bran as an adsorbent. It is known that, the advantages of using rice bran are biodegradable, environmental friendly and cheaper. The combination of ultrasonic and adsorption process will produce higher adsorption of lead from waste oil compared to the adsorption process alone.

1.3 Objective of Study

The objective of this research is to get the optimum condition towards lead removal from waste oil in the presence and absence of ultrasound

1.4 Scope of Study

In order to achieve the objectives, the following scopes have been identified:

1) To study the effect of solution temperature towards the heavy metal removal. The temperature of solution was adjusted to different values (40 – 90 °C) with presence and absence of ultrasound. 3 g of 0 – 200 µm of rice bran was used in this experiment. The temperature value at which the maximum lead removal is determines.

2) To study the effect of adsorbent dosage and particle size in presence and absence of ultrasound. These two parameters are varied between these ranges at optimum temperature:
   - Particle size: 0 – 200 µm, 400 – 500 µm and 630 – 800 µm
   - Adsorbent dosage: 1 - 6 g/100 mL

The value of adsorbent dosage and particle size at which the maximum lead removal were determined.

1.5 Rationale and Significance

Beside the treatment of waste oils by the traditional methods, this processing method gives alternative routes of increasing the yield of heavy metal removal. Instead of using adsorption process alone, the ultrasonic process is assisted to adsorb the metal ion. This will increase the efficiencies of heavy metal removal. The interest in the development of cost-effective methods for the removal and recovery of heavy metals has greatly increased because of the ecological awareness of the role of metals in the environment. Basically, it is preferable to provide new method with economic feasibility and user friendly concept.

CHAPTER 2

LITERATURE REVIEW

2.1 Waste Oil

Waste oil is defined as any petroleum-based or synthetic oil that, through use or handling, has become unsuitable for its original purpose due to the presence of impurities or loss of original properties. Waste oil can be disposed of in different ways, including sending the used oil off-site (some facilities are permitted to handle the used oil such as local waste disposal facilities), burning used oil as a fuel (some used oil is not regulated by burner standards, but others that are off-specification used oil can only be burned in either industrial furnaces, certain boilers, and permitted hazardous waste incinerators), and marketing the used oil (claims are made that the used oil is to be burned for energy recovery, it is then shipped to a used oil burner who burns the used oil in an approved industrial furnace or boiler). Among the metal impurities inside waste oil, lead is actually the major one. The lead content of the used motor oils is mainly caused by the use of tetraalkyl lead in the fuel.

One of the earliest researches involving waste oil was done by Fontana et al. in 1996. They invented the elimination of lead from used motor oils using ultrasonic lixiviation using nitric acid, the lead being recuperated as lead sulfate during the acid regeneration. As dumping waste oils causes a dramatic pollution of the water reserves, and furthermore burning waste oils containing lead is dangerous, their study was developed to decrease the lead content of waste oils.

Based on the previous study, the improvement and modification has been done by using ultrasonic process assisted with adsorption process in order to remove lead from waste oil. By combining these two processes, the removal of lead could be higher. Furthermore, use of rice bran as adsorbent is more user friendly, feasibility and economic compare with the chemical used in the previous study.

2.2 Lead Removal Using Low Cost Adsorbent

Lead is a hazardous waste and is highly toxic to humans, plants and animals. It causes plant and animal death as well as anemia, brain damage, mental deficiency, anorexia, vomiting and malaise in humans (Y. Bulut and Z. Baysal, 2005). Like mercury, another heavy metal, lead is a substitute for calcium in bony tissues and accumulates there. Lead is also poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. (P.C. Mishra and R.K. Patel, 2009).

Recently, most researches on low cost adsorbent were done in heavy metal removal by researchers for commercial purposes. Mishra and Patel (2009) studied different types of adsorbents that were activated carbon, kaolin, bentonite, blast furnace slag and fly ash to remove the lead and zinc ions from water. The effect of contact time, pH and adsorbent dosage on removal of lead and zinc by adsorption were investigated. The equilibrium time was found to be 30 min for activated carbon and 3 h for kaolin, bentonite, blast furnace slag and fly ash. Adsorbent doses were varied from 5 g/L to 20 g/L for both lead and zinc solutions. The result shows an increase in adsorbent doses increases the percent removal of lead and zinc.

H. Lalhruaitluanga et al. (2010) demonstrated that charcoal biomass from bamboo could be used as adsorbents for the treatment of Pb(II) from aqueous solution. In this study, The effect of chemical pretreatment on the adsorption of Pb(II) ions by MBRC and MBAC showed that 60% KOH pretreatment shows highest percentage of adsorption. The maximum biosorption of Pb(II) was found at pH 5. Maximum adsorption capacity was 10.66 mgg^{-1} for MBRC and 53.76 mgg^{-1} for MBAC. The FTIR analysis of MBRC and MBAC showed that different functional groups are involved in the adsorption of the metal ions. From their results, MBRC and MBAC can be efficiently used for the removal of Pb(II) from the aqueous solution.

2.3 Rice Bran as Low Cost Adsorbent

While developing new methods, economic feasibility and user friendly concepts are given much importance. In nature, there are so many materials which possess the properties of ion exchange and adsorption**.** Some materials are already in use even for commercial purposes. Activated carbon is the most widely used adsorbent (P.C. Mishra and R.K. Patel, 2009) only because of its more surface area. The cost of activated carbon is high which leads to limited uses particularly in developing countries. Hence in search of materials having similar properties, the attention has been diverted towards the agricultural and forestry product such as rice bran.

Rice bran is a by-product of the rice milling industry and the amount of rice bran available is far in excess of any local uses, thus frequently causing disposal problems (S.F. Montanher et al., 2004). For metal removal applications, the use of dead biomass or agricultural waste may be preferable, as large quantities are readily and cheaply available as a by product of various industries (K.K. Singh et al., 2005). Therefore, rice bran was chosen due to its granular structure, insolubility in water, chemical stability and local availability (S.F. Montanher et al., 2004)

Table 2.1: Rice bran characterization (S.F. Montanher et al., 2004)

Ash (%)	10.88
Humidity (%)	10.68
Total proton binding ligands (mol g^{-1})	17.00
Fibre (%)	11.58
Starch (%)	17.60
Protein (%)	12.70
Metals (mg kg^{-1})	
- Iron	73.10
- Magnesium	30.22
- Calcium	697
- Copper	7.13
SiO2 (%)	3.34
Acidity (mmol L^{-1})	6.23
Particle size (average diameter, m)	320
Surface area (m^2 g^{-1})	0.46

There is also a research done by Singh et al. (2005) on removal of Cr (VI) from wastewater using rice bran. In this study, the effect of different parameters such as contact time, adsorbate concentration, pH of the medium, and temperature were investigated. The novel biosorbent rice bran has been successfully utilized for the removal of Cr (VI) from wastewater. The maximum removal of Cr (VI) was found to be 99.4% at pH 2.0, initial Cr (VI) concentration of 200 mg l^{-1}, and temperature 20 ◦C. Based on the result obtained, they concluded that the removal of chromium was rapid in initial stages and became slower afterwards. Mass transfer studies confirmed that the rate of mass transfer from adsorbate to adsorbent was rapid enough.

Another research done by Yasemin and Zubeyde (2005) also use wheat bran as an adsorbent in order to remove lead from wastewater. The aim of this paper was to investigate the ability of WB to remove Pb ions from aqueous solutions. Under batch conditions equilibrium was attained within 60 min. It was found that the adsorption performance of WB is affected by initial metal concentration, sorbent dose, temperature, sorbent size, agitation speed and solution pH. Biosorption efficiencies increased with increasing contact time, temperature and agitation speed and decreased with increasing sorbent size. Adsorption of Pb(II) onto WB is an endothermic and spontaneous process.

2.4 Ultrasonic Process

Ultrasonic processing applies intense, high-frequency sound to liquids, producing intimate mixing and powerful chemical and physical reactions. It is well known that ultrasonic irradiation can significantly improve the reaction efficiency in chemical synthesis, mainly due to cavitation when mechanical vibrations are produced and transmitted into the liquid as ultrasonic waves. This phenomenon involves the formation, growth and implosive collapse of bubbles in liquids irradiated with high intensity ultrasound, creating shock waves, providing a unique set of conditions to promote chemical reactions and thus increasing the chemical reactivity in such systems (P.D.A. Mello et al., 2009).

The process of “cavitation” is, in effect, “cold-boiling” and results from the creation of chemical and physical reactions. Sonication processes have been applied limitedly to pretreatment for metal analysis and pre-extraction of metals, including Cu, Pb, Ni and Zn in order to recover precious metals. The use of ultrasound power has been investigated to speed up process because it has long been recognized that the cavitational effect created by ultrasound waves can break down the particle size, exposing a fresh surface and aggressively agitating the solution system. During the ultrasound treatment, particle dispersion can take place, which, in turn, causes an increase in the surface area available for the reaction (S.S. Hwang et al., 2007).

Combination of ultrasonic and adsorption process have already been done by other researches. According to Entezari et al. (2005), ultrasound facilitates and improves removal of Cd(II) from aqueous solution by the discarded tire rubber. In this study the ground discarded tire rubber was used for the sorption of cadmium from aqueous solution in the presence and absence of ultrasound. They investigated parameters such as ultrasonic waves, solution temperature, particle size of ground tire and others. In the presence of ultrasound the tire rubber was a more efficient sorbent for this pollutant than its absence. According to the results, the internal porous and film diffusions were both effective in the sorption process. The porous and film diffusion coefficients of the ground tire rubber were, respectively, about 1.8 and 2.7 times more in the presence of ultrasound than its absence. The effect of ultrasound on the sorption process could be explained by the thermal and non-thermal properties of ultrasonic field.

There is also a research done on extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid by Jinchuan Deng et al. (2009). In this study, the effects of nitric acid concentration and sonication time on the removal efficiencies of heavy metals from sludge were investigated and the extracted metals Cu, Zn, and Pb were determined. The results indicated that the removal efficiencies of Cu, Zn, and Pb increased with increases in nitric acid concentration and sonication time. Ultrasound alone was not effective enough to remove heavy metals from sludge and the role played by nitric acid predominated over that of ultrasound. However, ultrasound was synergistic with nitric acid when these were used together to extract heavy metals from sludge. Possible mechanisms of heavy metal extraction are also discussed.

Another research by Munoz et al. (2005) on combination of ultrasonic extraction and stripping analysis as an effective and reliable way for the determination of Cu and Pb in lubricating oils is discussed here. The determination of metals in lubricating oil has been used as an important way to prevent components failures, to provide environmental information and in some cases, to identify adulteration. In this work, an effective and simple procedure is proposed for Cu and Pb determination in lubricating oils.

CHAPTER 3

RESEARCH METHODOLGY

3.1 Introduction

The experimental procedure is done by referring to other study related ultrasonic process and removal of lead by other low cost adsorbents such as kaolin, bentonite, blast furnace slag and fly ash. It appears from the previous study that the effect of ultrasound on the sorption process can efficiently release heavy metal from waste oil. In this experiment, there are three variables that need to be considered which are adsorbent dosage, particle size and temperature of solution. The detailed procedure is described in the following.

3.2 Reagents, samples, and materials

Lead reference solutions were prepared from 1000 mg/L lead standard solution. Ultra pure water was used for preparing all reference solutions. Used lubricating oil samples were obtained at local workshop and were collected during oil changing operation in automotive vehicles. These samples were stored at room temperature.

3.2.1 Preparation of Adsorbent

The rice bran was manually ground and screen to eliminate the coarser sizes and to get homogenous particle size by passing the milled material through standard steel sieves (sieve shaker). Then, it was used for experiments without washing or any other physical treatment.

3.3 Instrumentation

An ultrasonic bath operating at 20 kHz was used for experimental procedure. The different regions in the ultrasonic bath were mapped to select the best irradiation positions. For comparative studies, a microwave extractor was used for the digestions of the lubricating oil samples. A graphite furnace atomic absorption spectrometer was employed for determination of lead in analysis procedure.

3.4 Experimental Design

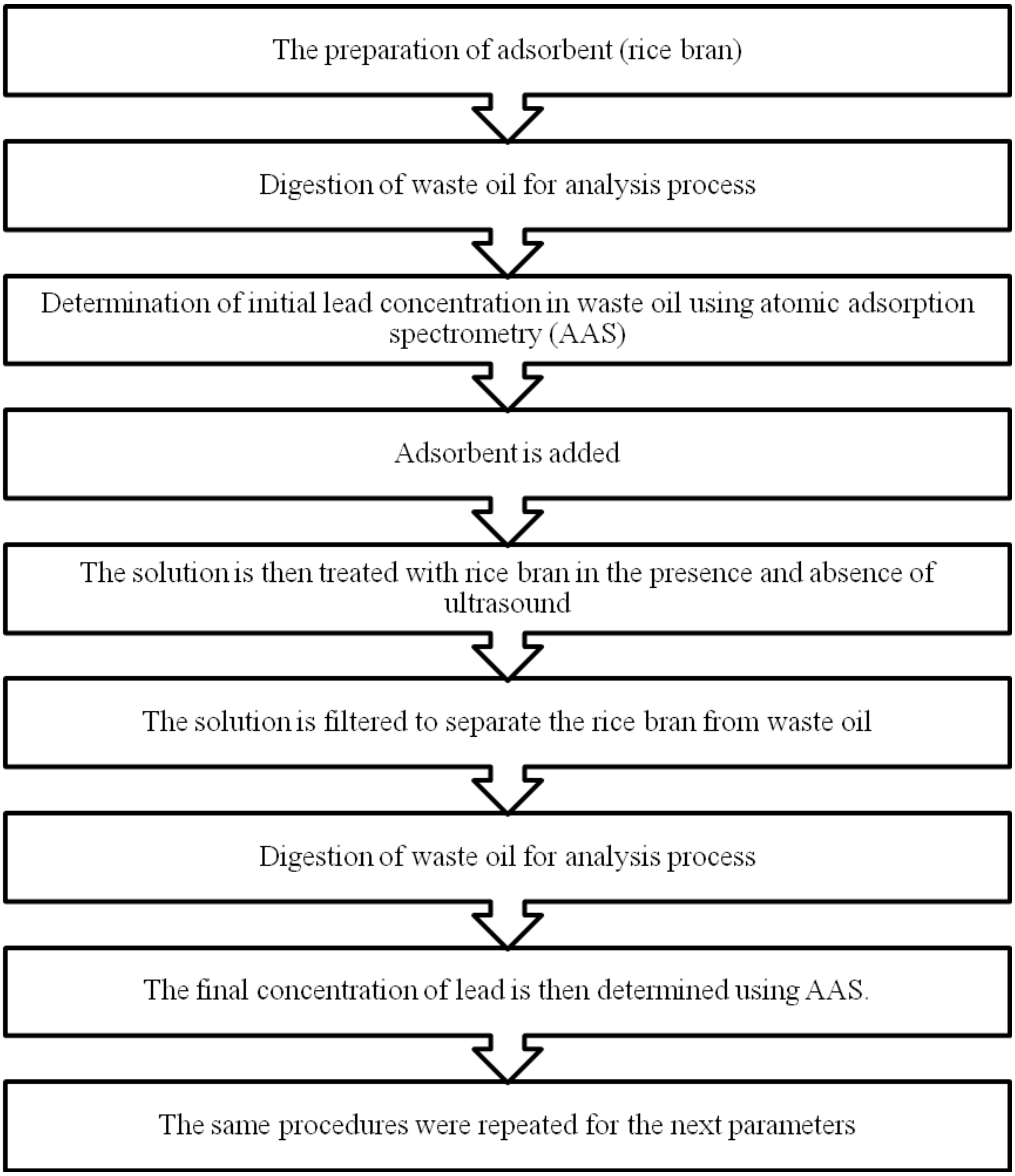

Figure 3.1: Experimental Procedure Flow Chart

3.5 Procedure

3.5.1 Temperature Studies

Batch experiments were conducted by adding 3 g of 0 – 200 µm rice bran to 100 mL of used lubricating oil samples with known initial lead concentration. The effect of temperature on the rate of adsorption process was observed by varying the temperature between the ranges 40 to 90 °C. The ultrasound exposure time was kept constant for 20 minutes and the temperature of the solutions during the US-assisted adsorption process was monitored. The experimental procedure could be performed for dozens of vessels simultaneously. After that, the mixtures were filtered, and the final lead concentration was determined using atomic absorption spectrometer.

Similar procedures were repeated at different temperatures for adsorption process in absence of ultrasound, with constant stirring. The temperature of solution in which give higher removal of lead considered as optimum temperature and was used for further study for the next parameter. The lead removal (%) was determined by the following equation:

$$Lead\ Removal\ (\%) = \frac{Co - Ct}{Ct} \times 100$$

Note:

Co = Concentration of lead at initial condition
Ct = Concentration of lead at any instant of time

3.5.2 Particle Size of Adsorbent Studies

The adsorbent particle size studies were conducted by adding 3 g of rice bran to 100 mL of used lubricating oil samples with known initial lead concentration. The effect of particle size on the rate of adsorption process was observed by varying the particle size between the ranges 0 – 200, 400 – 500 and 630 – 800 μm. The ultrasound exposure time and temperature of solution were kept constant, respectively, for 20 minutes and 85 °C. The particle size of adsorbent during the US-assisted adsorption process was monitored and the experimental procedure could be performed for dozens of vessels simultaneously. After that, the mixtures were filtered, and the final lead concentration was determined using atomic absorption spectrometer.

Similar procedures were repeated at different particle size of adsorbent for adsorption process in absence of ultrasound, with constant stirring. The range of particle size of adsorbent in which give higher removal of lead was used for further study for the next parameter.

3.5.3 Adsorbent Dosage Studies

The effect of adsorbent dosage on the rate of adsorption process was observed by varying adsorbent doses ranging from 1 to 6 g/100 mL. 100 mL of used lubricating oil samples with known initial lead concentration and 0 – 200 μm particle size of rice bran were used in this experiment. The effect of adsorbent dosage on the rate of adsorption process was observed at the solution temperature of 85 °C. The ultrasound exposure time was kept constant for 20 minutes and the adsorbent dosage of the solutions during the US-assisted adsorption process was monitored. The experimental procedure could be performed for dozens of vessels simultaneously. After that, the mixtures were filtered, and the final lead concentration was determined using atomic absorption spectrometer.

Similar procedures were repeated at different adsorbent dosage for adsorption process in absence of ultrasound, with constant stirring. The amount of adsorbent used in which give higher removal of lead considered as optimum adsorbent dosage.

3.6 Microwave digestion

For the digestion of lubricating oil in the microwave oven, a program similar as the one described in a previous study (R.A.A. Munoz et al., 2005) was adopted. It consists in transferring an aliquot of 0.1 g of the sample to be digested to the microwave vessel. After that, 9 mL of nitric acid (65%), and hydrogen peroxide (30%) were added together and applying of temperature at 200 °C for 10 minutes. From this treatment, a very clean solution was obtained and used for analysis process.