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RICE HUSK ASH WASTE IN REMEDIATION AREAS CONTAMINATED BY HYDROCARBONS

RICE HUSK ASH WASTE IN REMEDIATION AREAS
CONTAMINATED BY HYDROCARBONS

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Abstract

This paper presents a study to evaluate Rice Husk Ash adsorption potential in groundwater contaminated by BTEX (benzene, toluene, ethylbenzene and xylene) and TPH (total petroleum hydrocarbons). The methodology used in this research involved characterization of Porto Alegre/Brazil groundwater, characterization of adsorbents (AC and RHA) and laboratory and pilot scale assays (use of remediation system composed by: vacuum suction, aeration and adsorption filter). The results show high concentration and variability of BTEX and TPH in the groundwater studied. For benzene parameter, for example, it was obtained average concentration of 46.5 µg/L. According to the pilot scale study, it was observed decreases in TPH and BTEX ranging from 57.69% to 96.71% at suction system and 96.71% - 99.99% after adsorption mixed filter (50% RHA and 50% AC). The statistical tests ANOVA and Tuckey used here confirm, with a 95% confidence level, that the results obtained from the use of adsorption filter are significant. That is indicative of the importance of this treatment in order to guarantee process efficiency as well as confirm Rice Husk Ash functionality as adsorbent in adsorption filters applied to groundwater contaminated by hydrocarbons.

Key Words: Rice Husk Ash, Solid Wastes, Remediation of Areas, Hydrocarbons, Adsorption.

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Resumo

Esta pesquisa apresenta um estudo para avaliar o potencial de adsorção da cinza de casca de arroz no tratamento de águas subterrâneas contaminadas por BTEX (benzeno, tolueno, etilbenzeno e xilenos) e TPH (Hidrocarbonetos Totais de Petróleo). A metodologia utilizada envolveu caracterização da água subterrânea do município de Porto Alegre, Brasil; caracterização dos adsorventes, ensaios em escala de laboratório e em escala piloto (uso de sistema de remediação composto por: sucção à vácuo, aeração e adsorção). Os resultados demonstraram alta variabilidade e concentração de BTEX e TPH nas águas subterrâneas estudadas. Para o parâmetro benzeno, por exemplo, obteve-se concentração média igual a 46,5 µg/L. No estudo em escala piloto, percebeu-se decréscimos para TPH e BTEX variando entre 57,69% e 96,71% para o sistema de sucção e na faixa de 96,71% e 99,99% após filtro de adsorção misto (50% cinza de casca de arroz e 50% carvão ativado). Os testes estatísticos ANOVA e Tuckey realizados confirmam, a um nível de confiança de 95%, que os resultados obtidos com a utilização do filtro de adsorção são significativos. Isto denota a grande importância deste tratamento para garantia da eficiência do processo, além de confirmar a funcionalidade da cinza de casca de arroz como adsorvente em filtros de adsorção aplicados em água subterrânea contaminada por hidrocarbonetos.

Palavras chaves: Resíduos de cinza de casca de arroz, remediação de áreas, hidrocarbonetos, adsorção.

Introduction

Rice Husk Ash Waste

The necessity of research on solid industrial waste recovery has emerged on publications reviews. The growing demand for safe systems has encouraged the study of economic and technological alternatives so wastes can be introduced as raw material in other production cycles. Therefore, it is possible to reduce treatment costs as well as permanent disposal and also to offer secondary raw material to the market (Teixeira, 2001).

Rice husk ash (RHA) results from rice husk combustion while in thermal processes using this biomass to generate steam or energy. This waste is exempt from any hazardousness so its co-product recycling turns to be potentially safe. It is basically composed of silica and has great potential to be used as raw material for different industrial segments.

With an estimated production of 12 million tons/year for 2014 harvest Brazil is becoming the ninth worldwide producer in rice and the first if outside Asian market (IBGE, 2014). Considering that 23% out of the total rice harvested correspond to husk and 4% to ash it is assumed that more than 2.7 million tons of rice husk will be generated next year. If fully exploited while in energy process, it will be able to generate more than 450 thousand rice husk ash tons.

CCA usage as adsorbent material has aroused researchers' interest once commercial adsorbents (like activated –carbon) represent a high cost. According to Santiago *et al.* (2005), it happens because activated –carbon industrial production consist a high level of investment process involving chemical activation through acids and/or base and physical activation at high temperatures and pressure under controlled conditions. In Brazil, activated carbon has been commercialized at a cost of about U\$ 3.00 per kg.

In this sense, some unconventional low-cost materials have been studied for the same function. The fact that RHA is insoluble in water, that it exhibits good chemical stability and high resistance, and that it has a granular and porous structure proves it to be good adsorbent material (Nghah & Hanafiah, 2008).

In this way, Foletto *et al.* (2005) claim that many RHA studies applied to adsorptive purposes have been developed in different areas. As example, the author mentions the removal of metals in effluents and synthetic aqueous solutions, the removal of organic matter and effluents dyes as well as the removal of liquid-food purification. Other studies show that rice husk ash has great adsorptive properties and may be used in metal ions removal (Srivastava *et al.*, 2006; Srivastava *et al.*, 2008), in dyes (Mane *et al.*, 2007; Lakshmi *et al.*, 2009) and also in arsenic filtration found in water (Saha *et al.*, 2001).

Hydrocarbons Contaminated Areas

Concerning hydrocarbons contaminated areas, a relevant environmental issue refers to operational problems in gas stations underground tanks. The authors highlight this fact due to the proliferation of this type of business as well as to its installations and leaks (even if small volume).

In Brazil, Tiburtius & Zamora (2005) mention the existence of 27,000 gas stations likely to leak. This statement is based on the fact that the majority of those tanks is 25 years old and presents cracks and corrosion on their hull. Also, according to the authors, the number of gas stations with problems varies from 20% to 30% and in most cases leaks are perceptible only after its effects were detected.

The great concern is related, according to many researchers, among others: Corseuil *et al.* (1997), Watts *et al.* (2000), Corseuil *et al.* (2004), Ayotamuno *et al.* (2006), to potential contamination leaks over aquifers which could be used as drinking water supply. The justification according Tiburtius & Zamora (2004) is the high monoaromatic hydrocarbons toxicity (benzene, toluene, ethylbenzene and xylene – BTEX). These parameters, as mentioned in Patnaik (1999), have serious effects on inhalation, ingestion and contact.

An environmental evaluation is thus necessary to verify the extent and severity of the occurrence. The further action is related to these areas recovery and turning them as similar as possible to how they were before sinister. There is a growing number of remediation technologies widely discussed in the literature. From traditional interventions as “Pump and Treat”, “Adsorption” and “Steam Extraction” to more advanced and expensive technologies as heat injection and “air stripping”.

The adsorption process is commonly used to pull away the contaminant found in water once traditional methods (coagulation, flocculation, decantation, filtration and disinfections) are not sufficient to guarantee water quality mainly due to difficulties in removing heavy metals and dissolved hydrocarbons.

Concerning the remediation of areas contaminated by hydrocarbons, Ayotamuno *et al.* (2006) obtained removal results of TPH equal to 99.9% (initial concentration of 9304.70 mg / L) when studying activated carbon aiming at using it in the treatment of underground water which had been contaminated by crude oil and products of oil refining in Nigeria. Juneau Jr *et al.* (2007) using the treatment system (extraction well, "air stripping" tower, bioreactor with fluidized bed and polishing with activated carbon) which has been installed full scale (Fuel Station in New Hampshire, USA), reached 100% removal of BTEX with initial concentration ranging from not detected to 41390.0 µg/L. Yet Wirthensohn *et al.* (2009) also achieved 100% removal using adsorption filter with activated carbon as polishing for physicochemical treatment of groundwater contaminated by hydrocarbon at a gas plant in Vienna (Austria).

According to EPA (2001a), groundwater treatment time resulting from activated carbon adsorption systems can take from a few days up to many years depending on the following aspects: 1) the amount of pollutant in water and air; 2) type and quantity of hazardous chemicals in use; 3) size and number of the system columns and/or filters.

In light of the foregoing circumstances, evaluating the great rice husk ash waste generation, the existence of contaminated areas by hydrocarbons and analyzing the necessity of alternatives in adsorbent materials, this paper aimed to evaluate adsorption potential in rice husk ash for treating groundwater contaminated by BTEX and TPH (Total petroleum hydrocarbon).

Methodology

The study was conducted in 04 steps: 1) Characterization of groundwater (in full scale, it was meant to determine the concentrations of contaminants in water, the sampling and analytical parameters); 2) Characterization of Adsorbents (it was meant to compare the features of the activated carbon adsorbent and those of rice husk ash); 3) Laboratory scale assay (in a laboratory scale it was meant to test filters containing different adsorbents and the potential of

adsorption of TPH); 4) Pilot scale assay (meant to simulate a full-scale remediation system and the filter performance with rice husk ash).

Groundwater characterization

To determine the parameters from laboratory and pilot scale it was provided characterizations of groundwater in 03 gas stations located in Porto Alegre, State of Rio Grande do Sul, Brazil (gas stations A, B and C). All these commercial establishments were, at the time of collection, under active remediation process due to diesel or gasoline outpouring.

The groundwater samples were collected from the monitoring wells installed in the projects under study in sterile 1 liter amber glass bottles (TPH) and Vial Bottle (for BTEX). Per well, the volume of water collected was 1.5 liters. Once collected, the samples were stored in a cooler with ice to maintain temperatures between 0°C to 6°C. The samples were sent to the laboratory within 24 hours.

These samples were analyzed for concentrations of BTEX (benzene, toluene, ethylbenzene and xylene) and TPH (Total petroleum hydrocarbon) using EPA 8260-b; EPA 3510-d and EPA 8015-d methodologies. In one of the stages, in order to obtain a sample macro recognition it was scanned the following physical and chemical parameters: color; turbidity; conductivity; pH; series of solid, nitrogen and alkalinity; COT; DBO; DQO; phosphorus; Total and Thermotolerant Coliforms. All tests were guided by APHA (1995).

Adsorbents Characterization

For the experiment in laboratory and pilot scale, outlined in this research, it was used adsorption filters made of activated carbon and rice husk ash. The applied activated carbon was granular, obtained from chemical activation of burned coconut shell from a supplier in Paraná State, Brazil. The rice husk ash is a result of the combustion process in the boiler of a food company in Rio Grande do Sul, Brazil, that uses rice husk as fuel. In this continuous burning system rice husk is automatically provided, modulated according to the vapor pressure of the boiler. The material goes through the furnace on a sliding grid for 9 minutes. The heat in the furnace is at 900°C. The speed of the grid alters according to the amount of husk being fed and the air flow entering the system.

It is important to mention that the rice husk ash has been used in its natural form and hasn't undergone any kind of chemical or thermal treatment. Considering the results obtained by Kieling (2009), the rice husk ash gross sample was sorted out so to give consistency to the material by removing unwanted particles like unburned rice husks. The stage of sorting out was executed by a sieves shaker for 5 minutes. In order to remove the unwanted particles it was used a sieve mesh of only 1.2mm.

To facilitate the recycling of certain waste it is essential to study their characteristics through assays and appropriate methods. Thus, the rice husk ash and activated carbon were characterized by physical, chemical and microstructural properties.

The physical properties have been analyzed through the following parameters and analytical methodology references: pH and conductivity (Ng *et al.*, 2002); Loss on ignition (ABIFA, 2003a); Granulometry (ABIFA, 2003b), Specific Mass (ABNT NBR 6508, 1984 / ASTM D850, 2002).

Chemical analysis was performed on a Fluorescence Spectrometer of X-Rays by dispersive Energy, brand EDX 720 HS - Shimadzu. The mineralogical composition was performed by X-Ray Diffraction in Siemens D5000 diffractometer.

The microstructure of the rice husk ash was analyzed by scanning electronic microscopy. The micrographs were obtained by detection of secondary electrons by SEM equipment, Shimadzu SSX-550.

Laboratory Scale Assays

It was installed a laboratory scale system composed by: fiber reservoir (superior and inferior), silicone hoses, glass filters, booster pumps and PVC pipes. The superior reservoir had 6 simultaneous escapes to 6 installed filters in parallel. To dimension the filters in laboratory scale it was used a role model filter with activated carbon already installed in a real scale remediation system. Fig. 1 shows the installed system and the filter used in laboratory scale in detail.

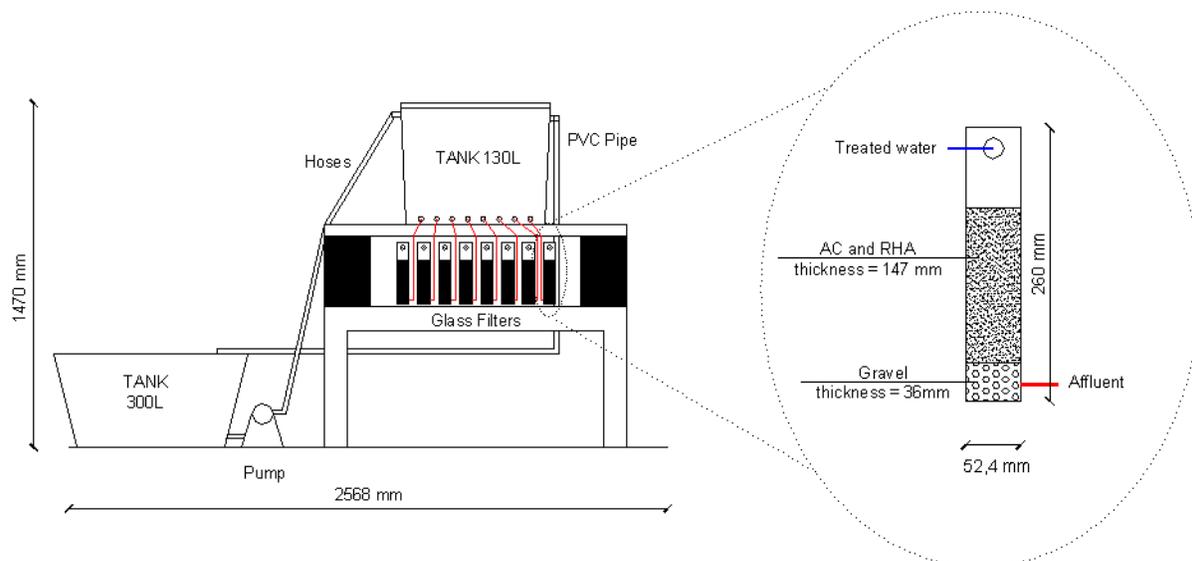


Fig 1: Laboratory scale test adsorption system

In experiments on bench scale, the bulk of adsorbent used was 602 g of rice husk ash and 539 g of activated carbon. This corresponds to a filling volume of 316.84 cm³ (diameter of 52.4 mm and height of 147 mm). The applied flow rate was 0.11 L / s, the speed of percolation of 2.6 cm / s and a final treated volume of 65L.

There have been accomplished 4 assays to analyze the feasibility of using rice husk ash as an adsorbent in the filters for groundwater contaminated by hydrocarbons. Assays number 1, 2 and 3 used adsorption filters made out of 100% RHA and 100% AC. In assay number 4 it was applied 100% AC, 100% RHA and a filter with 50% of AC and 50% of RHA. The groundwater sample was collected from a gas station with active remediation and it was stored in jerry cans.

TPH analyses samples were accomplished in an equalization tank (raw effluent sample) and after passed through filters (treated effluent). The parameters analyzed in each sample were TPH DRO (EPA 3510 and EPA 8015 D) – C10-C28 – diesel range; TPH GRO (EPA 8015) – C6-C10 – gasoline range; TPH Total (EPA 3510 and EPA 8015 D – C8-C40).

This phase of the research aimed at testing the filter system and the feasibility of using rice husk ash as an adsorbent material. With these results, it was possible to structure the pilot-scale assays which are detailed henceforward.

Pilot Scale Assays

The purpose of this testing in pilot scale was to simulate a suction sump installed in a contaminated groundwater area as similar as possible to the remediation system over a gas station in real scale. Hence, it was developed an experiment installed at University of the Sinos Valley (UNISINOS) in São Leopoldo, Rio Grande do Sul, Brazil.

In order to accomplish the tests, the following was provided: 1) synthetic floor profile and installation of suction sump to monitoring; 2) synthetic groundwater composed by rainwater and contamination in different proportions on diesel and gasoline; 3) remediation system made of water reservoir, injector, equalization tank, aerators and adsorption filters with 50% activated carbon and 50% rice husk ash (Fig. 2).

Synthetic contaminated groundwater was prepared using rainwater. Proportions of gasoline and diesel were added to this water in order to obtain concentrations of BTEX and TPH similar to those obtained in the stage of characterization of groundwater and in assays at laboratory scale.

For setting proportions, a laboratory test has been run up. In a 1-liter beaker, it was inserted deionized water and incorporated different proportions of gasoline. It was produced 5 samples according to the following proportions: 0.1%, 0.2%, 0.3%, 0.4% and 0.5% of gasoline in 1 liter of water. These samples were sent to an outsourced laboratory for testing the parameters of BTEX and TPH. It was noticed the increase of contaminants concentration as incorporated rate. In the analysis, the proportion 0.1% meant concentrations similar to the groundwater collected at a gas station and used in bench scale tests. Pilot scale testing characteristics are shown in Table 1.

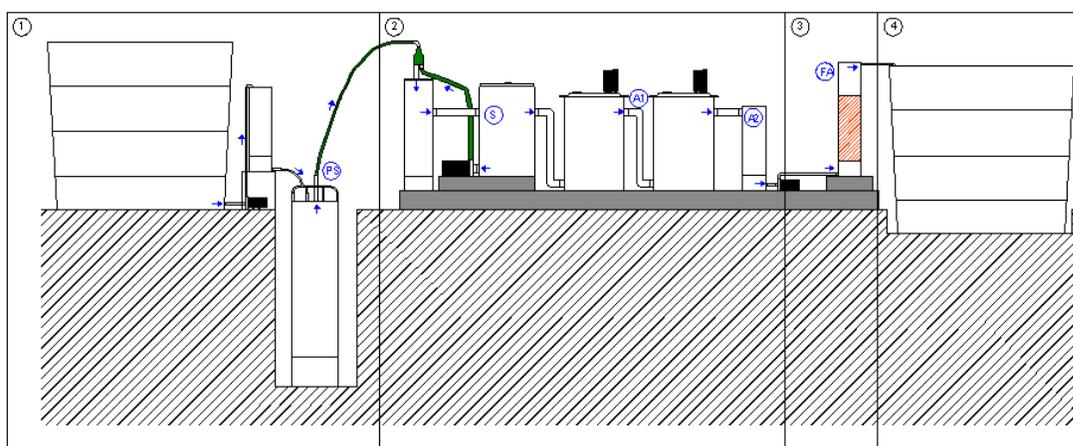


Fig 2: Remediation System on Pilot Scale

Legend: 1 – Mix and supplying reservoir and suction sump (PS); 2 – Suction system (S) and aeration (A1 / A2); 3 – Adsorption Filter (FA); 4 – Treated water reservoir

Table 1. Pilot scale testing characteristics

Test	Gasoline and Diesel Concentration	Time (minutes)	Sample Placement
1	5L (gasoline) + 5L (diesel)	0*, 60, 120, 180, 240*	PS, S, A1, A2, FA
2	5L (gasoline) + 5L (diesel)	0*, 60, 120, 180, 240*	PS, S, A1, A2, FA
3	5L (gasoline) + 5L (diesel)	0*, 60, 120, 180, 240*	PS, S, A1, A2, FA
4	10L (gasoline) + 10L (diesel)	0*, 60, 120, 180, 240*	PS, S, A1, A2, FA
5	10L (gasoline) + 10L (diesel)	0*, 60, 120, 180, 240*	PS, S, A1, A2, FA
6	10L (gasoline) + 10L (diesel)	0*, 60, 120, 180, 240*	PS, S, A1, A2, FA

Legend: PS (suction sump), S (sump), A1 (aerator 1), A2 (aerator 2) and FA (Adsorption Filter)

* PS collection time period

The tested experimental apparatus presented a synthetic soil with a permeability coefficient equal to $7.0 \times 10^{-2} \text{ m / s}$. The flow treatment was equal to 0.031 L / s and the hydraulic detection time consisted of 8 hours.

The treatment efficiency was analyzed through 06 assays of 4 hours each summing up 30 system tests in a study for the parameters: BTEX (EPA 8260) – Benzene, Toluene, Ethylbenzene and Xylene; TPH DRO (EPA 3510 and EPA 8015 D) – C10-C28 – diesel range; TPH GRO (EPA 8015) – C6-C10 – gasoline range; TPH Total (EPA 3510 and EPA 8015 D – C8-C40).

Results and Discussion

Groundwater Characterization

The characterization (Table 2) demonstrates great variability of results and high contaminants rates present in the studied groundwater, therefore being above intervention level expectation according to national regulation CONAMA 420 (2009). The variability and high rates of contaminants are also reality in other Brazilian cities as well as in the global set.

Table 2. BTEX and TPH groundwater concentration in Porto Alegre

Site	Groundwater Concentration ($\mu\text{g/L}$)				
	Benzene	Toluene	Ethylbenzene	Xylene	TPH
A	41.3	37.9	34.4	179.0	12617.0
	45.4	5.71	35.2	183.0	22391.0
B	13.1	4.1	2.0	6.7	490.0
	83.3	29.1	9.1	37.8	631.5
	94.4	4.1	3.8	15.8	2348.5
	3072.3	6267.7	1049.2	5596.4	62833.8
C	1.7	<1	<1	<3	3500.0
<i>Average</i>	<i>478.7</i>	<i>1058.1</i>	<i>188.9</i>	<i>1003.1</i>	<i>14973.1</i>
<i>Standard Deviation</i>	<i>1144.2</i>	<i>2552.2</i>	<i>421.7</i>	<i>2251.6</i>	<i>22574.6</i>
<i>Maximum</i>	<i>3072.3</i>	<i>6267.7</i>	<i>1049.2</i>	<i>5596.4</i>	<i>62833.8</i>
<i>Minimum</i>	<i>1.7</i>	<i>4.1</i>	<i>2.0</i>	<i>6.7</i>	<i>490.0</i>
Research Level					
<i>CONAMA N° 420 (2009)</i>	<i>5</i>	<i>700</i>	<i>300</i>	<i>500</i>	<i>-</i>

EPA (1997), for example, demonstrates in an American study, initial BTEX concentrations ranging between 6 and 24 mg/L. For benzene parameter this variation is from 3 to 600 mg/L. Bass *et al.* (2000), according to a data survey of 49 study cases on contaminated areas in United States, have verified initial BTEX concentration ranging from 24 to 198,000 $\mu\text{g/L}$. For TPH, the authors found initial concentration from 240 to 34,000 $\mu\text{g/L}$. In German northeast, Afferden *et*

al. (2011) demonstrated benzene initial concentration (after accident in 2007) varying from 13.046 to 18.625 µg/L; toluene from 6.7 to 8.0 µg/L; ethylbenzene from 31.0 to 50.0 µg/L; xylene from 63.7 to 82.5 µg/L. In Austria, Wirthensohn *et al.* (2009) demonstrated contaminants in groundwater varying between 295 - 806 µg/L for BTEX and 247 - 547 µg/L for Benzene. In Taiwan, Chen *et al.* (2010) demonstrated initial BTEX concentration ranging from 39 to 2838 µg/L (Benzene = 15 - 743 µg/L; Toluene = 2 - 712 µg/L; Ethylbenzene = 6 - 419 µg/L; Xylene = 16 - 964 µg/L). In Brazil, however, phreatic aquifer contamination data over Duque de Caxias Refinery in Rio de Janeiro demonstrated, by Abdanur & Nolasco (2005), initial BTEX concentration ranging from 9.748 mg/L to 65.883 mg/L. For benzene, the variation was from 0.747 mg/L to 11.433 mg/L. Mariano *et al.* (2007) describes contaminant initial concentration in Santa Bárbara d'Oeste (São Paulo) varying from 56.1 to 4702 µg/L of BTEX (Benzene: 4.0 – 57.0 µg/L; Toluene: 4.0 – 69.0 µg/L; Ethylbenzene: 4.0 - 4330 µg/L; Xylene: 4.0 - 372 µg/L).

Over site A it was also checked other physicochemical parameters. The results demonstrated the presence of TPH, BTEX and other contaminants as pH (6.89), Turbidity (54.0 NTU), Total Coliforms (< 23.0 NMP/100mL), Thermotolerant Coliforms (12.0 NMP/100mL), Conductivity (697 µS/cm), Phosphorus (0.673 mg/L), Total Nitrogen (2.92 mg/L), Ammoniacal Nitrogen (3.01 mg/L), OD (0.404 mg/L), DBO (172.0 mg/L), DQO (197.4 mg/L), COT (230.7 mg/L), Total Alkalinity (67.3 mg/L), Total Solids (534.0 mg/L). It was noticed that these compounds are not related to operation and/or leak of fuel at the site. It was in fact due to other sources of contamination, probably household sewage.

Adsorbents Characterization

The characterization results report that the activated carbon presents predominantly organic composition with a loss on ignition of 98.4%. Rice husk ash has a predominantly inorganic composition with a loss on ignition of 7.2%.

Referring to the PH value established for the samples, both presented alkaline pH, 9.3 for activated carbon and 8.7 for rice husk ash. The activated carbon higher pH indicates the adsorbent activating process as a result of the use of bases. The electrical conductivity of activated carbon (227.5 µS/cm²) was higher than the value found for the ash (81.7 µS/cm²), indicating a greater presence of ions in activated carbon resulting from chemical activation. The densities are similar, 1.7 g / cm³ for the activated carbon and 1.9 g / cm³ for the rice husk ash. In terms of particle size, the rice husk ash presents itself thinner compared to activated carbon. The particle size distribution of the activated carbon ranges between 3.35 and 0.85 mm, while the one of rice husk ash lies between 1.7 and 0.053 mm.

Chemical analysis indicates that silicon (85%) is the major component found in rice husk ash, presenting traces of other elements such as iron, manganese, calcium, potassium and phosphorus.

For activated carbon, the inorganic fraction showed silicon, sulfur, iron, copper, calcium, potassium and phosphorus. Among these elements it was observed a higher concentration of potassium. The high potassium values found for activated carbon associated to the alkaline pH of the material indicates a possible activation with potassium hydroxide.

In XRD assays, although evidenced presence of peaks in the XRD pattern of X-ray, it is observed that the gross RHA and segregated RHA have the halo of formlessness that corresponds to the deviation of the baseline between the angles of 15 ° and 30 °, indicating the amorphicity of the material. According to the peaks this silica ash may be present in the form of cristobalite. The XRD pattern of activated carbon indicates that the material is amorphous.

The microstructure of rice husk ash can be observed through the micrographs shown in Fig. 3.

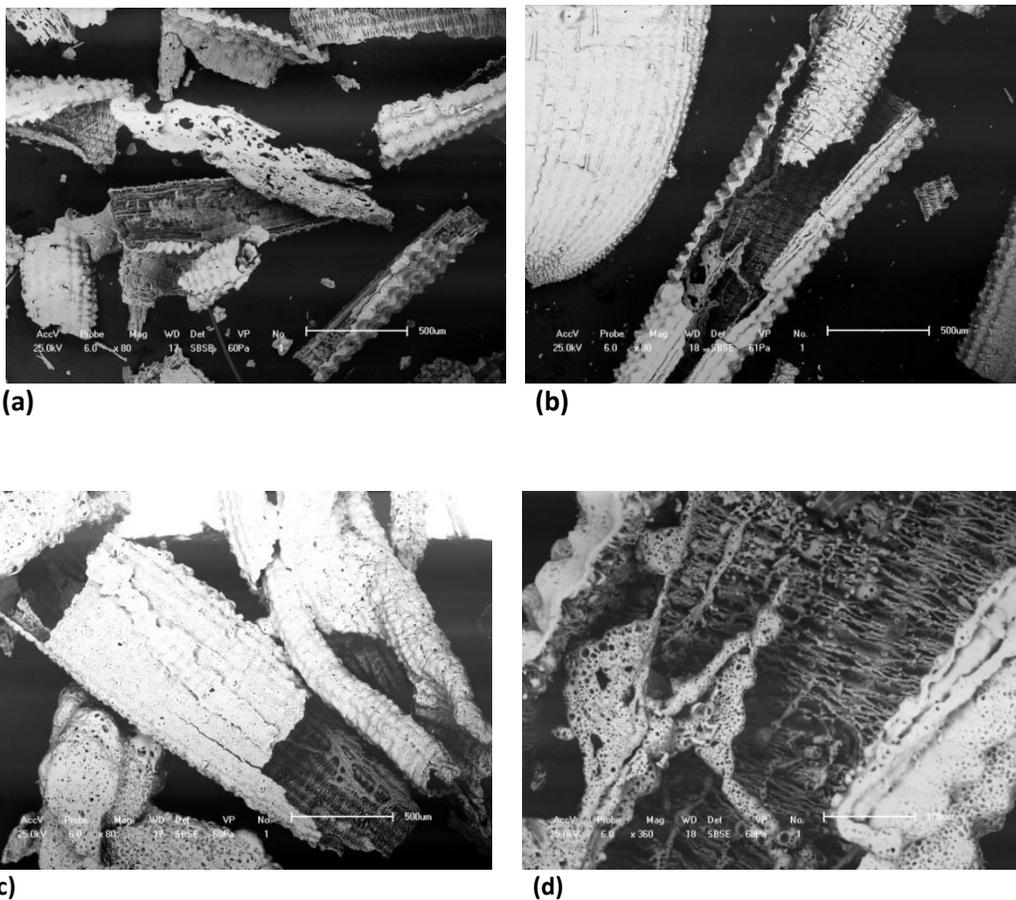


Fig 3: Micrographs of the RHA: (a), (b) and (c) increase of 80X - (d) increase of 360X

Analyzing the micrographs (a), (b) and (c) it is observed that the burning of RHA is not uniform, resulting in particles with different particle size resulting from the burning temperature and residence time during the combustion process.

In micrograph (d) it is found that the RHA particles are formed by two parts: an outer, consisting of a denser structure; another inner, more porous which indicates the potential of its use as an adsorbent.

Laboratory Scales Assays

The laboratory scales assays are shown in Table 3.

Table 3. The laboratory scales assays results

Tests	TPH initial ($\mu\text{g/L}$)	Filters	Maximum % TPH Removal	Time*
1	1629.0	Filter with RHA 100%	58.5%	14 min
1	1629.0	Filter with AC 100%	100%	52 min
2	626.0	Filter with RHA 100%	100%	48 min
2	626.0	Filter with AC 100%	100%	64 min
3	1013.0	Filter with RHA 100%	46.5%	12 min
3	1013.0	Filter with AC 100%	100%	70 min
4	555.0	Filter with RHA 100%	100%	60 min
4	555.0	Filter with AC 100%	100%	90 min
4	555.0	Filter with AC 50% and RHA 50%	100%	90 min

* System's maximum operation time when there is no adsorbent saturation

It was noticed in assays 1, 2 and 3 that the filters made of rice husk ash present a reduction of contaminants. However, saturation is faster than in filters containing activated carbon. It is also to be highlighted that in TPH higher initial concentration (1 and 3) those filters containing rice husk ash did not eliminate completely the contamination. In opposition to what has been observed in activated carbon filters which present 100% removal regardless initial concentration.

Moreover, it is important to mention that 100% rice husk ash filters presented problems of clogging of the adsorbent interrupting the filter water stream. This can be associated to the low granulometry of the ashes. In this sense, for experiment 4 filters with 50% rice husk ash and 50% activated carbon have been prepared.

Thus, the results of assay 4 show that 100% carbon filters and those mixed (50% AC and 50% RHA) behave similarly during 90 minutes monitoring once they adsorb 100% of contaminants in this period. This same efficiency is not observed in 100% rice husk rice filters with presence of saturation after 60 minutes testing.

From these analyses it was observed the potential use for rice husk ash as an adsorbent in filters for contaminated groundwater treatment by hydrocarbons. It also enabled to set the constructive criteria of the pilot scale experiment below.

Pilot Scale Assays

There are two remarks to be specified regarding this assay: 1) in the majority of the assays, benzene parameter has not been identified; 2) when there were inserted 0.2% of gasoline and 0.2% of diesel, the concentration of the contaminants have not increased as expected.

The first fact can be justified by the rate of volatilization of benzene. It is estimated that by the time when the contaminants were mixed with water, there has been loss of these concentrations.

Secondly, it was perceived difficulties in dissolving diesel and gasoline in the water due to the large volume ratios, differently from those used for the laboratory tests. It was noted the presence of free phase in the reservoir, which confirms this assumption.

Thus it was not possible to vary the initial concentration for the tests. Even the ANOVA test performed demonstrated that the 06 assays were similar, in other words, there has not been any statistical variance between the initial concentration of TPH and BTEX parameters in the suction sump.

From this fact on, the determination of the average decrease found in each equipment tested (Table 4) shows that approximately 57.69% - 96.71% of contamination was removed with the installed suction equipment. Pump and Treat system combined with "air spargin" treatment studied by Kieling *et al.* (2010) in 10 gas stations in Porto Alegre/RS show removal efficiency for BTEX equal to 100%. The same "air spargin" treatment demonstrated by EPA (1997) through studies accomplished in contaminated areas in United States confirms removals that vary from 59% to 100%. Bass *et al.* (2000) and Khan *et al.* (2004) also detected 99% removal with the same technology. With air injection, Afferden *et al.* (2011) obtained 100% BTEX removal in 611 days monitoring. In the same way, concerning "air stripping", EPA (2001b) reports that once well conducted these systems can reach up to 99% removals.

Table 4. Average decrease of BTEX and TPH parameters for the remediation system studied

Parameter	Average initial concentration ($\mu\text{g/L}$)	Average decrease in %			
		Suction	Aerator 1	Aerator 2	Adsorption Filter
Benzene	6.7	96.71	96.71	96.71	96.71
Toluene	449.6	71.43	98.03	99.86	99.86
Ethylbenzene	112.2	69.14	94.66	99.66	99.68
Xylene	548.8	69.73	96.25	99.78	99.79
TPH DRO	30123.8	58.47	71.03	82.53	99.99
TPH GRO	1415.9	67.36	96.71	99.98	99.98
TPH Total	31534.6	57.69	73.43	84.34	99.99

For the here tested equipment after treatment in adsorption filter a range from 96.71% to 99.99% of final decrease for BTEX and TPH has been achieved. This result is similar to that obtained by Ayotamuno *et al.* (2006); Juneau Jr *et al.* (2007) and Wirthensohn *et al.* (2009).

ANOVA test, by using the software IBM SPSS 22 version, demonstrated significant difference (95% confidence interval) among BTEX and TPH concentration results comparing suction sump, suction, aerators and adsorption filter and that confirms the equipment efficiency. There was no exclusion of any data in the statistical analysis.

However, according to Tuckey's analysis it is possible to observe significant differences by comparing Suction Sump and its Suction capacity (for all parameters analyzed). TPH parameters show substantial differences between suction and aerator and also aerator 2 and suction and adsorption filter. Yet, there is no significant difference in the results from aerators and aerators and adsorption filters. This set of data allows the option for aerator exclusion in the treatment system by choosing the maintenance of only suction followed by adsorption filters. Fig. 4 shows the high reduction when comparing the treatment types tested.

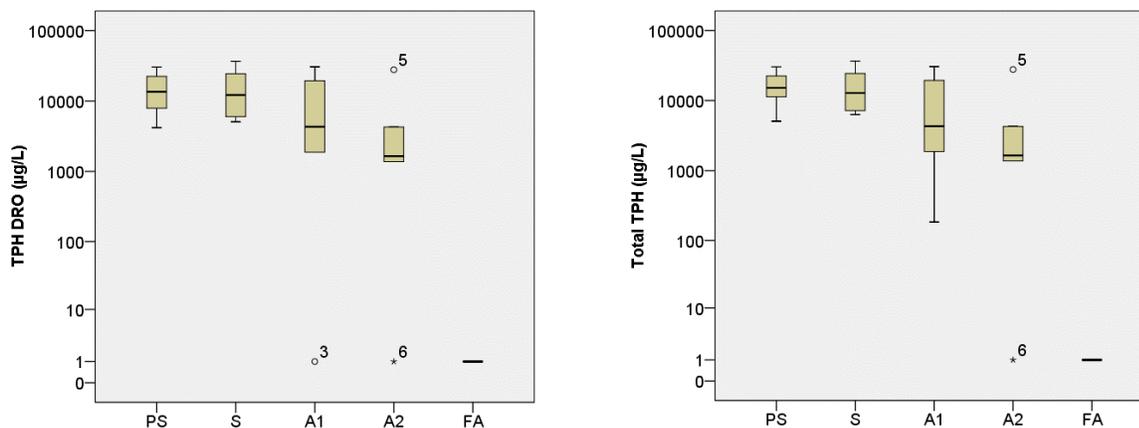


Fig 4. Total TPH reduction results for 240 minutes

For BTEX parameters, the processes that promote Air Stripping reduce these concentrations at minimum concentration levels, meeting the criteria established for the level of research CONAMA N° 420 (2009). Nevertheless, Fig. 4 shows that non-volatile compounds need final polishing. It stands out the high decrease comparing aeration treatment for adsorption filters. That represents the great importance of this treatment/equipment in order to guarantee process efficiency and functionality configuration of rice husk ash as adsorbent in adsorbent filters applied to groundwater contaminated by hydrocarbons.

The complete system tested for this study demonstrated to be efficient in removing hydrocarbons present in groundwater. With detention time of 8 hours the equipment promoted water treatment providing full compliance, considering the analyzed physicochemical parameters (BTEX and TPH) with national legislation.

The cost of the complete equipment is estimated at US\$40,000 (approximately US\$20/m³ treated water). The treatment capacity is 900m³/day of contaminated groundwater.

In relation to the adsorption system, compared with the conventional filter, the main advantages of the use of the adsorption filter built with 50% AC and 50% RHA for the polishing process were the reuse of RHA waste, and the reduction of environmental impacts caused by the production of AC and of operation costs. Considering the replacement of adsorbent every 1000 h and the similar behavior of the composite filter observed in laboratory tests, compared with the 100% AC filter, the reduction of operational costs of treatment may be from US\$0.14/m³ to US\$0.07/m³ when a 50% RHA filter is used.

Regarding the disposal of rice husk ash waste contaminated by hydrocarbon after treatment by adsorption, in Brazil, they are usually sent to industrial landfill similar to what currently occurs with activated carbon. Other alternatives are: composting, incineration and co-processing.

Conclusions

Rice husk ash waste was confirmed in this paper as a potential adsorbent to be used, as adsorbent filter, in remediation technology in groundwater contaminated by hydrocarbons.

The results demonstrated the importance of studying gas station areas contaminated by hydrocarbons once the concentrations found in the studied groundwater vary from 1.7 µg/L to 3072.3 µg/L, for benzene, for example. These levels are above from those permitted by CONAMA 420 (2009) regulation, in which benzene's is 5 µg/L.

The comparative test among adsorbents (RHA - rice husk ash and AC - activated carbon), performed in lab, showed efficiency results similar to those between adsorbent filters with 100% activated carbon and mixed filters (50% AC and 50% RHA). This result enabled these filters to be applied in pilot scale.

By these means, the remediation technology proposed by this research, composed by vacuum suction, aeration and adsorption filter (50% AC and 50% RHA), demonstrated concentration decreases for BTEX and TPH ranging from 57.69% to 96.71% for suction system. Referring to the results achieved, after polishing using adsorption filter, the obtained removals varied from 96.71% to 99.99%. Statistical tests (ANOVA and Tuckey) confirm the need of polishing treatment by using adsorption filter.

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