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ARSENIC REMOVAL FROM GROUND WATER

RESEARCHES AND PRACTICAL IMPLEMENTATION CONDUCTED AT

INSTITUTE OF CHEMISTRY, VIETNAMESE ACADEMY OF SCIENCE AND TECHNOLOGY

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Abstract.

The paper presents the arsenic removal from ground water by adsorption onto synthetic manganese dioxide prepared by electrochemical method.

For designing the adsorption column, dynamical adsorption study was accomplished under different operation conditions and phosphate concentration in treating water to obtaine the dynamical adsorption capacity of arsenic to manganese dioxide adsorbent as well as the loss of capacity under flow conditions characterized by mass transfer zone.

Arsenic and ammonium removal from ground water was also investigated by phytogenous method. Cyperus alternifolius planting on sand layer was used as filtration media for field investigation. Results for arsenic and ammonium removal efficiency of filtration unit for about one year are reported.

1. Introduction.

Many ground water sources being used for domestic purposes are contaminated with high arsenic concentration. To prevent the human health threat it must be removed or reduced to a reasonable concentration level. Several technologies have been developed and some of them have practical applications.

Groundwater sources contaminating with arsenic are mostly the wells belong to individual farmer family in rural areas and diffusely distributed. This specific feature requires appropriate treatment methods with respect of:

- safety of the water quality.
- low capital and running costs.
- easy operation and maintaining.

In addition, the numerous water sources are characterized by variable concentration of other constituents (Fe, Mn, P, organic matter), which affect the removal performances of the treatment system.

The methods chosen for arsen removal for such situations are the adsorption onto manganese oxide materials and the combination of sand filtration with plant cultivation.

2. Research activities.

2. 1. Manganese dioxide preparation and its adsorbility to arsenic.

As known, arsenic from ground water can be removed by adsorption onto aluminum and different iron oxides, ion exchange, precipitation with ferric salt. These treatment technologies often require the pre-oxidation step to convert the As(III) to As(V) due to difficulties of removing As(III) by

above mentioned procedures. The technology consists of two steps is rather not conventionally to apply for small scale treatment in rural region. Adsorption of arsenic onto manganese dioxide could overcome this trouble due to oxidatability of manganese dioxide, that means manganese dioxide plays both an oxidative catalyst and an adsorbent in the case of arsenic treatment [1, 2].

Preparation of manganese dioxide by chemical and electrochemical method and assessments of their adsorbility to As(III), and As(V) were the researches performed in our labor.

Manganese dioxide was prepared by chemical precipitation (CMD1, CMD2) and by electrochemical method (EMD).

The products are characterized by different methods: SEM, XRD, BET, PZC (Figure 1, 2). The characteristics of products are summarized in table 1.
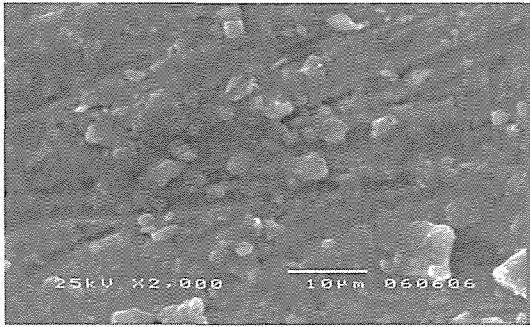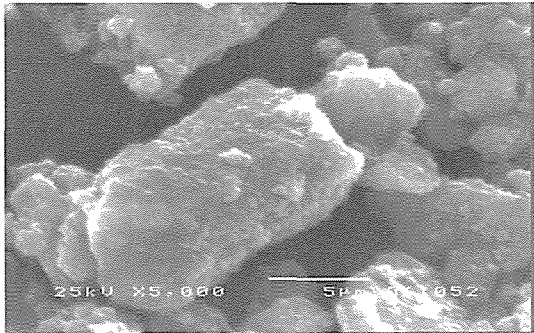

Fig 1. SEM picture of EMD

Fig 2. SEM picture of CMD 2

Table 1. Characters of manganese dioxide.

Sample	CDM1	CDM2	EDM
Surface area (m^2/g)	75,0	42,9	55,0
Manganese type	δ - MnO_2	Ramsdellite	α - MnO_2
PZC (range)	6,0	6,0	6,0
Representative size (μm)	1 - 2	5 - 10	5 - 10

The adsorbility of manganese dioxide was evaluated by measuring the adsorption isotherm for As(III) and As(V) at different pHs. (Figure 3, 4). Isotherm date were treated by Langmuir isotherm equation to obtain the maximal adsorption capacity (table 2).
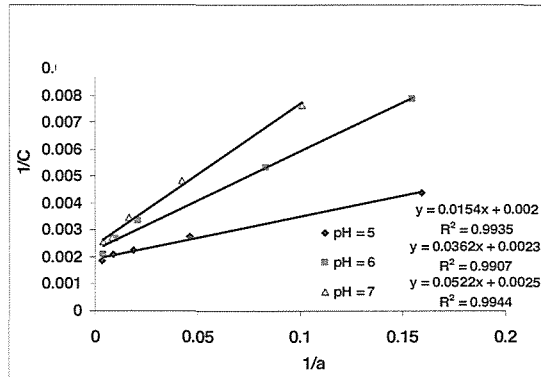

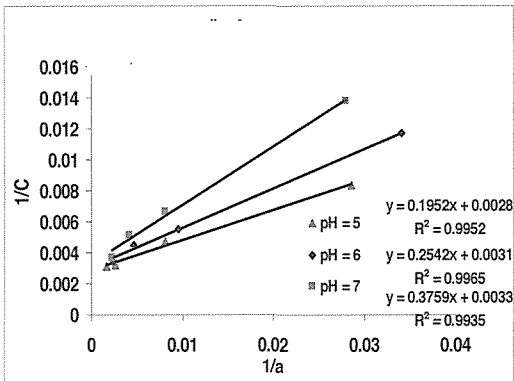**Fig. 3.** Adsorption isotherm of As (III) on CMD 1 (linearlized Langmuir equation)

Fig. 4. Adsorption isotherm of As (V) on CMD 1 (linearlized Langmuir equation)

Table 2. Adsorption capacity a_m (g/kg) of manganese dioxide

Capacity \ pH	a_m of CMD1		a_m of CMD2		a_m of EMD	
	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)
pH = 5,0	1,000	0,500	0,714	0,357	0,833	0,417
pH = 6,0	0,769	0,435	0,588	0,322	0,667	0,370
pH = 7,0	0,625	0,400	0,476	0,303	0,526	0,345

From above results could be considered that almost manganese oxide modifications are able to adsorbe arsenic, the adsorption capacity depends upon the surface area.

2. 2. Arsenic adsorption in column.

Practical application of arsenic adsorption is implemented under flow condition or in column where the adsorption capacity (dynamical) is influenced by several operational factors, such as flow rate, grain size, the height of adsorbent layer and is never reached the statical adsorption capacity (values under static conditions of labor experiment).

To evaluate the adsorption column performances, the Adam- Bohart model describing the breakthrough curve [3] is used:

$$t = \frac{a_o.H}{C_o.v} - \frac{1}{k.C_o} \ln\left(\frac{C_o}{C_b} - 1\right) \qquad (1)$$

$$\text{or } t = \frac{a_o}{C_o.v}(H - L) = \frac{a_o}{C_o.v}.\eta \qquad (2)$$

with

$$L = \frac{v}{k.a_o} \ln\left(\frac{C_o}{C_b} - 1\right) \qquad (3)$$

a_o: statical adsorption capacity corresponding to initial (influent) concentration C_o. L: the mass transfer zone. k: formal kinetical constant. H: the height of adsorbent layer. C_b: breakthrough concentration (10 µg/l for arsenic as standard value); v: flow velocity of water through column; t: working (service) time. η: the utilization degree of column.

From equation (2), the working time could be predicted from the adsorbility of adsorbent (a_o), the quantity of adsorbent mass in the column (H) and the mass transfer zone presenting the kinetical process (see eq. (3)) and the operation parameters (C_o, v).

a_o, k are mainly dependent on the nature of adsorption system in actual operating condition (temperature, pH, adsorbent grain size, non - arsenic contaminants). η presents the column utilization degree ($a_o.\eta$ corresponding to dynamical adsorption capacity) depending mainly upon the kinetical constant k; L $\rightarrow$ 0, η $\rightarrow$ 1,0, dynamical capacity $\rightarrow$ statical capacity when k $\rightarrow$ ∞, that is the case of ideal or equilibrium adsorption in column.

For practical applications, the assessment is focused on the a_o (corresponds to C_o) and L for a individual water source.

From these values, the working time of a column can be determined or in other words an adsorption column can be designed.

Measuring the outlet concentration of arsenic at different times (breakthrough curve) and at different height of adsorbent layer, a set of breakthrough curves can be constructed (Fig 5).
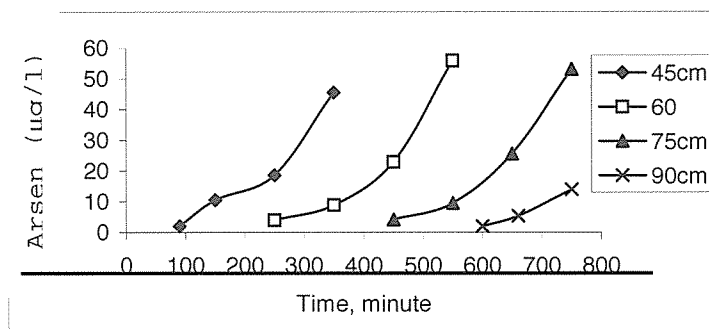
Fig 5. The adsorption breakthrough curve of arsenic on MF-97.

By fixing the breakthrough concentration C_b (10 µg/l for arsen), taking the working time at C_b from breakthrough curves at different height (Fig 6), a_o and L can be calculated by using eq. (2).
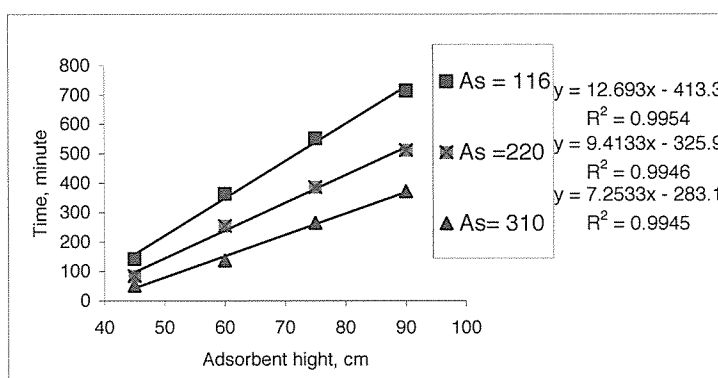

Fig 6. The working time of column versus the adsorbent layer.

Table 3 represents the experiment data of a_o, L for the adsorption system MF-97 (MF-97 is the commercial product developed in Institute of Chemistry, the modified manganese oxide are) under different conditions (velocity, innitial arsenic concentration, phosphate and organic matter.

Table 3. Dynamical adsorption characteristics of system MF-97.

Influence of exp. Conditions		L (cm)	a_o (µg/cm^3)
Concentration C_o V = 6 bed volume/h	$C_o = 55$µg/l	15	5.03
	$C_o = 104$µg/l	19	7.36
V = 3 bed volume/h	$C_o = 116$µg/l	33	6.54
	$C_o = 220$µg/l	35	9.19
	$C_o = 310$µg/l	39	9.98
Flow rate v $C_o = 310$µg/l	$Q = 3.V_{h^!t}$/h	39	9.98
	$Q = 6.V_{h^!t}$/h	42	9.39
PO_4^{3-} - Influence C_o=310µg/l, v= 3 bed volume/h	$PO_4^{3-} = 0$ mg/l	39	9.98
	$PO_4^{3-} = 2$ mg/l	41	6.62
	$PO_4^{3-} = 5$ mg/l	42	3.29
Influence of Hardness (H) and organic matter COD (Mn) C_o= 310µg/l, v= 3 bed volume/h	H=100mgCaCO$_3$/l COD (Mn) = 1 mg O$_2$/l	39	9.98
	H=500mgCaCO$_3$/l COD (Mn) = 20 mg O$_2$/l	39	9.73

From the data of table 3, some facts could be extracted:

- High arsenic concentration in water could not reduce the working time of column in linear proportionality to concentration due to high adsorption capacity at high initial concentration.
- Adsorption capacity and mass transfer zone are weakly influenced by flow rate.
- Adsorption capacity of MF-97 to arsenic is strongly reduced by the presence of phosphate.
- Adsorption rate is rather high (6 bed volume/h, approximately to adsorption of organic matter onto activated carbon are ion exchange on anionit resin). However, because of the high mass transfer zone (40 cm), the utilization degree could be enhanced by increasing the column height.

2. 3. Arsenic and ammonium uptake by plants.

Many ground water sources in Song Hong Delta are heavily polluted by ammonium (about 80% wells with ammonium concentration higher than 5 mg/l), simultaneously with arsenic. Removing both constituents by plant cultivation was the research topic performed in our labor. Several plants can uptake heavy metals as well as ammonium and phosphate as nutrient for growth. They are can be used for soil remediation and water purification [4]. Criteria for selecting plants for the purposes of removal of arsenic and ammonium are:

- High uptake capacity to arsenic and ammonium.
- High biomass production.
- Alive in a wide range of climate conditions.
- High oxygen transport to rhizome and root zone.

Cyprus plant (Fig 7) could adapt such requirements via labor investigations. Its uptake rate:

For arsenic: 0,38 $\mu g/(g. d)$

For NH_4-N: 0,38 $\mu g/(g. d)$

For PO_4-P: 0,38 $\mu g/(g. d)$

This plant was used for construction a protype of planted filter to remove arsenic and ammonium.
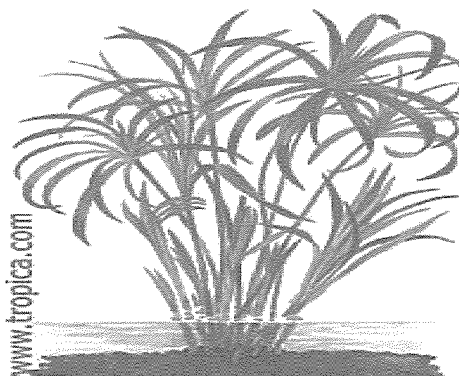

Fig 7. Cyperus alternifolius

3. Practical implementation.

3. 1. Arsenic removal by MF-97 column filtration.

Arsenic removal by column filtration technique was intended to use for family scale living in rural regions. Conventionally, ground water is exploited and simply treated by aeration and sand filtration to remove iron. The treated water is then stored in the tank for daily usages. Water from the storage tank is filtered upward through the column containing MF-97 with a velocity ranging 2 to 4 bed volume depending on the water level within the tank. The column has inner diameter 12 cm and the height 60 cm containing 10 liter MF-97 (Fig 8).

Fig 8. MF-97 column install in Ha Nam (November 2001).

In Cooperation with Institute of geography (VAST), in November 2001, 40 filtration units were installed in different locations in Ha Nam Province to evaluate the arsenic removal performances of filtration column. Arsenic concentration in waters to be filtered ranges from 60 to 230 µg/l. Periodic analyses (for 2 years) of filtered water shown that the remaining arsenic concentration was below 15 µg/l, almost lower than 10 µg/l.

The work was extended in year 2004, about 150 filtration columns were installed.

In 2005, UNICEF Viet Nam pointed to use MF-97 for arsenic treatment in Ha Nam in the manner: the farmers were provided with MF-97, the users made the column by themselves (from steel or plastics). Recently, they are experienced on the use of MF-97 for arsenic removal in their owner houses.

3. 2. Arsenic and ammonium removal by combination of sand filtration and plant cultivation.

A pilot plant was constructed to investigate the possibility of using cyperus alternifolius for removing both arsenic and ammonium from ground water. Design of the system through is depicted in figure 9.

The system was operated in two modes: simple filtration (M5) and two tank connected in serie (M4).

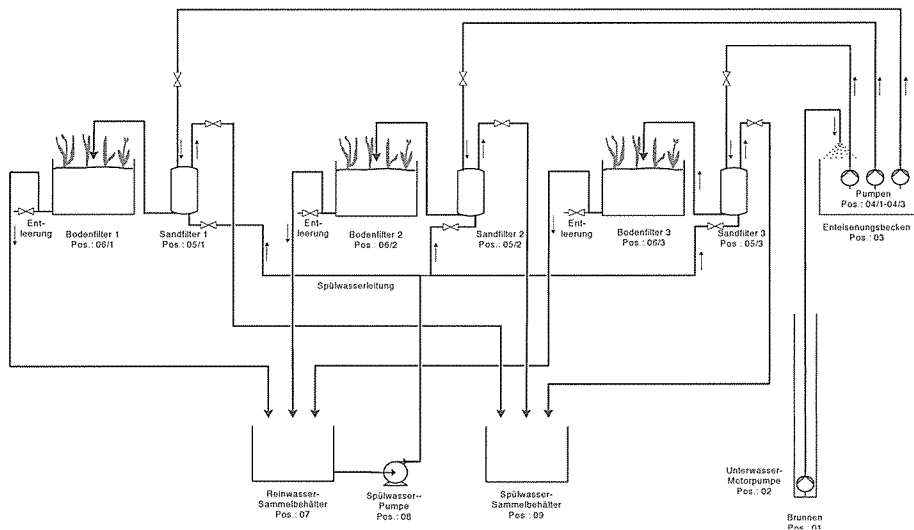The system was installed in Thuong Tin, Ha Tay and began to operate in Feb. 12th, 2005.

Fig 9. Design a filtration system.

Fig 10. Filtration system with plant cultivating.

The ground water was first treated for iron removal by aeration and sand filtration. The filtered water using for the investigation has following characteristics:

pH: 8,08 - 8,44.

Ar (μg/l): 105 - 220

Fe (mg/l): <0,02

PO_4-P (mg/l): 1,01 - 1,63

NH_4- N (mg/l): 21,3 - 23,8

The flow rate was designed 80 l. m^{-2}. d^{-1}.

Results of field investigations are presented in figures 11, 12, 13, 14. The analysis of arsenic, ammonium, nitrite and nitrate was conducted weekly.
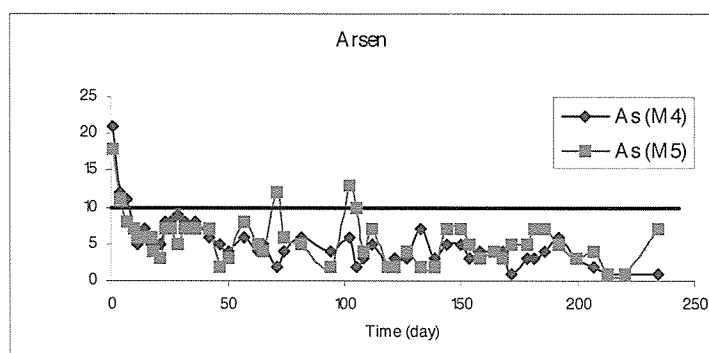
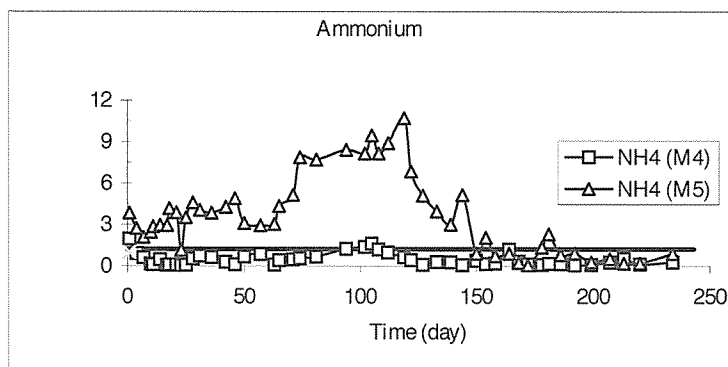**Fig 11.** Arsen concentration remaining in treated water.

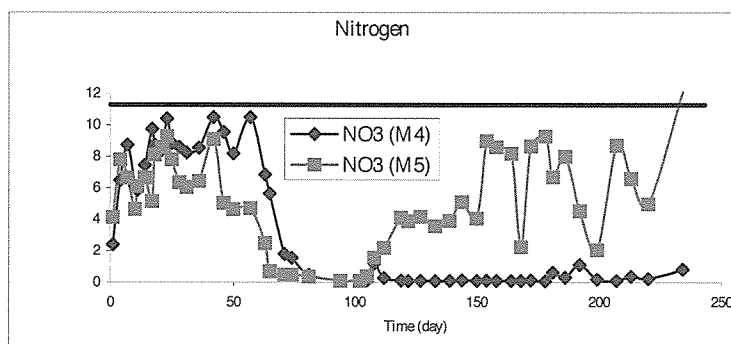**Fig 12.** Ammonium concentration remaining in treated water.

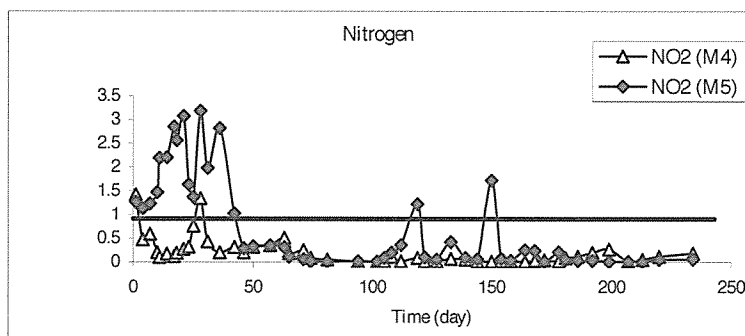**Fig 13.** Nitrate concentration remaining in treated water.

Fig 13. Nitrite concentration remaining in treated water.

Arsenic removal.

After 12 days operation (temperature about 17 - 22°C), the removing capacity for arsenic was achieved more than 90%, the treated water is met the standard criteria for drinking purposes for both operating modes. Only 2 from 41 analysis data for simple filtration were not achieved the standard value.

Nitrogen removal.

In the treatment system, several nitrogen removal mechanisms could occur simultaneously: uptake by plants, nitrification, denitrification processes. The contribution of each process to total nitrogen removing is changed with time of operation and difficult to distinguish. After certain time, the efficiency of the operation of the tank in serie mode showed high and met the drinking water quality.

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