# Metals Removal from Shallow Groundwater Using Simple and Low-Cost Technique

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## ABSTRACT

This work was motivated by the need to develop a simple and low cost technique for the removal of trace metals from shallow groundwater in various parts of Egypt. The technique uses Clay Pots filled with locally available materials such as charcoal, cast iron turnings and sand. This work is a scientific appraisal of the 3-Clay Pots method (Khan et.al., 2000) for the purification of water and its viability in Egypt. To evaluate the method various water chemical parameters such as Electrical conductivity (EC) and pH were measured. The water quality was further investigated by measuring the concentrations of trace metals and other major cations using the ICP-OES. The complete conversion of $Fe^0$ to nonmagnetic Hydrous Ferric Oxide (HFO) as the most active component for metal removal is indicative of an oxidizing environment that is sustained by continuous diffusion of air through the porous clay pots. All parameters indicated that the resulted water quality meets and exceeds USEPA, WHO, and Egyptian standards for drinking water.

## INTRODUCTION

The purification of drinking well water from trace metals naturally found in shallow wells extracted by hand pump is of great concerns. This water might be used for drinking purposes in some parts of Egypt. An array of methods and technologies are available for the purification of water from trace metal contaminants (EPA, 1999). These are coagulation- filtration, lime softening, activated alumina, ion exchange, reverse osmosis, electrodialysis, nanofiltration and in-situ treatment of well water (Rott, et. al., 1993). A simple and low cost filtration system was tested for its efficiency in removing arsenic, other trace metals and anions from the groundwater in Bangladesh and known as '3-Kolshi method'(Khan et.al., 2000). Such method was tested for its efficiency in removing metals and other impurities from the shallow groundwater in some rural areas of Egypt.

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## EXPERIMENTAL WORK

The filtration system described here consists of three fired unglazed clay pots used as a reservoir for drinking and cooking water. Figure 1, shows the schematic diagram of this filtration system. The pots (top A, middle B, and bottom C) are placed on top of each other in a steel or bamboo frame for ease of maintenance. Each pot has a volume of about 18 liters. The top and middle pots are perforated with small holes (~0.5 cm diameter), and covered with pieces of synthetic (polyester) material from inside The middle Pot was then filled with 2 kg sand, 1 kg wood charcoal (1 cm$^3$ pieces) .The top Pot has 3-kg of cast iron turnings and 2 kg of coarse sand on top of the iron turnings. All the filling materials are pre-cleaned to completely remove dust and dirt before the filtration system is assembled. Water is slowly fed to the top Pot and collected at the bottom pot. The efficiency of the filtration system was tested after discarding the initial 3-4 batches (10-1, each) of water. Washing the filtration system with 4L of hot water cycle each week keeps the filtered water free of pathogenic loads
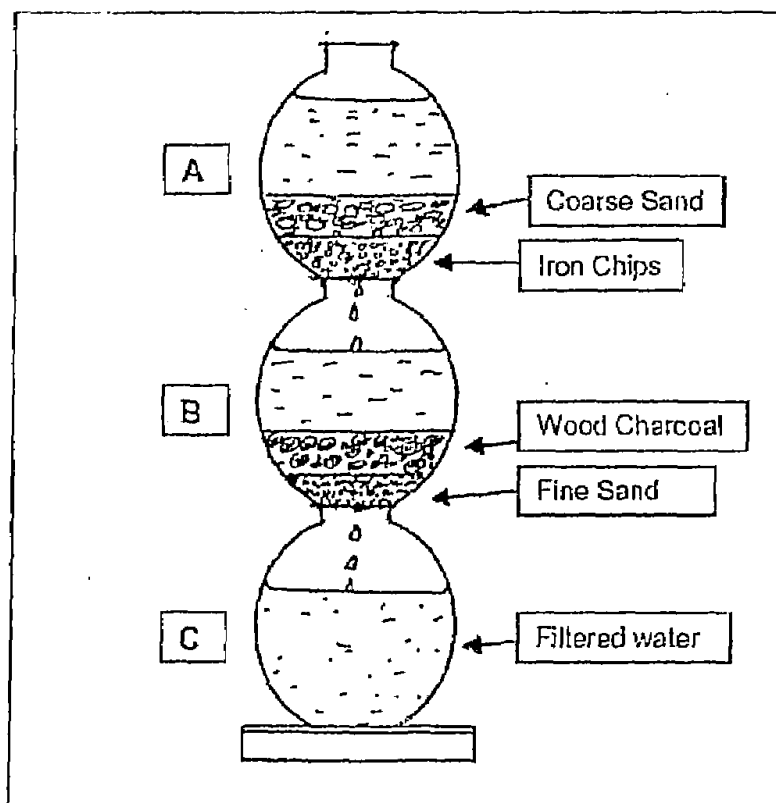


Fig.1 Schematic diagram of a 3-ClayPot setup for water purification (Khan et.al., 2000).

Groundwater from hand pumps was collected in pre-washed high-density polyethylene (HDP) 20 liter tank. Filtered water was decanted into pre-washed (high-density polyethylene) 1 liter sample collection bottles and immediately analyzed or acidified by $HNO_3$ to pH below 2. Water samples were analyzed before and after filtration using Perkin Elmer Otptima 3000 ICP-OES. Anions were analyzed preserved without acid addition using Ion Chromatography from Dionex model DX500. Total alkalinity, concentrations of $CO_3^{2-}$ and $HCO_3^-$ were determined by acid-base micro-titration of groundwater (Snoeyink et. al., 1980). Electric conductivity (EC) was measured using a direct readout from a temperature compensating conductivity meter, HANNA model HI-8820N, pH was measured in the laboratory using a microprocessor pH meter HANNA Model HI-9321. The flow rate was adjusted to about 7 L/hr. The effluent flow rate was measured by collecting water in measuring cylinders for fixed times. Water samples after filtration were stored in clean transparent plastic bottles to monitor color changes during storage.

## RESULTS AND DISCUSSION

Analytical results of groundwater samples of five hand pumps are summarized in Table 1. No color changes, suspended materials or sediments were recorded over a month monitoring. Data included in Table 1 shows that the concentrations of Fe greatly decreased and in sample 5 it reached a concentration less than the detection limit of ICP-OES (0.01mg/l). The concentration of Mn also decreased to less than 0.1 mg/L. The decrease in the two metals reflect their removal by the filtration system and the formation of hydrous oxide precipitates. Other trace metals are removed by co-precipitation with iron such as Ca, Sr and Ba that were removed at percentages of 20%, 20%, 30% respectively. The concentration of Mg recorded a slight decrease at 6%. A small increase of about 8% in alkali metal ions ($Na^+$, $K^+$) concentration was observed. This is attributed to the ion exchange of these ions which exist within the silicate sand lattice structure with the Ca and Mg cations in water or dissolution of K and Na in water (Langmuir, 1997). A slight increase in Vanadium concentration in some filtered water may be due to the presence of V in cast- iron turnings. Zinc and lead concentrations were decreased by

more than 50%. Other trace metals (Cd, Cr, As, Cu) did not change or remained below the detection limit of ICP-OES.

Table. 1 Analytical data of water taken from five hand pumps before and after filtration

| Sample | | Well No.1 | | Well No.2 | | Well No.3 | | Well No. 4 | | Well No. 5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| parameter | unit | Befor | After | Befor | After | Befor | After | Befor | After | Befor | After |
| pH | – | 7.22 | 7.98 | 7.44 | 7.83 | 7.31 | 7.81 | 7.46 | 7.56 | 7.39 | 7.78 |
| E.C | us/cm | 917 | 840 | 1630 | 1427 | 1650 | 1480 | 1220 | 1110 | 1120 | 1060 |
| Ca | mg/l | 80.4 | 70 | 116 | 85 | 127 | 90 | 85 | 67 | 95 | 73 |
| K | mg/l | 8.18 | 8.6 | 15.8 | 17 | 12.4 | 13.2 | 7.46 | 8.2 | 5.77 | 6.2 |
| Mg | mg/l | 20 | 18.7 | 42 | 39 | 40.5 | 38 | 35 | 32.5 | 32.9 | 30.7 |
| Na | mg/l | 75 | 82.6 | 152 | 163 | 158 | 168 | 120 | 130 | 83.6 | 90.3 |
| Cl | mg/l | 110 | 117 | 190 | 195 | 200 | 203 | 160 | 165 | 138 | 143 |
| SO4 | mg/l | 70 | 83.27 | 90 | 98 | 100 | 110 | 70 | 77 | 73 | 79 |
| PO4 | mg/l | 0.03 | 0.06 | 0.02 | 0.035 | ND | ND | ND | ND | 0.03 | 0.042 |
| HCO3 | mg/l | 300 | 246 | 525 | 443 | 556.3 | 440 | 420 | 360 | 380 | 300 |
| Ba | mg/l | 0.135 | 0.07 | 0.219 | 0.1 | 0.219 | 0.134 | 0.143 | 0.08 | 0.115 | 0.08 |
| Fe | mg/l | 2.13 | 0.2 | 3.82 | 0.1 | 2.75 | 0.1 | 4.95 | 0.15 | 2.35 | < |
| Pb | mg/l | 0.02 | 0.008 | 0.032 | 0.01 | 0.025 | 0.009 | 0.02 | 0.009 | 0.14 | 0.01 |
| Mn | mg/l | 0.35 | 0.016 | 0.967 | 0.082 | 0.9 | 0.07 | 1.34 | 0.093 | 0.957 | 0.074 |
| V | mg/l | ND | 0.01 | ND | 0.01 | ND | ND | ND | ND | ND | ND |
| Sr | mg/l | 0.711 | 0.5 | 1.24 | 0.9 | 1.09 | 0.78 | 0.822 | 0.603 | 0.787 | 0.575 |
| Zn | mg/l | 0.269 | 0.11 | 1.25 | 0.535 | 0.79 | 0.4 | 0.339 | 0.17 | 0.285 | 0.14 |
| Cd | mg/l | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Cr | mg/l | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| As | mg/l | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Cu | mg/l | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

The decrease in $HCO_3-$ concentrations could be due to the slight increase in pH additionally the slight increase in $SO_4^{2-}$, $Cl^-$, and $PO_4^{3-}$ might be due to the increase in pH and corresponding decrease in metals solubility because of metal precipitation leaving free anions in solution, nevertheless are within the maximum allowable limits for drinking water (Table 2). Measurement of Electric conductivity is also essential to

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understand the effect of overall filtration process in terms of soluble ionic components passing through the filtering media. Table 1 shows that the Electric conductivity of the solution decreased by about 10 % on the average due to the net decrease in mg equivalent sorbed or ions precipitated in the process. The pH of the filtered water slightly increased possibly as a result of decrease in soluble iron concentration as a Lewis acid and decarbonation.

Table 2 Comparison of the average of filtered water quality with those of USEPA, WHO, and Egyptian standards

| Constituient | Average of fillerd water | USEPA 1996 | WHO guideline 1993 | Egyptian Ministry of Health 1995 |
|---|---|---|---|---|
| pH | 7.79 | 6.5 - 8.5 | 6.5 - 8.5 | 6.5 - 9.2 |
| Ca | 77 | ..... | ..... | 200 |
| K | 10.64 | ..... | ..... | ..... |
| Mg | 31.78 | ..... | ..... | 150 |
| Na | 126.78 | ..... | 200 | 200 |
| Cl | 164.6 | 250 | 250 | 500 |
| SO4 | 89.454 | 250 | 250 | 400 |
| HCO3 | 357.8 | ..... | ..... | 500 |
| Ba | 0.0928 | 2 | 0.7 | |
| Fe | 0.11 | 0.3 | 0.3 | 0.3 |
| Pb | 0.009 | 0.015 | 0.01 | 0.05 |
| Mn | 0.067 | 0.05 | 0.1 | 0.1 |
| Sr | 0.6716 | ..... | ..... | ..... |
| Zn | 0.271 | 5 | 3 | 5 |
| Cd | ..... | 0.005 | 0.003 | 0.005 |
| Cr | ..... | 0.1 | 0.05 | 0.05 |
| As | ..... | 0.05 | 0.01 | 0.05 |
| Cu | ..... | 1 | 1 | 1 |

To understand the chemical speciation of groundwater, a computational geochemical model, *Visual MINTEQ* was used with the inputs shown in Table 1.The speciation model shows $Ca^{2+}$ , $Fe^{2+}$ , $K^+$ , $Mg^{2+}$ , $Mn^{2+}$ , $Na^+$,$Zn^{2+}$ ,$Cl^-$, $CO_3^{2-}$ , $SO_4^{2-}$ , $NO_3^-$ , and $NO_2^-$ as the major components and $CaHCO_3^+$, CaCO3 (aq), MgCO3 (aq), $MgHCO_3^+$, $MnHCO_3^+$, $H_2CO_3$(aq), and $HCO_3^-$, as the major species under oxic condition.

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The model also predicts that the concentration of Fe, Mn, and Ca, exceeds their solubility product limits as hematite ($Fe_2O_3$), bixbyite ($Mn(OH)_3$), , Calcite ($CaCO_3$), and Dolomite ($CaMg(CO_3)_2$), respectively and thus precipitate out under oxic condition. Similar oxic conditions prevail in the 3-Pots- filtration system.
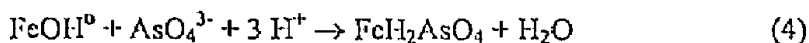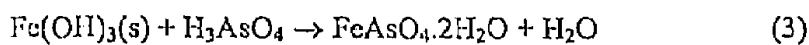
### Role of metallic Iron in metal Removal

Elemental iron (zero valent iron) is one of the most effective agents for environmental remediation of inorganic (Wilson, 1995) and organic (dechlorination of chlorinated solvents, etc.) (Powel, et. al., 1995). The use of metallic iron to remediate metal contaminated sites has increased because it is nontoxic and inexpensive. A satisfactory explanation of reaction chemistry should consider significant changes that occurred in pH values and major ion concentrations. Some diagnostic changes include increased pH values, increased concentrations of Fe, and decreased concentrations of Ca, and $HCO_3^-$. These changes in fluid chemistry are consistent with the effects of $Fe^0$ corrosion. As $Fe^0$ dissolves $Fe^{+2}$ is released, protons are reduced to elemental $H_2$ (Eq.1).

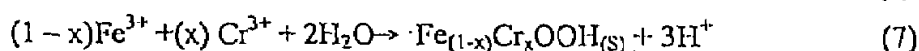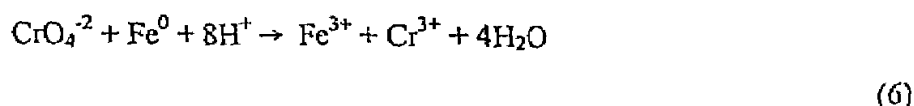Dissolved Ca and $HCO_3^-$ concentrations decrease because of precipitation of calcite that is triggered by the increased pH value. As calcite precipitates, the release of $H^+$ helps maintain a low pH value (Eq.2) (S. J. Morrison 2002)
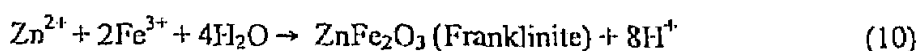
$$Fe^0 + 2H^+ \longleftrightarrow H_2 + Fe^{2+} \qquad (1)$$

$$Ca^{2+} + CO_2(g) + H_2O \longleftrightarrow CaCO_3(s) + 2H^+ \qquad (2)$$
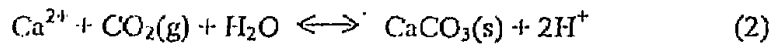
Zero valent iron used to remediate arsenic the possible reactions of arsenate with hydrous iron oxide are shown below where [$FeOH^0$] represents oxide surface site (Mok and Wai, 1994; Hering et al., 1996). Immobilization of arsenic by hydrous iron oxide, as shown in Eqs. 3 to 5, requires oxidation of arsenic species into As pentavalent form for higher efficiency arsenic removal is dependent on pH.

$$Fe(OH)_3(s) + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O \qquad (3)$$

$$FeOH^0 + AsO_4^{3-} + 3 H^+ \rightarrow FeH_2AsO_4 + H_2O \qquad (4)$$

$$FeOH^0 + AsO_4^{3-} + 2 H^+ \rightarrow FeHAsO_4^- + H_2O \qquad (5)$$

A range of Fe(0) and Fe(II) bearing materials promoted reduction and precipitation of Cr(VI) (Deng and Stone, 1996a,b; Blowes et al., 1997; Buerge and Hug, 1997, 1999). The net reactions of Cr(VI) reduction with Fe(0) and coprecipitation of Cr(III) and Fe(III) are:

$$CrO_4^{-2} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O$$

(6)

$$(1 - x)Fe^{3+} + (x)\ Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH_{(s)} + 3H^+ \qquad (7)$$

In this study the remediation of Zn was explained by precipitation of a known mineral as Franklinite( $ZnFe_2O_3$) the solubility of Franklinite is the most insoluble of Zn mineral depending on the Fe(III) mineral controlling the activity of $Fe^{3+}$.coprecipitation of Zn(II) and Fe(III) are explaine by Eqs 8 to 11(W.L.Lndsay,1979)

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad (8)$$

$$Fe^{+2} \rightarrow Fe^{3+} + e^- \qquad (9)$$

$$Zn^{2+} + 2Fe^{3+} + 4H_2O \rightarrow ZnFe_2O_3 \ (Franklinite) + 8H^+ \qquad (10)$$

Franklinite may be amorphous and other cations of similar size may partially substitute for $Zn^{2+}$. Added to this Iron oxides may form analogous minerals with other trace elements like $Cu^{2+}$, $Mn^{2+}$, $Co^{2+}$, also Dissolved $Mn^{2+}$ often forms carbonate minerals rhodochrosite (MnCO3), so $Mn^{2+}$ remediation was explained by the Eq.11:

$$Mn^{+2} + CO_2(g) + H_2O \rightarrow 2H^+ + MnO_3 \ (rhodochrosite) \qquad (11)$$
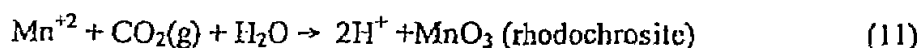
**Role of soluble Iron in metal Removal**

Dissolved iron is a natural component of most groundwater. Besides causing pots and pans to become brown, at high concentration dissolved iron can be toxic to small infants. Table 1 clearly shows that the concentration of soluble iron originally present in the well water decreased significantly, from an average of 3.2 mg/l to an average of 0.1 mg/l, which is below the permissible level for most cases. Dissolved iron, primarily present as Fe(II) in groundwater plays a very significant role in removing trace cations and anions. In contact with air Fe(II) is oxidized to Fe(III) and precipitates as $Fe(OH)_3$,

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hydrous ferric oxide (HFO: $Fe_2O_3$, $2-3H_2O$), $Fe(HCO_3)_2$ etc. Iron is present in the filtration system as zero valent iron, ($Fe^0$) in the pot A and in Groundwater mostly as soluble $Fe(II)$ species. Since the filtered water is nearly free from iron, therefore the oxidation products of zero valent iron and the oxidation of $Fe(II)$ species to nonmagnetic hydrous ferric oxide HFO (Dzombak et. al., 1990) are quantitatively retained in the top and middle pots. Previously, we reasoned that trace metals were quantitatively removed by compound formation or adsorption on HFO (Khan et.al., 2000).

## CONCLUSIONS

The filtration system presented here is promising as it uses locally available materials and no chemicals are used. The overall water quality obtained from the 3-Clay Pots is compared with that of standards of USEPA, WHO, and Egyptian standards in Table 2. The study clearly indicated that water quality obtained from 3-Clay Pot meets the international and Egyptian standard.

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