Fabrication of Microporous Water Filter Using Titanium Dioxide Particles, Silica Particles, and Polyethylene Glycol

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Abstract. We report the fabrication of microporous filter for use in filtering both inorganic and organic substances from liquid materials. Titania (TiO_2) anatase was used as the main material for this filter. Polyethylene glycol (PEG) with average molecular weight of 20,000 was also used as additive to control the formation of pores, especially pore sizes. The mixture of titania and PEG was pressed into cylindrical tablet shape at room temperature and then simply heated inside a furnace up to temperature where the PEG decomposed into gas to leave only connected titania particles. The use of titania as base material for the filter allows the organic substances that trapped inside the filter pores to be easily removed by heating up the used filter at above decomposition temperature of the trapped organics. We also made other filter by adding small amount of silica (SiO_2) particles to reduce the size of the pores as well as to improve the mechanical strength. We observed that filters containing silica particles, with smaller in size compared to titania, resulted in better mechanical strength, smaller in pore sizes and better filtering results in term of turbidity and dissolved oxygen (DO) content. This method is potential for development of larger scale and cheaper water filters for use in various applications.

Keywords: *microporous-sized filter; titania; water filter.*

1 Introduction

Water is one of basic needs which unreplaceable by any other materials. In some countries or regions, people are still using soil water from the well to fulfill their daily needs or using tap water in their houses. However, these water sources have their own problems. For example, soil water could be contaminated with *E.coli* bacteria and tap water pipes might be leak to permit the water contaminated with bacteria on their way to houses. Indeed, contaminated drinking water is still a cause of major outbreaks of diarrheal diseases not only in developing but also in developed countries [1,2].

Drinking water quality could have a big impact on someone's health in the future. For people who have a well in their houses, they usually get their

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drinking water by simply boiling the water for several minutes. In fact, micro sized organic materials might still exist inside the boiled water and occasionally cannot be removed from the water just by that simple heating. These organic materials could cause negative effects to people's health. Therefore, before boiling the water, it is important to make sure that the water is free from microorganism.

Filtration is a mechanical or physical operation to separate solids from fluids (liquids or gases) by giving a medium to allow the fluid to flow through but the solids in the fluid are trapped in the medium [3]. However, the separation of solids and fluids depends on the size of the pores, the thickness of the filter medium, and the mechanisms that occur during filtration.

Some people use water filter to improve their water quality. There are so many water filters released in the market. In general, those filters are used to filter microorganism like *E.coli* bacteria to improve the water quality. In the medical world, water filter are used to produce sterile water for use in washing the surgical tools. Most water filters in the market are not reusable and cannot be used for long term activities. Having used for several times, the waste might stuck inside the filter and sometimes it is difficult to clean manually. Researchers in Germany have proven that most of water filters in the market, with plastic as its main material, are not safe for use for more than a week [4]. They even found that the total bacterial counts in filtered water (using commercial filters) in around 64% of households were higher than the count in tap water of the same household. The filtered waters were contaminated with bacteria, fungi and moulds. Those microorganisms could grow in water, and in 5 of 13 tested filter materials, the contamination can reach up to 2,000 mould colonies in each water container. Therefore, to ensure the water filtration is clean, people must replace water filter within less than one week.

Titania is a semiconductor materials having relatively large optical band gap. It meets very wide application area such as in cosmetics, sunscreen, painting materials, coating materials, solar cells, and photocatalysts for decomposition of organic pollutants in water or air. Titania is also used as reinforced fillers in composite materials and as filler in polymer electrolyte nanocomposites for improving the ionic conductivity. Titania is available in markets at relatively low price. Most titania materials sold in market are in the form of powder at various particle sizes.

From geometrical point of view, arrangement of spherical or spherical-like particles always result in pores between particles. It is impossible to fully fill a certain space with particles without leaving pores. The size of the pores between particles might be smaller than the particle size, depends on the structure of particle arrangement. As illustrated in Figure 1, ideal arrangement in **a** (triangle or hexagonal) and **b** (cubic) produce small pores, while in **c** (random arrangement) produces larger pores. Porosity of material is defined by the ratio of pores volume to the total volume of space occupied by material. Porous materials are candidate for developing filter, either for liquids or solids. Since the pore sizes in materials made by compacting particles depend on the particle size, the development of filter using particles as a source material permits to control the pore sizes by just using particles of different sizes. In addition, using inorganic materials such as titania as source material, instead of organic materials such as membrane, permit to develop reusable filters, where contaminated filter can be used again by just heating it at a certain temperature to decompose trapped organic waste.

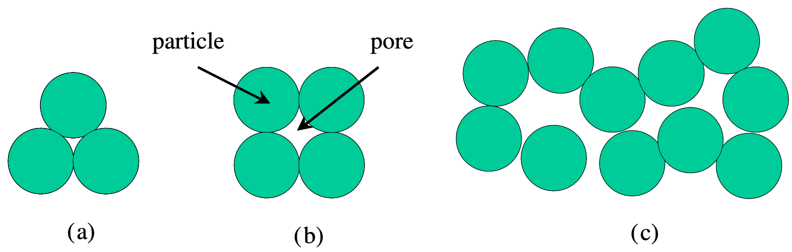

Figure 1 Compacting of spherical or spherical-like particles always result pores between them: (a) ideal arrangement in triangle or hexagonal, (b) ideal arrangement in cubic and (c) random arrangement.

In this paper, we report the development of reusable water filter using titania as the source material. Many authors have reported the use of titania as filter or photocatalyst materials either in dense or porous structures [5-10]. To the best of our knowledge, there is no report on the preparation of porous tinania for use as filter using a simple pressing and simple heating method using titania powder as precursor. This method is potential for development of large scale titania-based filters. Some reported methods such as dip-coating [6], sol-gel [7], and aerosol templating [9] are generally time consuming and difficult to be extended into mass production.

Even though applications for titania are limited by its relatively poor mechanical properties, we could use it as a cleanable filter by creating porous inside a pressed titania powder. In addition, the photocatalytic activity of titania is potential for exhibiting self cleaning and disinfecting properties under exposure to UV or visible radiation. The photocatalytic mechanism is simply illustrated in Figure 2.

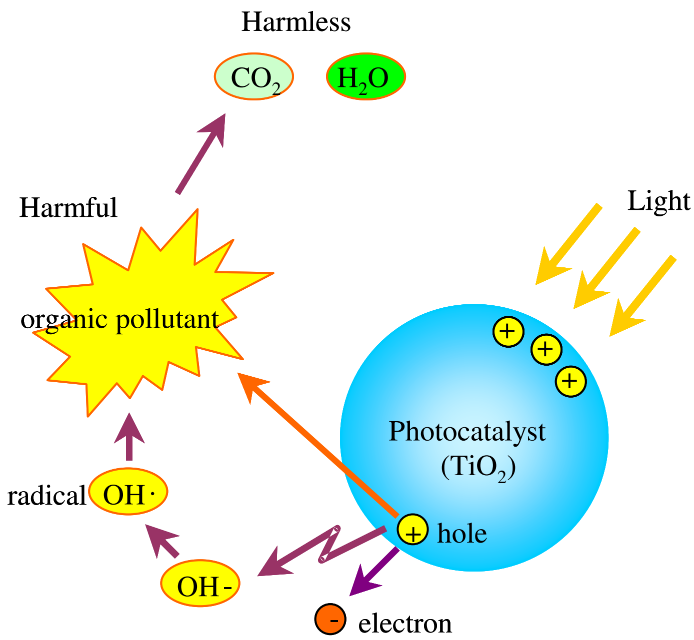

Figure 2 Photocatalytic process using titania particles.

When titania particles are irradiated with light of energy greater than their energy band gaps, electrons and holes are produced in the conduction and valence bands, respectively. These electrons and holes have high reductive potential reactions on the surfaces so that photocatalytic reactions are induced. In the presence of O_2 and H_2O, the photo-formed electrons and holes easily react with molecules on the titania surfaces to produce O^{2-} and OH radicals, respectively. These O^{2-} and OH radicals have very high oxidation potential, induced the complete oxidation reaction of various organic compounds such as toxic halogen [11]. Various reaction steps can be illustrated as following

$$TiO_2 + hv \rightarrow TiO_2(h^*_{vb} + e^-_{cb})$$

$$TiO_2(e^-_{cb}) + O_2 \rightarrow TiO_2 + O^{2-}$$

$$TiO_2(h^*_{vb}) + H_2O_{ad} \rightarrow TiO_2 + OH^-_{ad} + H^+$$

$$TiO_2(h^*_{vb}) + (\text{organic compounds})_{ad} \rightarrow TiO_2 + H_2O + CO_2$$

Such high photocatalytic reactivities of photo-formed electrons and holes can be expected to induce various catalytic reactions to remove toxic compounds and can usually be applied for reduction or elimination of polluted compounds in air such as NO_x, cigarette smokes as well as oxidizing them into CO_2. In water, such toxins as chloroalkenes, specifically trichloroethene and tetrachloroethene as well as dioxin can be completely degraded into CO_2 and H_2O. These properties make the material a candidate for sanitary applications.

The focus in this report is the production of porous filter using titania as a base material and testing the filtration process for polluted waters. Photocatalytic properties will be investigated in our next works.

2 Experiment

In this experiment, we used a simple mixing, pressing, and simple heating method to create the micro porous filter. From this method, we finally achieve the best result in creating titania water filter. The schematic of the method of synthesis is shown in Figure 3.

The form of all the three material used in experiment are in the powder form. Titania and PEG are mixed by hand shaking for several minutes until we the titania powder were fully covered by PEG (homogeneous mixture). The heating temperatures to ensure slow decomposition of PEG inside the sample are about 100 ^oC to 200 ^oC since PEG powders evaporate at temperatures 120 ^oC to 180 ^oC. After achieving a perfect mixing (based on the eye viewing), the mixture was then pressed into a cylindrical-shaped tablet. Other filter was made by adding a small amount of silica particles in the mixture of titania and PEG. After achieving a perfect mixing of titania and PEG, silica particles powder was added, followed by mixing and shaken for several minutes until silica particles looks disappeared inside the mixture. The next step was pressing the mixture to form a cylindrical-shaped tablet using a handy pressing machine. No control of the pressure was made at this time because the pressing machine was not equipped with a pressure or load indicator.

After the pressing process, the material was then heated up to 1000 ^oC to increase the bond's strength between titania particles and to decompose PEG. The final filter materials then consisted only titania and silica particles. The role of PEG was just to control the pore size during formation of filter materials. Silica particles, due to smaller in size, increased the number of "contact hands" belongs to tinania particles so that improved the strength of materials, compared to when using only titania for making filter.

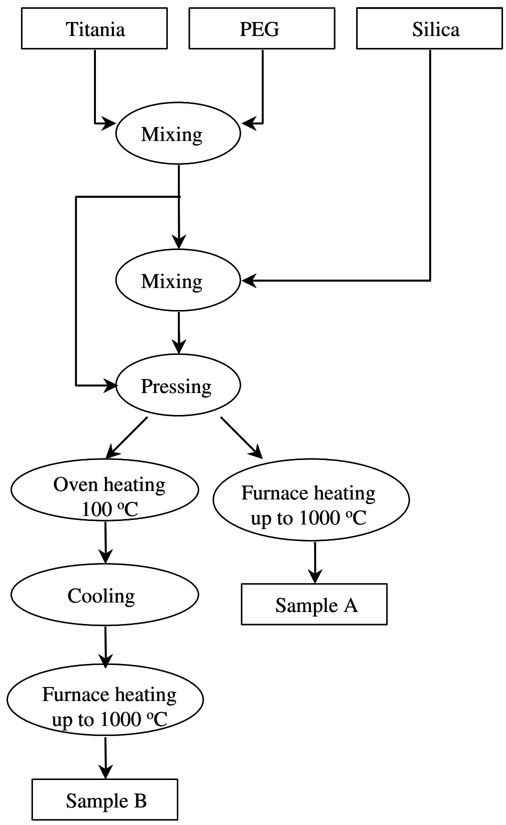

Figure 3 Schematic of synthesis of titania-based microporous filter.

In this experiment, we performed two methods of heating. In the first method, the pressed material is directly heated inside a furnace in a low temperature for several minutes. We did this step to allow the titania particles bond stronger before decomposition of the PEG. After that, the material was heated at a high temperature for several hours to maximize bond strength between titania particles and to decompose PEG. This process must occur slowly to allow the PEG did not decompose suddenly so that the bond between titania particle would not damaged and broken. In the second method, the pressed material was heated inside a kitchen oven, instead of a furnace, at 100 °C for about two hours. After that, we moved the material into the furnace to be heated just like in the first method.

The morphologies of the material were characterized using a scanning electron microscopy (SEM JEOL JSM-6360 LA). The filtering properties of the material were tested using soil water and textile waste. The visible appearance of the material was taken using a digital camera. The DO parameter was determined using a Winkler titration method using solutions of $Na_2S_2O_3$, NaOH, KI, and $MnSO_4$, and suspension of starch.

3 Results and Discussion

After performing two different heating methods, we obtained materials with different strength. We assigned material that has been treated with the first heating method as material A and that with the second heating method as material B. From pictures in Figure 4 we can see clearly that material B looks more solid than material A. Even though we have not comprehensively tested the mechanical strength of the materials, we believe that material B is stronger than material A by performing a simple pressing test. Material B could support load up to 2.5 kg without breakage, while material A could only support up to 0.5 kg. This result is very important, since strong material (such as material B) could handle a pressure from the tap water [12].

Adding silica particles powder as filler resulted in a stronger material having smaller pore sizes. To compare the morphology result, both materials prepared with and without silica particles powder were characterized with a SEM. Figure 5 shows samples prepared without silica powder (a) and with silica powder (b). Figure 6 is the same pictures at high magnification. Without silica powder the resulted material looks brittle. Material prepared without silica has bigger pores (> 0.5 μm in size) and less contact between titania particles, while material prepared with silica has smaller pores (might be less than 0.1 μm in size) and better contacts between particles were observed. By comparing Figures 5(a) and (b) or Figures 6(a) and (b), it is clear that the average sizes in Figures 5(b) or 6(b) are smaller that the corresponding pictures in Figures 5(a) and 6(a). It indicated that the sizes of silica particles are smaller than titania particles. Due to small in size of silica compared to titania, the silica particles filled big pores between titania particles to create new pores having smaller sizes. At present we were unable to measure the pore size using commonly known methods, such as Brunauer-Emmet-Teller (BET) method, because of unavailability of the equipment. However, from SEM pictures in Figure 6 we can deduce the size of the pores is in submicrometers.

Figure 4 Pictures of materials (a) A and (b) B taken with a digital camera.

After optimizing the preparation method, the filter material was then used to filter a soil water. For a better comparison, we used more than one filter materials that have been synthesized at different compositions. We made various filter by varying the mass fraction of titania and PEG as well as with and without adding silica particles powder. Before performing process of filtration, we inspect how fast clean water could flow through the filter materials. Table 1 shows the comparison of flow rate of clean water through the filters. Each filter was tested four times. The highest flow rate was obtained at filter prepared at tinania:PEG = 6:4 w/w and the slowest was observed at filter prepared at tinania:PEG = 7:3 w/w + silica particles. These results are acceptable since the first filter has the largest pore size while the last filter has smallest pore sizes.

Table 1 Comparison of flow rate of clean water at different filters.

	Flow rate (ml/s) of clean water at different filters		
	Titania/PEG = 6:4 w/w	**Titania/PEG = 7:3 w/w**	**Titania/PEG = 7:3 w/w + silica particles**
Test 1	8.3	3.7	2.7
Test 2	9.1	4.9	3.0
Test 3	15.0	5.0	3.0
Test 4	15.0	5.0	3.0

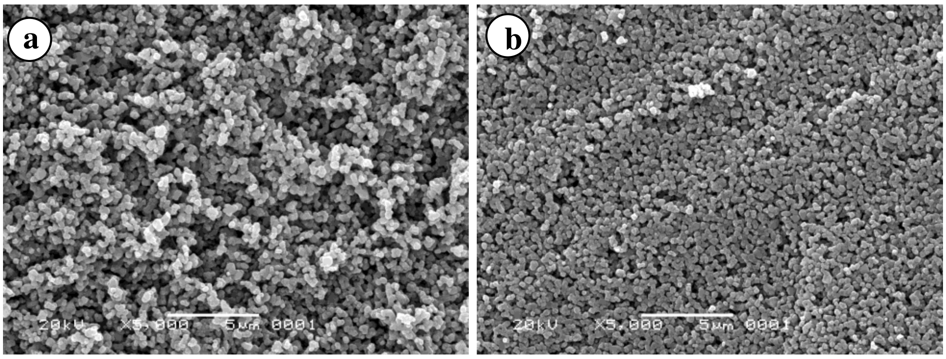

Figure 5 SEM images of filters: (a) prepared without addition of silica particles and (b) with addition of silica particles. The length of scale bar is 5 µm.

After performing a filtration process on the soil water we observed the turbidity of the soil water decreased. The best result of decreasing the turbidity as found when filtering the soil water with titania:PEG = 7:3 + silica particles filter. Figure 7 shows the picture of soil water before filtering and after filtering with the titania:PEG = 7:3 + silica particles filter.

In addition to filtrating the soil water, we also used the material to filter textile waste. The DO of the waste was measured before and after filtration process. Since filter material resulting in the best reduction of turbidity of the soil water was tinania:PEG = 7:3 + silica particles, we used this material to filter textile waste. We found the DO of the textile waste before the filtration was 0.8. After filtration, the DO increased to 3.8, i.e., the increasing up to 480% from the value before filtration.

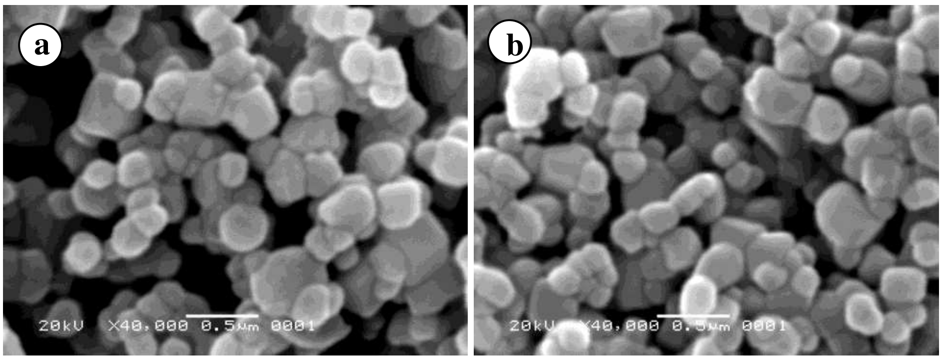

Figure 6 SEM images of filters at higher magnification: (a) prepared without addition of silica particles and (b) with addition of silica particles. The length of scale bar is 0.5 mm.

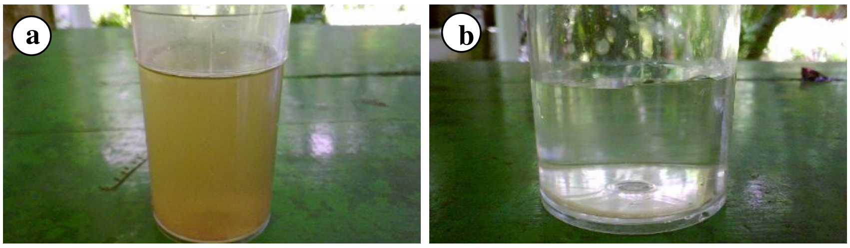

Figure 7 Pictures of soil water: (a) before filtering process and (b) after filtering with the titania:PEG = 7:3 + silica particles filter.

We have mentioned that a reusable filter than can avoid the growth of bacteria inside the filter is necessary. By using titania as the main material, this filter can be cleaned by heating it up in the furnace. Having used the material to filter toxic waste, the material was heated up to 400 ^{o}C for about 15 minutes inside furnace. As shown in Figure 8, after heating process, organic materials that trapped inside the filter has disappear from the filter due to burning process.

The more we add PEG powder to the mixture, the more porosity we can get from the filter material. However, bigger porosity means bigger microorganism could pass the filter. Therefore we have to optimize the speed of water flow inside the filter material and the pore sizes. To get a better result, we have made four filters at different titania and PEG fraction, i.e. titania:PEG = 6:4 w/w, 7:3 w/w, 8:2 w/w and 9:2 w/w. After checking the water flow rate, the 8:2 w/w and 9:1 w/w filters cannot filter 30 ml of clean water below one minute and the 6:4 w/w filter did not show a satisfying result when filtering soil water. So the best composition was the 7:3 w/w filter since it had a strong particle bond to handle water flow.

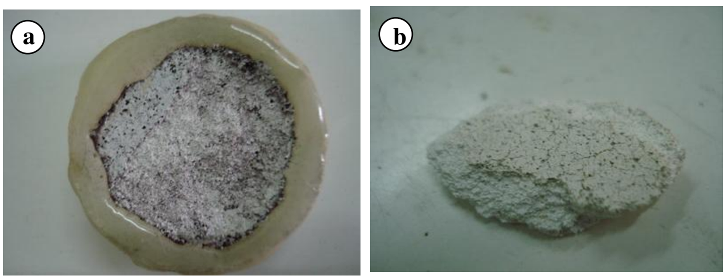

Figure 8 Pictures of titania filters (a) after filtering textile waste and (b) after heated at 400 ^{o}C.

Silica particles powder plays a role as filler to the material. By adding silica particles powder, the material became more solid because silica particles could fill large pores between titania particles. The mass fraction of silica particles added to the mixture was silica particles mass:titania mass = 0.1:5 g/g. Adding silica particles fraction below 0.1:5 g/g produced no effect on the filtration. It is proven by filtrating soil water that using filter containing silica particles mass fraction of less than 0.1:5 g/g resulted in similar result with filtering soil water using filter made without silica particles. On the other had, adding silica particles fraction above 0.1:5 g/g greatly reduced the speed of water flow through the filter.

Silica particles could prevent particle movement in titania material in course of water flow. If silica particles did not perfectly mix in the suspension, silica particles function as filler will not work well when the material used to filtering water. We found that in textile waste filtration, result of the DO from filter with perfect mix is 3.77, i.e. better than filter without perfect mix of 2.91. Without adding silica particles, filter material became brittle after several time used to filter soil water. This happen because the bond between titania particle were not strong enough to handle the flow of water through it. Simple testing was also made to prove the improvement of filter strength when adding silica particles. After performing 10 times of filtration process, a filter containing titania only was about to break, while a filter containing titania and silica was still in good condition.

We have tested that titania water filter filtration could purify soil water, but the same process could not happen with textile waste water. Even though the textile waste turbidity did decrease, but the final result was not as clear as soil water filtration result. However this filter could increase the DO value of the textile waste. Titania ability as a photocatalyst to disinfecting properties under exposure to UV radiation could not effectively applied here because the disinfecting process occur in about 5 to 6 hour.

We also determined the porosities of filters by a simple method. The volumes and masses of the filter were measured. Based on the measured masses of the filters and the theoretical masses when the materials were dense titania (using titania mass density of 4.23 g/cm^3), the porosity can be calculated using a formula porosity = (theoretical mass – measured mass)/theoretical mass. The porosities of filters made at different compositions of titatia and PEG are listed in Table. 2

Table 2 Porosities of filters made at different compositions of titatia and PEG

Titania/PEG (g/g)	**Porosity (%)**
6:4	75.8
7:3	71.7
8:2	68.1
9:1	55

Darcy's law is frequently used to explain the transport of single phase fluids flow in microscopically disordered and macroscopically homogeneous porous materials [13-15]. It is simply assumed that the global permeability κ relates the average fluid velocity v through the pores with the pressure drop ΔP measured across the system via a relation $v = -\kappa\Delta P / \mu\Delta L$, with ΔL the length of the sample in the flow direction and μ is the viscosity of fluid. Multiplying both sides with fluid density and defining $J = \rho v$, as the amount of mass flow per unit time per unit area, we have $J = -\rho\kappa\Delta P / \mu\Delta L$. This equation is similar to electric current equation, $J = I/A = \sigma(\Delta V/\Delta L)$, with I the electric current, A the cross section, and ΔV the potential different between two cross sections separated by a distance ΔL, and σ the electrical conductivity. The factor $\rho\kappa / \mu$ plays similar role with σ in the electric current flow. This similarity allows the adoption of equation that explains the effective conductivity in a conductive fillers/insulating matrix composite to be used for calculating the effective permeability of porous materials [16-18].

The effective permeability, κ, of the filter can be expressed by the following relation [19]:

$$\kappa = (W_g^*)^{1+1/D}\kappa_1 + (1 - W_g^*)\kappa_e^*, \tag{1}$$

where

$$W_g^* = \phi W_g, \tag{2}$$

$$W_g = 1 - \frac{(1-\phi)^2 \beta^*}{(1-\beta^*)^2 \phi}, \tag{3}$$

β^* is the smallest root of equation

$$\phi(1-\phi)^{n-2} = \beta^*(1-\beta^*)^{n-2}, \tag{4}$$

ϕ is the porosity, κ_1 is the permeability of empty space, κ_e^* is the solution of the following equation,

$$\phi(1-W_g)\frac{\kappa_1 - \kappa_e^*}{\kappa_1 + (n/2-1)\kappa_e^*} + (1-\phi)\frac{\kappa_2 - \kappa_e^*}{\kappa_2 + (n/2-1)\kappa_e^*} = 0, \tag{5}$$

κ_2 is the permeability of solid material, n is the effective number of "contact hands" between particles, and D is the fractal dimension. Equations (1)–(5) have been successfully used to explain the effect of porosity on the liquid permeability of holocene and pleistone basaltic andesite in the Oregon Cascades containing different pore sizes reported by Saar and Manga [20].

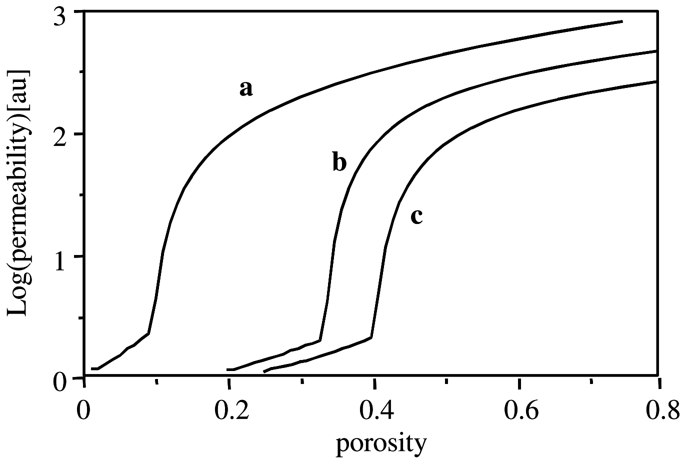

Figure 9 Effect of porosity on the permeability of porous materials. Calculation was performed using **a**: (n =12, κ_1/κ_2 = 1000 for left curve), **b**: (n = 4, κ_1/κ_2 = 800 for middle curve), and **c**: (n = 3.5, κ_1/κ_2 = 500 for right curve). The fractal dimension of porous filters were assumed to be D = 2.5.

Figure 9 is example of effect of porosity on the permeability of porous materials. Calculation was performed using **a**: (n = 12, κ_1/κ_2 = 1000 for left curve), **b**: (n = 4, κ_1/κ_2 = 800 for middle curve), and **c**: (n = 3.5, κ_1/κ_2 = 500 for right curve). The fractal dimension of gels were assumed to be D = 2.5.

4 Conclusion

Material mixing when creating water filter with this method must be perfect, in order to get maximum result in filtrating the water. Before heating up the filter material to decompose PEG, the bond between titania particles must be strong enough to prevent from breaking. The best titania:PEG fraction was found 7:3 w/w with addition of silica particles mass fraction (relative to titania mass) of 0.1:5 g/g. At this fraction the filter could filtrate 30 ml soil water into clean water within ten seconds and increased dissolve oxygen rate about 480% in a textile waste. With 1.5 – 2 μm porosity, microorganism filtration is possible and bacteria growth inside the filter could be avoided because the filter in cleanable by heating process.

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