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ABSTRACT

EXPERIMENTAL ANALYSIS FOR OPTIMUM ARSENIC REMOVAL FROM GROUND WATER

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ABSTRACT

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Introduction

Water is particularly vulnerable to contamination with toxic chemicals discharged by various industries. Heavy metals in water are one such group of contaminants having serious consequences for aquatic life and human beings. The metals of major concern are aluminum, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel and zinc [8]. In this study we carried out experiments to find the optimum arsenic removal from ground water. Many approaches can be used to remove arsenic to have a concentration below the value imposed by law, but most of the systems are expensive and not suitable for small water systems with limited resources. Therefore we studied arsenic removal through adsorption because the system can be simple to operate and cost-effective.

Arsenic effects on humans and worldwide distribution

It can be further released into the environment through natural activities such as volcanic action, erosion of rocks and forest fires, or through human actions.

Elevated concentrations of arsenic are found in groundwater in many regions around the world, like Bangladesh, India, in some areas of China, Chile, Argentina, Mexico, Hungary, Taiwan, Vietnam, Japan, New Zealand, Germany and the United States; in Italy, high arsenic level can be found in Campania, in the area of Campi Flegrei. One of the major sources of arsenic exposure by the general population is drinking water; arsenic in drinking water may have affected more than 100 million people worldwide.

The International Agency for Research on Cancer (IARC) has determined that inorganic arsenic is carcinogenic to humans, but it has also dangerous non carcinogenic effects.

In order to reduce health risk, the World Health Organization (WHO) recommended a maximum arsenic concentration of 10 μgl^{-1} in drinking water in 1993 (this is the MCL Maximum contaminant level). The EPA (*United States Environmental Protection Agency*) adopted the WHO guideline of 10 μgl^{-1} of arsenic as the drinking water standard in 2001, and this standard was adopted by Italy in 2001 too thanks to the D.Lgs.31/01/2001.

Methods of arsenic removal

A variety of treatment processes have been examined for arsenic removal, but most of the systems are expensive and not suitable for small water systems. More attention is given to arsenic removal through adsorption because the system can be simple to operate, suitable for small water systems and not expensive. In this study we investigated the applicability of several different adsorbents in removing arsenic (in the inorganic forms As(V) and As(III), more toxic than the organic forms) from water through adsorption.

Adsorbents

Several adsorbents were tested for their ability on arsenic removal. The adsorbents tested are:

- Activated Carbon (AC): It is the generic term used to describe a family of carbonaceous adsorbents with a highly crystalline form and extensively developed internal pore structure. It's characterized by a very large surface area per unit volume because of an enormous number of fine pores. Due to its high degree of microporosity, just one gram of activated carbon has a surface area of approximately 500 m^2. Some of the more common raw carbon sources include wood, sawdust, lignite, peat, coal, coconut shells, and petroleum residues.

- Activated Alumina (AA): It is prepared by dehydration of $Al(OH)_3$ at temperatures of 300-600°C. Depending on the particle size, the surface area of activated alumina can range anywhere from 50-880 m^2/g, but is typically chosen between 100-300 m^2/g (a high surface area to weight ratio): it has a lot of very small pores, almost like tunnels, that run throughout it.

- Adsorbents modified: We developed different iron-containing adsorbents for arsenic removal, someone based on untreated AC and someone else based on untreated AA. Some of these adsorbents contained also different amount of limestone; indeed literature has shown that the adsorption on activated carbon can be significantly increased by treatment with various metal compounds, since arsenic adsorption onto Virgin AC was minimal and regeneration was difficult, so it cannot be directly applied for arsenic treatment. The adsorbents developed are:

  a) 20g AC + 30ml $Fe_2(SO_4)_3$ + 12g Limestone

  b) 20g AA + 30ml $Fe_2(SO_4)_3$ + 12g Limestone

  c) 20g AA + 30ml $FeCl_3$

  d) 20g AA + 30ml $Fe_2(SO_4)_3$ + 6g Limestone

  e) 20g AC + 30ml $Fe_2(SO_4)_3$ + 6g Limestone

Experimental

The ability of adsorbents for arsenic removal was evaluated through both batch and column studies. Batch experiments were carried out to obtain the adsorption isotherms of arsenic with several adsorbents. In particular, we investigated if the Langmuir and Freundlich isotherms are models that satisfy our experimental data. Anyway the adsorption isotherms do not give accurate data for fixed bed systems and therefore the practical applicability of the adsorbent was ascertained in the column operation. Other batch experiments were carried out to determine the best pH for arsenic removal and to investigate the sulfide effect on the adsorption of arsenic.

Batch studies – Adsorption isotherms

The isotherm is a relation between the amount of adsorption (adsorbate per unit mass of adsorbent) and equilibrium concentration of the adsorptive; every adsorbent has its own. Thanks to isotherm we can determine how much pollutant could the adsorbent hold at a fixed temperature: once a certain amount of arsenic has been adsorbed on the adsorbent surface, the process reaches and equilibrium, and at this point a longer contact time will not result in more adsorption.

Procedure: each centrifuge tube was loaded with 50 ml aged tap water contaminated with arsenic in 8 different concentrations: (0,5ppm 10ppm 20ppm 30ppm 40ppm 50ppm 60ppm 70ppm) and 0.1 g of adsorbent. Each centrifuge tube was let mixing for 2 hours. During the experiments the pH was maintained constant at 7.0 ± 0.3, with 1.0M NaOH and 5 wt % HCl. Then each centrifuge tube was centrifuged at a rotational speed of 9000 rpm for 5 minutes. This experiment was carried out for As(V) as well as As(III), but for As(III) nitrogen compressed has been used for 15 minutes to avoid the possibility that arsenite could be oxidized to arsenate.
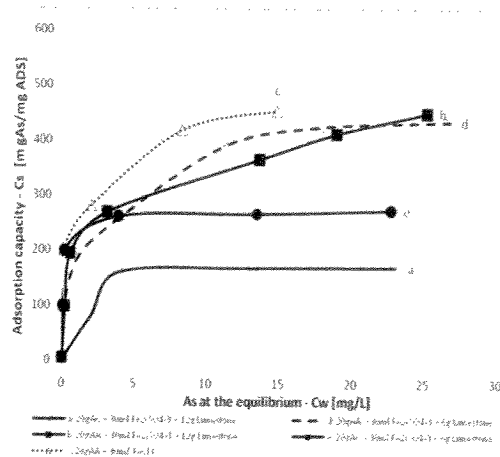
Results:

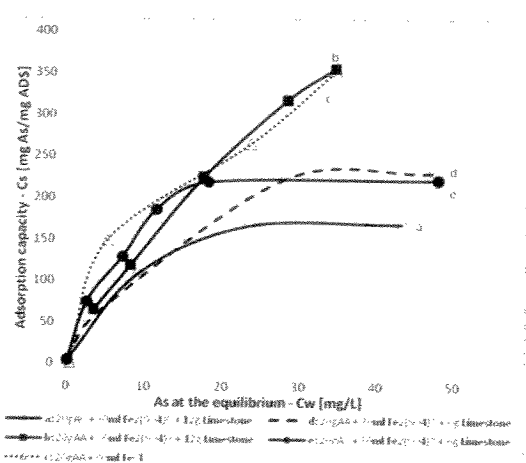**Fig. 1 - As(V) Adsorption isotherms**   **Fig. 2- As (III) Adsorption isotherms**

Comparing the isotherms in Fig.1, we can see as the best adsorbent for the removal of As (V) under our experimental conditions is the adsorbent c with a percentage of removal range from 75,48% to 99,70%; indeed this sample reaches the equilibrium later than the other samples. The worst adsorbent seems to be the adsorbent a with a percentage of removal ranged from 20,69% to 84%. We can do similar considerations for the adsorption isotherms of As(III) in Fig.2: the best adsorbents for the removal of arsenite is the adsorbent c, with a percentage of removal range from 20,8% to 74,2% and the worst one is the sample a. Anyway as shown in the literature, our results confirm that arsenate is more effectively removed by ferric hydroxides and oxides than arsenite. Moreover we investigated if the Langmuir and Freundlich isotherms are models that satisfy our experimental data. The adsorption on every sample can't be described

using the Langmuir or the Freundlich equation, except for the adsorption on the sample *e* that can be described using the Langmuir model and the adsorption of arsenite on the sample *b* that can be described using the Freundlich equation.

Batch studies – pH effect

The pH of the aqueous solution is an important controlling parameter in the adsorption process. A variation of pH may significantly decrease arsenic adsorption, and therefore we studied its effect on the process of adsorption.

Procedure: each centrifuge tube was loaded with 0,1 g of adsorbent was loaded in a centrifuge tube with 50 ml of aged tap water contaminated with 300 ppb of arsenic. Each centrifuge tube was maintained at the established pH values (pH values used: 4, 5, 6, 7, 8, 9, 10, 11) using 5 wt % HCl, 1.0M NaOH and 10M NaOH solutions. After 1 hour mixing, the pH has been checked and adjusted to the established pH value and then let mixing for another hour. The final pH was checked and then each sample was centrifuged at a rotational speed of 9000 rpm for 5 minutes. Also this experiment was carried out for As(V) as well as As(III), but for As(III) nitrogen compressed has been used for 15 minutes to avoid the possibility that arsenite could be oxidized to arsenate.
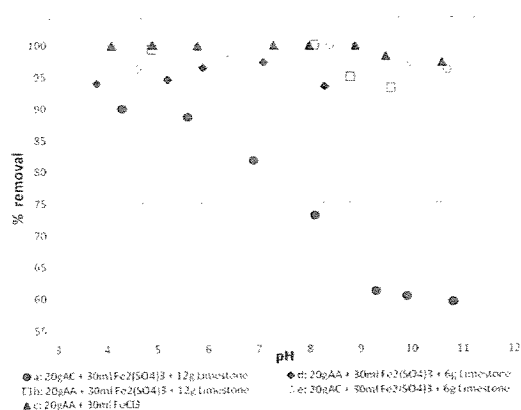
Results:

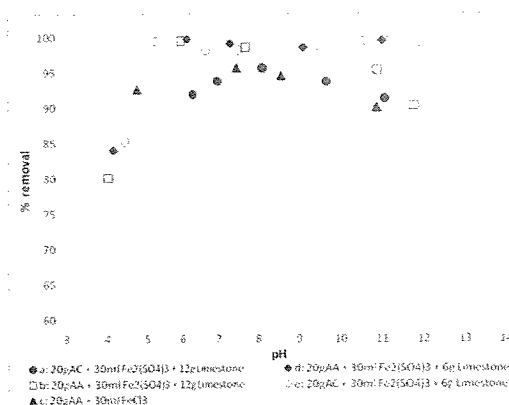**Fig. 3 - Effect of pH on arsenate adsorption**

**Fig. 2 - Effect of pH on arsenite adsorption**

The uptake of arsenite is much less than that of arsenate for AA in most pH conditions, and the uptake remains almost constant for pH less than around 9, and then dropped significantly for higher pH conditions. Anyway significant decrease in arsenate and arsenite adsorption was not observed until the pH was increased to more than 9.0, suggesting that the material should be effective for the majority of water supplies, which normally have a pH range from 6.5 to 8.5.

Batch studies – S^{2-} effect

Another parameter that can influence the adsorption of arsenic is the presence of anion in the water: the anion could compete with the arsenic in adsorption on the media, and therefore its presence may significantly decrease arsenic adsorption. Screening tests were carried out to investigate the sulfide effect on the adsorption of arsenic by two different media made with activated carbon and activated alumina.

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Procedure: These studies were conducted starting from an initial concentration of arsenic of 600 ppb in aged tap water. In each centrifuge tube of 50 ml containing the contaminated solution, we added different concentrations of S^{2-} (0,1ppm 0,5ppm 1ppm 5ppm 10ppm) and then we loaded 0,1g of adsorbent samples and let mixing for 2 hours. During the experiments the pH was maintained costant at 7,0 ± 0,2. In the end each centrifuge tube was centrifuged at a rotational speed of 9000 rpm for 5 minutes. This experiment was carried out for As(V) as well as As(III), but for As(III) nitrogen compressed has been used for 15 minutes.

Results:
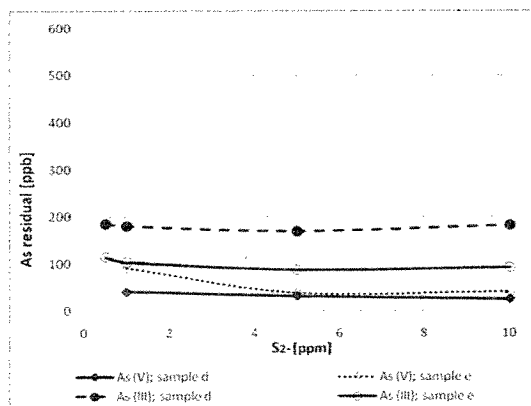
Fig. 5 - Sulfide effect on As adsorption by media Fe-AA and Fe-AC

The sulfide influences the media based on AC more than the media based on AA, confirming literature. Anyway as the concentration of sulfide increases in the range of concentration that we studied, there isn't a big influence in removing arsenic: the arsenic residual has a constant value while the concentration of S^{2-} increases.

Column studies

The adsorption isotherms do not give accurate data for fixed bed systems and therefore the practical applicability of the adsorbent was ascertained in the column operation. To reach this purpose we made column studies in order to find the breakthrough curves for different adsorbents, both for arsenate and arsenite.

Removal of arsenic from water was achieved in flow continuous mode: experimental tests were conducted using a small column of 1cm diameter and 10cm height. The effluent was collected at the bottom of the column through a 2mm diameter orifice. The adsorbent was packed into the column carefully to avoid air bubbles and make sure an intimate contact between the adsorbent and the water. A bed volume of 5 ml of adsorbent was used, and during the filtration about 2cm of water was assured above the bed. Samples at the bottom of the column were collected at definite intervals of time (about 24 hours) and analyzed to estimate arsenic concentration. A flow rate (Q) of 2mL/min was used for all the experiments, which gives an empty bed contact time (EBCT) of 2,5 min. In particular for the experiment carried out for As(III), nitrogen compressed has been used for all the duration of the test to avoid the possibility that arsenite could be oxidized to arsenate.

As (V) results

The results in Fig 6 clearly demonstrated that the Virgin AC is not suitable for arsenate removal, because the arsenate residual in the water is always higher that the limit imposed by the law. Instead for the column with Virgin AA the effluent concentration reached 10 ppb MCL at around 1500 EBV.

In Fig. 7 it is demonstrated that the modified adsorbents based on AC increased the arsenate removal capacity of Virgin AC: using them the concentration residual in the water was lower than MCL in 600EBV for the sample *a* and in 700EBV for the sample *e* and so for the modified adsorbents based on AA. The modification of the Virgin AA with iron compounds improved the capacity of removing arsenate too: the column containing the sample *d* shows that the effluent concentration reached 10 ppb at around 4500 EBV, the one containing the sample *b* shows the MCL at around 5000 EBV and the column containing the adsorbent *c* reached 10 ppb at approximately 5500 EBV (Fig.8). Moreover also the presence of limestone in the adsorbents contributes to improve the capacity of removing arsenic, even if its contribute is not so important as the one of the iron compound.
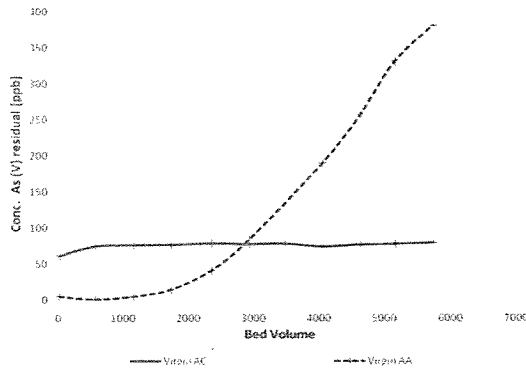

Fig. 6 – As (V) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Virgin adsorbents. Cin=600ppb, Q=2mL/min.
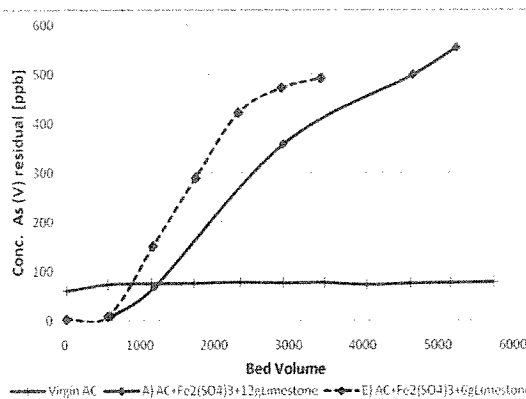

Fig. 7 - As (V) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Comparison between adsorbents based on AC. Cin=600ppb, Q=2mL/min.
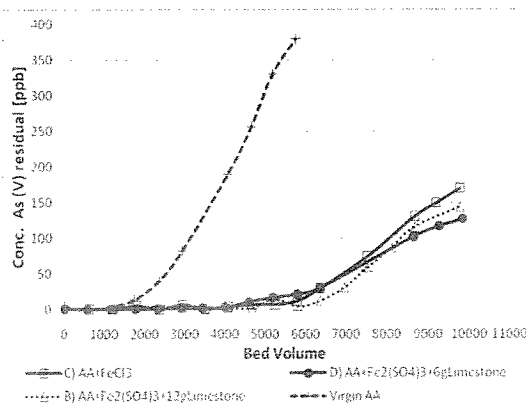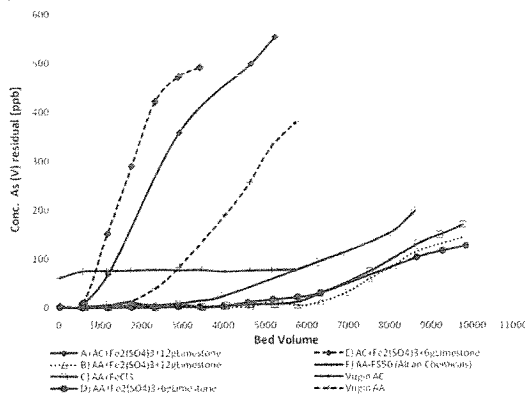

Fig. 8 - As (V) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Comparison between adsorbents based on AA. Cin=600ppb, Q=2mL/min.

In the end in Fig.9 we compared all the adsorbents with one in commerce based on AA (from Alcan Chemicals). The time to reach the MCL is around 3000EBV, before than our modified adsorbents based on AA. Probably this happens because our modified adsorbents contain an higher amount of iron compared with the amount of iron in the adsorbent in commerce (this supposition is confirmed by the color: our adsorbents are darker than the adsorbent from Alcan Chemicals). This means that our adsorbents have an higher arsenic removal capacity than the one in commerce, but this means that our adsorbents are more expensive too.

Fig. 9 - As (V) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Cin=600ppb, Q=2mL/min.

As (III) results

Virgin AC is not useful for arsenite removal, while Virgin AA is able to remove arsenite, and the effluent concentration is lower than MCL in about 500EBV (Fig.10). As for the arsenate removal, in Fig.11 and Fig.12 we can see as the modified adsorbents has improved the capacity in removing arsenic of the virgin adsorbent, both for Virgin AA and Virgin AC. In particular the column containing the adsorbent d (based on AA) reaches the MCL in around 2100EBV, while the one containing the sample c (based on AA) reaches MCL in 3100EBV. Anyway the adsorbents based on AA have a better arsenite removal.
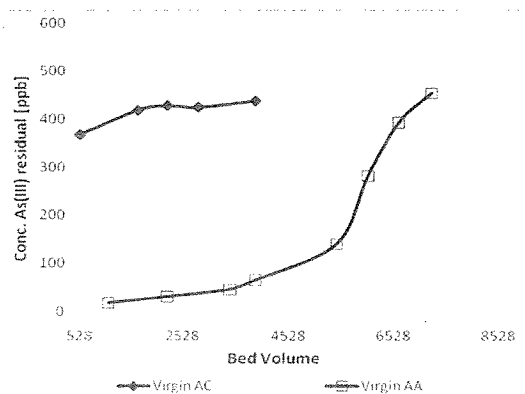
Fig.10 - As (III) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Virgin adsorbents. Cin=600ppb, Q=2mL/min.
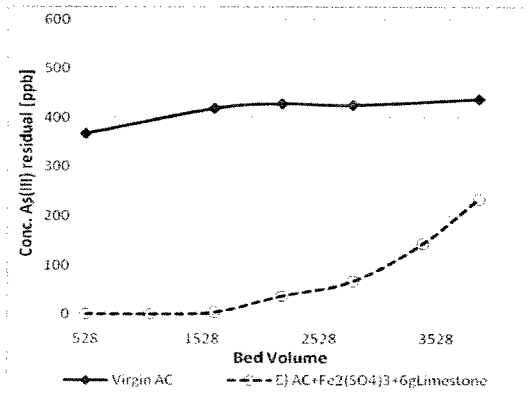
Fig.11 - As (III) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Comparison between adsorbents based on AC. Cin=600ppb, Q=2mL/min.
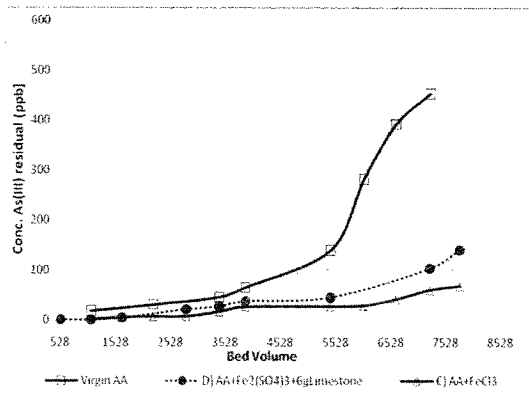

Fig.12 - As (III) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Comparison between adsorbents based on AA. Cin=600ppb, Q=2mL/min.

Comparing the results, we can say that arsenate is more effectively removed by ferric (hydr)oxides than arsenite, in accord with literature. Lastly, confirming the results obtained with the batch tests, the best adsorbent seems to be the adsorbent c, because it last longer than the other samples before the effluent concentration reaches the MCL of 10ppb.

Finally in Fig.13, we studied the effect of 2ppm of S^{2-} in water contaminated by As(III) we found that this anion didn't significantly affect arsenite removal on the adsorbent d based on AA, while the adsorbent e (based on AC) has a great decrease in capacity of adsorption arsenite in presence of S^{2-}. Moreover modifing the adsorbent b based on AA using a pretreatment with 5ml of 100 ppm Mn solution (KMnO$_4$), the effluent concentration reaches the value of MCL at around 1300EBV (compared with 1700EBV without pretreatment): hence this new adsorbent shows a worst capacity of arsenite adsorption.
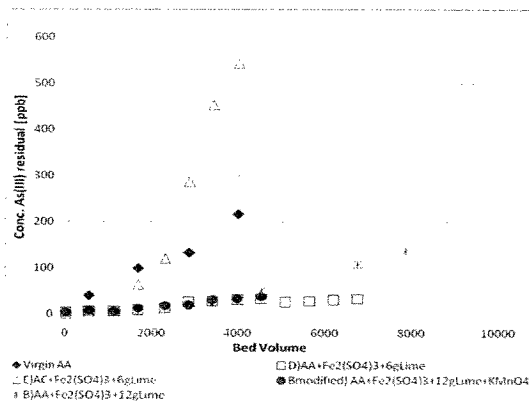

Fig.13 - As (III) - Arsenic concentration in the effluent as a function of empty bed volume (EBCT=2,5min). Influence of S^{2-}. Cin=600ppb, Q=2mL/min.

Future development

Summarize all the studies we can conclude that adsorbents based on Activated Alumina and iron-containing reduce effectively arsenic concentration in water through the process of adsorption, giving an effluent concentration lower than the limit of 10ppb suggested by WHO and received by our legislation. The pH at the typical value for drinking water and the presence of S^{2-} in low concentration don't influence significantly the process. Therefore this method could be developed in the future thinking to an application on a larger scale and also to a reasonable cost, because in many cases it could be applied for small systems in poor areas of the world.