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The removal of copper in water using manganese activated saturated and unsaturated sand filters

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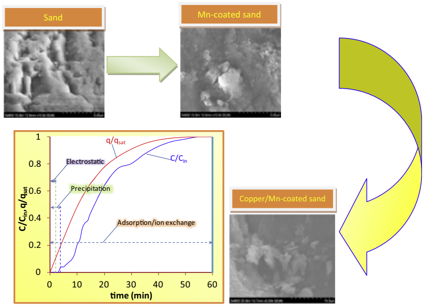
HIGHLIGHTS

- ▶ Copper is widely distributed in the environment and can have several health effects.
- ▶ Activated unsaturated sand filter was effective for Fe and Mn but not studied for Cu.
- ▶ AUSF was indeed found effective for removing copper from water.
- ▶ Removal mechanisms were suggested and supported by experiments.

GRAPHICAL ABSTRACT



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ABSTRACT

Activated unsaturated sand filter (AUSF) is one among the few of the filtration technologies utilised to treat metal bearing waters. AUSF utilises activated sand as its filter media and operates under naturally flowing air to ensure unsaturated condition. In this study, manganese-activated sand was used for the removal of copper. Activation of the sand increased its BET surface area by 21% at 0.071 mg Mn/g sand and Mn leaching was significant only at pH < 4.5. SEM/EDS showed clusters of crystalline manganese oxides coating the sand surface and newborn copper hydroxides occupying sand surface after exposure to copper-bearing-water. A tracer study revealed that the gas voidage in the filter increased from 0.143 to 0.294 as the water flow rate reduced from 74.4 to 16.4 mL/min, which ensured better water aeration and increased copper removal. The ratio of manganese to sand was a key parameter as it increased almost exponentially the removal capacity of the AUSF. On the other hand, copper removal increased linearly with the inverse of the sand particle size, which indicates the importance of the surface area in the process. However, unexpectedly, when the inlet copper concentration increased from 3 to 20 mg/L, the filter capacity reduced by about 50% from 0.020 to 0.011 mg Cu/g sand. Based on the results obtained, mechanisms by which copper was removed in AUSF were proposed and they were found to vary as function of time [electrostatic attraction ($t < 2$ min); precipitation ($t < 3.8$ min), and adsorption/ion exchange ($t < 60$ min)].

1. Introduction

Several research studies have demonstrated the presence of high concentrations of heavy metals in ground waters [1] and surface waters [2,3]. Heavy metals are not biodegradable and tend to accumulate in living organisms causing several health effects. For instance the presence of copper in water can cause vomiting, diarrhea, stomach cramps, nausea, greenish or bluish stools and saliva and may have severe effect in the brain and liver of people with Wilson's disease [4,5]. Elevated intake of Cu may cause liver and kidney damage, and sometimes death, particularly in children [4,6,7]. Copper reaches water supplies through discharges from anthropogenic activities such as mining and smelting, industrial activities, municipal wastes and sewage sludge [4,6–8] and also from natural sources such as sea salt sprays, windblown dusts,

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volcanogenic particles and decaying vegetations [4]. The removal of copper from water is hence very important in order to protect water supplies and human health.

Precipitation followed by filtration tends to be the most common technique used due to its simplicity [9]. Essentially, precipitation involves changing the dissolved metal ions into insoluble solid state species by a chemical reaction with a precipitant such as alkali or sulphide. It is common that the insoluble solids are removed by filtration, which involves fully submerged filter media in water [10,11]. Integration of the two steps (i.e. precipitation reaction and filtration) in one step seems beneficial. To this end, this can be achieved by filtration on reactive media and such technique is termed as activated unsaturated sand filter (AUSF), which was first studied by Paramarta et al. [12] for the removal of iron and manganese. Basically AUSF is an activated granular filter media (e.g. sand) operating under unsaturated conditions (i.e. water does not fully occupy all the filter pores). The activation of the media can be done by $KMnO_4$ solutions and previous studies have shown that this technique leads to faster reaction rates of metals removal [13–15]. Moreover, the presence of water-free pores in the filter aerates the water which also promotes the chemical reactions in solution [12]. Solid metal species formed as a result of the precipitation reaction precipitate and are removed on the same filter media. Since this treatment technique combines both precipitation and filtration processes in a single unit, it offers the advantage of not requiring a separate sedimentation unit. AUSF was found an effective alternative for treating iron and manganese from water and was able to achieve concentrations that met for example the Indonesian water standards (Fe: 0.3 mg/L, Mn: 0.1 mg/L) or even below. Besides, AUSF costs were significantly low as compared to those reported by the Indonesian water utility [12,16].

Despite the fact that AUSF technique was efficient to remove Fe and Mn, currently there are only a very limited number of research studies on AUSF removal of other metals and this study is the first of its kind to investigate copper removal from water in AUSF. The performance of AUSF in removing copper at different operating conditions was hence investigated in this study. In addition, the hydraulic performance of AUSF using tracer studies and characterisation of the activated sand were made. Suitable mechanisms for copper removal supported by experimental results were also suggested in this study.

2. Materials and methods

All chemicals were purchased from Fisher Scientific, UK, and were of reagent grade. Water solutions containing copper ions (Cu^{2+}) were prepared from copper nitrate ($Cu\ (NO_3)_2{\cdot}3H_2O$). All aqueous solutions were prepared in Milli-Q water (Q-H_2O, Millipore Corp. with resistivity of 18.2 MΩ cm). All solutions were prepared at initial pH and copper concentrations so that the solubility product of the copper hydroxide ($K_{sp} = 2.35 \times 10^{-20}$ at 20 °C) was not exceeded to avoid precipitation. The filter media used in this research was natural, uncrushed silica sand fractions B (1.18 mm–600 μm) and C (600 μm–300 μm) (standard sand BS 1881–131:1998 from David Ball Specialist Sand, UK).

2.1. Activated sand preparation

First, the sand was sieved to a 0.850 mm diameter fraction using Russell Sieve (Russell Finex, Model 17300). Then the activated sand was produced by drying the sieved sand at 105 °C in an oven for about 12 h then soaked with $KMnO_4$ 0.01 N for about 24 h and washed with water before being dried again at 105 °C in an oven for about 12 h [16,17]. The activated sand was then cooled to room temperature and stored in plastic containers before being used in the experiments. The mass of manganese that effectively coated the sand per unit mass of sand, γ_{Mn}, was determined by nitric acid digestion using the US EPA method EPA 3050B.

2.2. Analytical

Copper concentrations were analysed using Bicinchoninate method (Hach method 8506: spectrophotometer DR-2400, CuVer® 1 Copper Reagent Powder Pillow, concentration range 0.04–5.00 mg/L, wavelength range 400–880 nm, Automatic Wavelength Selection), which is approved by the US Environmental Protection Agency. Samples at higher concentrations than the method range were diluted before analysis. In this method, the copper is determined by the reaction with a salt of bicinchoninic acid (2,2-biquinoline-4,4-dicarboxylic acid) contained in CuVer® 1 reagent to form a purple coloured complex in proportion to the copper concentration. The coloured complex is then measured by the spectrophotometer (Hach DR-2400). The accuracy of the method was also checked with a Varian 240FS AAS and the correlation factor R^2 was 0.9904. HNO_3 (10%) was added to the sample solutions to reduce the pH to less than 6 in order to stabilise the metal ion and prevent precipitation.

Point of zero charge of the activated sand was determined by the mass titration method [18]. Briefly, the method involved adding certain masses of sand (0.01%, 0.1%, 1%, 5%, 10%, 20%, 30%, 40%, 50% and 60%) to Milli-Q water in a beaker. This beaker was sealed and placed on a shaker for 24 h. The resulting pH values were measured at the end of the experiment. Acid and alkali resistance tests were also carried out by soaking the manganese-coated sand in Milli-Q water at room temperature for 24 h at pH values adjusted in the range 2–11 ± 0.1 using HNO_3 and NaOH [19].

The activated sand was also characterised using photomicrography of its exterior surface acquired by Scanning Electron Microscope (SEM) (Hitachi S-4800, Oxford Instruments). The distribution of elemental concentrations for the sand samples was investigated using the mapping analysis of SEM/Energy Dispersive X-ray Spectroscopy (EDS). Samples for SEM/EDS were placed on a circular carbon film (9 mm diameter) and/or a quick drying silver paint (Agar G302, Agar Scientific, UK) to avoid influence of any charge effect and sample movement during the SEM operation. In addition, the surface area of the prepared sand was determined by the Brunauer, Emmet, Teller (BET) method using nitrogen adsorption at 77.3 K technique (NOVA 2000e Surface Area & Pore Analyzer).

2.3. Activated sand filter

A schematic diagram of the activated sand filter is depicted in Fig. 1. The filter used in this research was made of a QVF glass col-

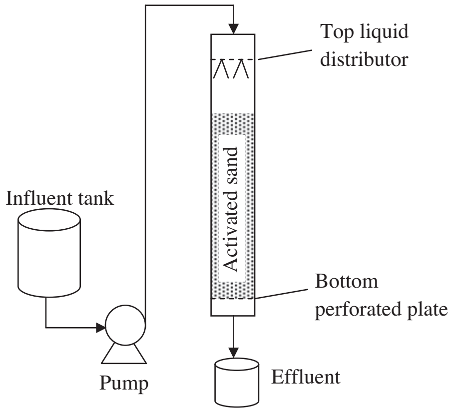

Fig. 1. Schematic diagram of the AUSF.