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Efficacy of combining colloidal TiO_2 or colloidal Ag coatings with the ceramic water purifier for use in rural and per-urban Sierra Leone

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Abstract

This paper aims to assess the potential of combining the photo catalytic properties of titanium dioxide (TiO_2) as a low cost, low energy and low environmental impact water treatment method with the Point of Use ceramic water purifier (CWP) developed by Potters for Peace (PfP) in order to provide a WHO standard drinking water solution suitable for use in rural and peri-urban Sierra Leone. Current pot designs include a colloidal silver (Ag) coating, which adds an antimicrobial layer and prevents the formation of bio-fouling. This paper presents the efficacy of colloidal TiO_2 materials to remove humic substances, ubiquitous organic contaminants and pathogens in solution and later results will be presented to compare this to Ag and $AgNO_3$ both in solution and as coatings for the CWP using CWP's obtained from Potters for Peace, Nicaragua, under environmental conditions similar to those in Sierra Leone.

1. Introduction

Over 5000 children are dying daily because of water related diseases (WHO and UNICEF 2005) and 900 million remain without access to safe and reliable water supplies (DFID 2008). In developing countries where political and economic factors prevent the management and maintenance of small scale or centralised systems, and particularly in the rural and peri-urban areas where the infrastructure and services required for such systems are not in place, this leaves point of use (POU) systems as the only option for water purification (Peter-Varbanets et al. 2009). The ceramic water purifier (CWP) has the means to provide a sustainable, low cost solution to water purification with a 46% reduction in diarrhoeal diseases (Sobsey et al. 2008) and at only $10 per filter (Lantagne et al. 2007) Replacement is required only upon breakage and research by (Sobsey et al. 2008) has shown the mean life expectancy of the CWP to be 2 years with a 2% per month disuse rate of which 67% was due to breakage of either the filter of the receptacle.

1.1. The Ceramic Water Purifier: Microfiltration Unit

The CWP operates as a batch microfiltration membrane system. Microfiltration operates by a sieving mechanism driven by gravity through a porous membrane with pore sizes in the range of 0.1-10µm (Sheikholeslami 2007). The CWP's average pore sizes can range up to 3µm, this results in some viruses and bacteria passing through with the permeate and in the case of natural organic matter, specifically humic acids as well as PAH's will pass through the filters pores unless fouling levels increase resulting in pore blocking of the membrane.(Varbanets et al. 2009).

1.2. The Ceramic Water Purifier: Current Practices

The CWP design, developed by Potters for Peace (PfP), a Nicaraguan based non-profit organisation, uses a colloidal silver (Ag) coating supplied by Argenol (Spain), which some factories have recently replaced with silver nitrate ($AgNO_3$).

Recent results obtained from surveying filter factories production methods (Reyner 2009) highlight the diversity shown between filter factories suggesting that despite Potters for Peace's initial training, the long term sustainability of factories is jeopardised where lack of education, supply chains break down and the economy is not is place. It has however been shown that in order to increase the sustainability of a technology an appreciation and understanding of the technology and the scientific and engineering principles behind it preferably with a practical based learning approach is required. This provides the foundation of knowledge, skills and values needed for sustainable development and technology integration (Byars et al. 2009). In the words of E.F.Schaumacher (1973):

"Development does not start with goods; it starts with people and their education, organisation and discipline"

Of the 25 factories interviewed (Reyner 2009) 83% are currently using colloidal Ag and 17% use $AgNO_3$. Of those factories using colloidal Ag, 47% obtain it in its liquid form and 67% in the powdered form. There is also variety not only in the type and suppliers of the colloidal Ag but also in the methods of application as 56% submerge their filters which is recommended by (Oyanedel-Craver and Smith 2008), 33% paint the filters with Ag, whilst 11% bake colloidal Ag into the filter

It is of current concern the lack of data comparing the effects of $AgNO_3$ to colloidal Ag and the concern that Ag both increases the cost of the filter and it not being a local resource in many developing countries makes sourcing it costly and less practical. With the current studies being carried out and focusing on the feasibility of POU drinking water solutions for Sierra Leone, and Sierra Leone having one of the world's largest rutile deposits, investigations are being made to determine the suitability of colloidal TiO_2 as a suitable alternative coating for the CWP.

1.3. Colloidal TiO_2: A water treatment process

A summary report by Malato et al. (2009) shows that TiO_2 has the potential to not only inactivate microorganisms which resisted UV-A radiation but also has the potential to reduce and remove hazardous organic contaminants present in water which can interfere with other water treatment methods and in the case of chlorine form harmful bi-products (Liu et al. 2008). The report concludes that solar TiO_2 photo catalysis is cost-efficient; sustainable; is robust and posses low risk to humans and the environment. In this light experiments to evaluate the potential for TiO_2 photo catalysis to be combined with the CWP to provide a sustainable and low cost solution for POU water treatment in Sierra Leone have been started.

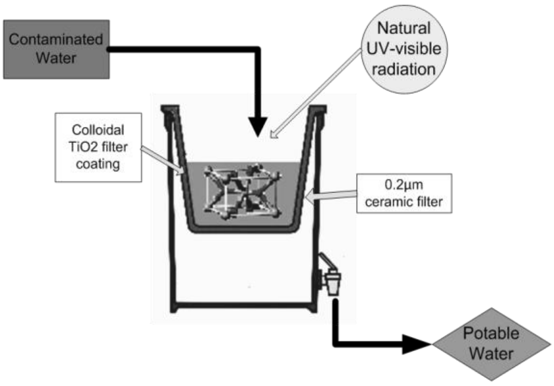

Figure 1: Process Flow Diagram: TiO_2 coated CWP

1.4. A combined approach

Attempts to provide a low cost water treatment solution which helps to build local economies; has low capital costs; employs simple production methods and uses local resources fits Schumacher's definition of intermediate technology (Schumacher 1973) and makes for a sustainable and long term water treatment solution. Figure 1 shows the proposed design combining the CWP with a colloidal TiO_2 coating to achieve a high purity water treatment solution.

The final objectives of this research are: (1) to investigate the efficacy of colloidal TiO_2 as a suitable alternative coating for the CWP for Sierra Leone; (2) to compare and assess the suitability of colloidal TiO_2, colloidal Ag and $AgNO_3$ for use as CWP coatings; (3) to address issues faced in putting the technology into practice particularly with attention to the variation in factory standards and codes of practice in the use of $AgNO_3$ as an alternative CWP coating to colloidal Ag; and (4) to assess issues of filter fouling and the ability of TiO_2 and colloidal Ag play in reducing this.

2. Materials and Methods

TiO_2 (anatase) (Sigma Aldrich, 99.7% purity, <25 nm) used as received. Leonardite humic acid standard (International Humic Substances Society-USA, carboxyl 7.46 mol/kg C, phenolic 2.31 mol/kg C, Log KA1 4.56 and Log KA2 9.72) used as received. Phenanthrene (Acros Organics, purity > 98%) stock solutions prepared in methanol (Sigma Aldrich, HPLC grade). Colloidal Ag (Argenol, Collargol), $AgNO_3$ (Fisher) used as received. Other chemical consumables (Sigma Aldrich and Fisher Scientific, HPLC grade) used as received. All experiments are conducted in high grade glassware. Clay pots supplied by Ceramistas por la Paz, filter factory AquaFiltro, Ciudad Sandino, Nicaragua were used as received (pore size, 0.2 µm). To validate the efficiency of the treatment, environmental water was tested. Water was collected from the River Almond (N 55'58 502''; W 3' 18 177''; Scotland) and characterised for organics (EPA Method 1664).

Batch experiments were conducted in triplicates during 7 days under controlled temperature (26-310C) and pH 7 in presence and absence of: (1) light; (2) TiO_2, 10mg l^{-1}, (3) Leonardite, 40 mg l^{-1}; (4) Phenanthrene, 0.8 mg l^{-1}. As a source of light, a lamp which simulates natural daylight (Arcadia, 18W) was used. 2.5ml samples were collected daily for analysis of phenanthrene, leonardite and pathogens. This was increased to 3ml due to interference of the TiO_2 in the natural river water samples after 66hours. Samples were extracted in hexane to monitor phenanthrene concentration in the organic phase and humic substances concentration in the aqueous phase, using 2.5ml or 3ml hexane respectively at a ratio 1:1 sample: hexane. The extracts were analysed using a Heλios γ UV spectrometer at 254nm wavelength for phenanthrene concentration in the organic phase and humic substances concentration in the aqueous phase. The organic extract was further analysed using high performance liquid chromatography (HPLC, Perkin Elmer) coupled with a diode array detector.

The four untreated filter pots obtained from the AquaFiltro will be applied with a colloidal coating by painting pots, to imitate factory methods, with: (1) TiO_2, (2) colloidal Ag, (3) $AgNO_3$, and (4) blank. Batches of 8L of water will be filtered daily and samples taken to show the ability of the pots to reduce the level of contaminants, humic substances, pathogens and TOC to indicate removal ability and fouling rates of the pots combined with the different coatings.

3. Results and Discussion

Collaboration has been carried out with Potters for Peace and fellow researchers to evaluate current practices in filter factories in order to highlight problems and successes with the current technology and to look for ways to improve the filter design. From correspondence it has been made apparent that several different practices are being used by filter factories and with recent initiatives which have been made to research and improve the current filter design and write up common codes of practice there is still significant variation across the different factories in their use of materials to make the pots and methods of application of the colloidal solutions (Reyner 2009). Whilst material variation is expected depending upon resource availability, research and investigation into the effectiveness and suitability of the selected materials should first be conducted to ensure the standard and quality of water still meets WHO requirements.

The need for use of local skills and materials to provide a sustainable solution has been considered in the selection of materials and design chosen. With Sierra Leone having one of the world's largest rutile deposits TiO_2 is an obvious choice of material for the country compared to colloidal Ag which involves importation and therefore adds a barrier with respect to both the economic and supply chain distribution factors, both of which are key factors to the products successful implementation (Sobsey et al. 2008).

Preliminary results obtained using TiO2 to treat river water in dark conditions are shown in Figures 3 and 4.

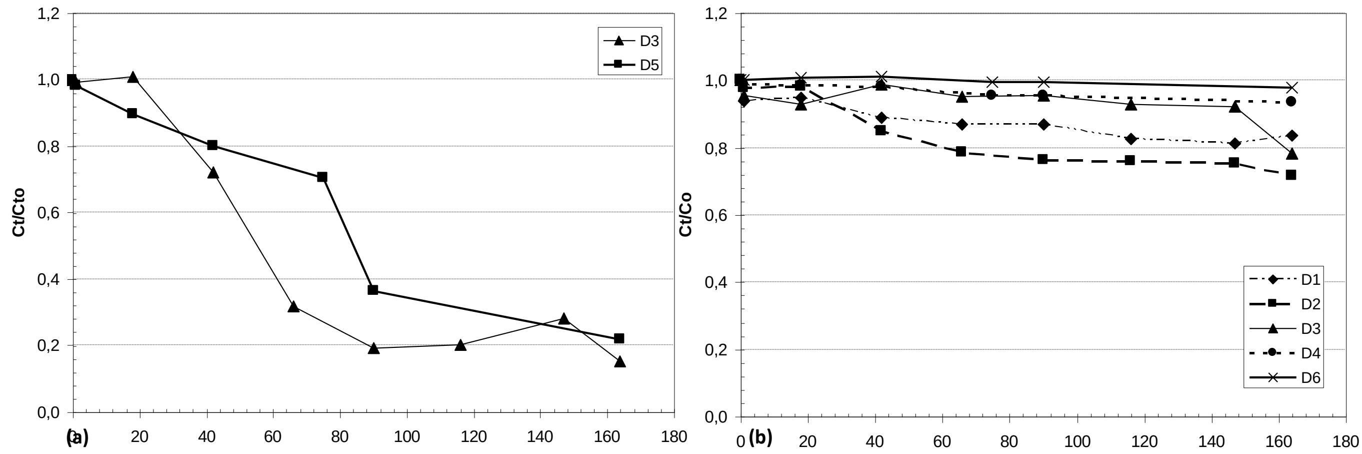

Figure 1: (a) Reduction of humic substances and (b) phenanthrene concentration in solution (as monitored by a UV-Vis Spectrometer) using colloidal TiO_2 in dark conditions (D1: Natural River Water; D2: Natural River Water + TiO_2; D3: Natural River water +TiO_2 + Phenanthracene; D4: Ultra Pure Water + Leonardite + TiO_2; D5: Ultra Pure Water + phenanthracene + TiO_2; D6: Ultra Pure Water + Leonardite; D7: Ultra Pure Water + TiO_2).

Figure 3 (a) shows a reduction in the level of phenanthrene in solutions D3 and D5. D2 and D3 suggest a similar pattern in reduction to that of D4 as shown in fig.3 (b) indicating the presence of humic substances in the natural sample and their removal through the addition of TiO_2.

Figure 4 presents the results obtained from chromatographic analysis which corroborate the results obtained from UV-Vis analysis, demonstrating a clear reduction in phenanthrene concentration in solution during the first 92 hours. Further investigations as to whether natural light will result in a faster removal of PAH's are being carried out.

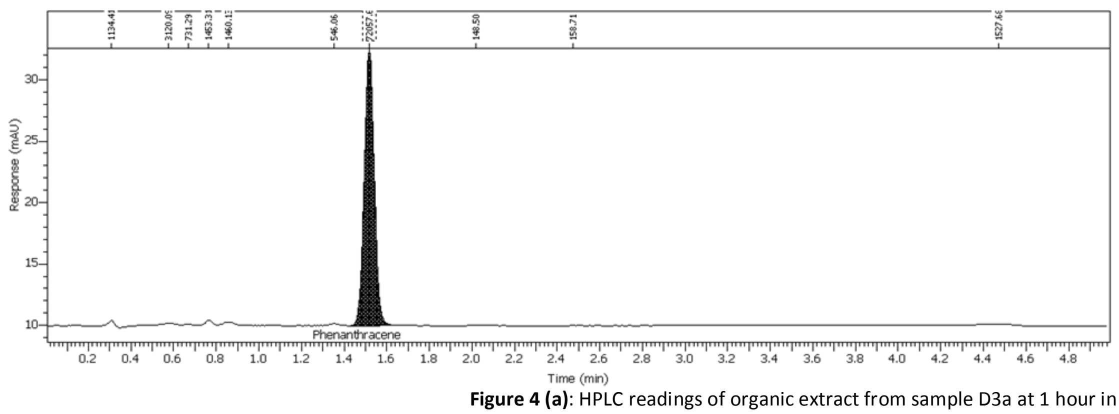

Figure 4 (a): HPLC readings of organic extract from sample D3a at 1 hour in dark conditions

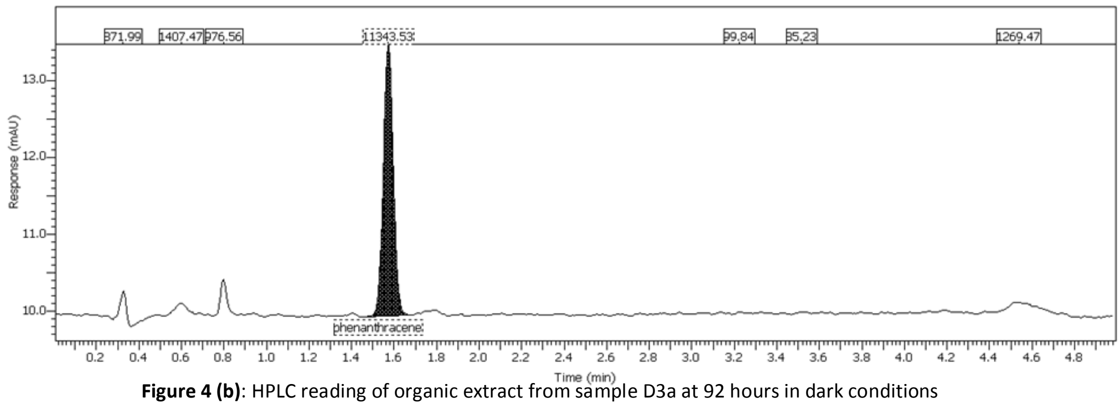

Figure 4 (b): HPLC reading of organic extract from sample D3a at 92 hours in dark conditions

Whilst levels of reduction are not as significant as hoped in the time frame provided it is expected that this will increase with the addition of natural light and even more significantly under UV light. However for the purposes of the application to be combined as a water treatment solution using local resources, natural light is the source present in Sierra Leone.

Recent experiments into the investigation of nanophotocatalyst (Liu et al. 2009) shows that the P-123 functionalized TiO_2 can achieve a 95% reduction in phenanthrene in a 20 minute time period under visible light conditions (λ>420nm) with 40 minutes irradiated stirring before irradiation with a 300W Xenon lamp. Whilst the same time scale may not be able to be achieved with pure TiO_2, if residence times of approximately 1-2 hours could be achieved, then this would allow water a satisfactory contact time in the filter with the flow rate being 2L/hr. Further residence time could be gained by the coating of the ceramic receptacle with TiO_2.

4. Conclusion

Results show similar trends between samples D2 and D4 suggesting a decrease in humic substances present in the natural water samples in the presence of TiO_2. This demonstrates TiO_2's effectiveness at reducing and removing contaminants and humic substances without light.

Reduction in the level of phenanthrene has been observed from both UV-vis absorbance spectra and the HPLC chromatography. Whilst levels of reduction are not as high as hoped for, it is expected that with the addition of natural light that the reaction time will decrease ensuring a more achievable residence time for the CWP as shown by (Liu at al. 2009) then this would confirm the suitability of pure TiO_2 leading to investigations of its performance as a filter coating for porous clay.

At this stage further investigation is still required before a complete conclusion can be reached. With the evidence shown for TiO_2's ability to reduce the level of phenanthrene and leonardite indicating the presence of PAH's and humic acids shows that it will not only have the potential to provide microbiological reduction but also has the added benefit of providing a means to reduce levels of natural organic matter (NOM) preventing harmful bi-products forming and ensuing the processed water is of potable standard. With the correct implementation through investigation of low cost materials; local resources and ensuring education and appreciation of the technology both for the manufacturers as well as for the customers it has the potential to be a powerful tool in treating water for Sierra Leone providing not only health benefits but also with the potential to enhance local economies and social structures.

Further investigation will be conducted into:

- The impact of natural light on TiO_2 efficiency.
- The efficacy of colloidal Ag to treat pathogens and humic substances.
- The performance of the pots when coated with TiO_2, colloidal Ag and $AgNO_3$ to remove contaminants, humic substances and pathogens.
- The local needs in Sierra Leone for successful implementation of the CWP.

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