VIETNAMESE ACADEMY OF SCIENCE AND TECHNOLOGY
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REMOVAL OF ARSENIC AND MANGANESE IN UNDERGROUND WATER BY MANGANESE DIOXIDE AND DIATOMITE MINERAL ORES

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WEPA-2008

INTRODUCTION

Arsenic contamination in underground water was found in various countries of the world as Bangladesh, India, China, Mexico, America and ect .

30-40 million people of Bangladesh, 13 million people in America, are now at risk of As contamination.

As and concentration at higher level than the WHO recommended value be found of 51% in the tube-wells in Bangladesh .

The geology of the Red river in **Vietnam** likes the geology of Ganges River in Bangladesh also has been finding the As contamination in underground water some provinces as Hanoi, Hatay, NamDinh, HaNam and etc.

Mn level above the admissible standards are found both in the Red River and Mekong River.

GROUND WATER QUALITY

No	Parameter and pollutant	Unit	Limitation value
1	pH value		6,5 ÷8,5
2	Colour	Pt - Co	5 ÷50
3	Hardness (as CaCO3)	mg/l	300 ÷ 500
4	Total solids	mg/l	750 ÷1500
5	Arsenic	mg/l	0,05
6	Cadmium	mg/l	0,01
7	Chloride	mg/l	200 ÷ 600
8	Lead	mg/l	0,05
9	Chromium (VI)	mg/l	0,05
10	Cyanide	mg/l	0,01
11	Copper	mg/l	1,0
12	Fluoride	mg/l	1,0
13	Zink	mg/l	5,0
14	Manganese	mg/l	0,1 ÷0,5
15	Nitrate	mg/l	45
16	Phenol compound	mg/l	0,001
17	Iron	mg/l	1 ÷ 5
18	Sulphate	mg/l	200 ÷ 400
19	Mercury	mg/l	0,001
20	Selenium	mg/l	0,01
21	Fecal coli	MPN/100 ml	Not detectable
22	Coliform	MPN/100 ml	3

Parameter limits and maximum allowable concentrations of pollutants in ground water in Vietnam

GROUND WATER QUALITY

A broad survey of arsenic pollution in the 12 provinces of the Red River Delta, Mekong Delta and Central area was carried out from Nov. 2003 to Apr. 2004 by IET and UNICEF.

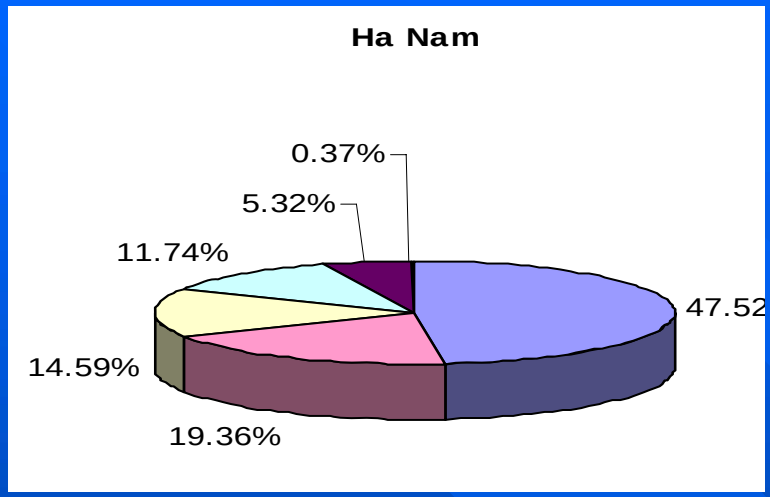
12,439 water samples were tested with As in 419 communes of 33 districts in the 12 provinces

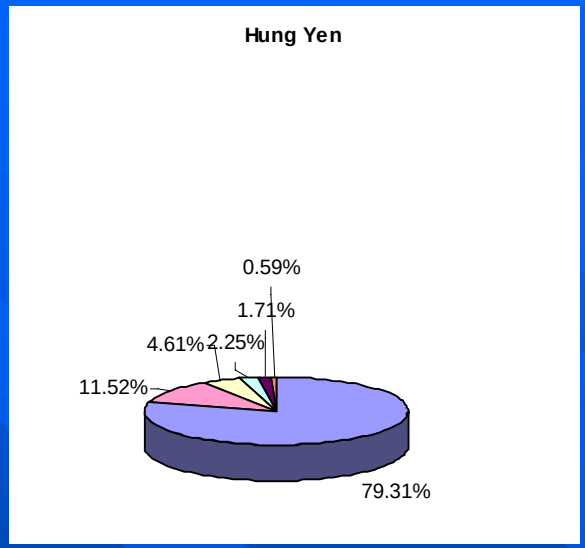
As> 0.01 mg/L (34.92%)
As> 0.05 mg/L (21.07 %)
As >0.05 mg/L (39.15%)

In that

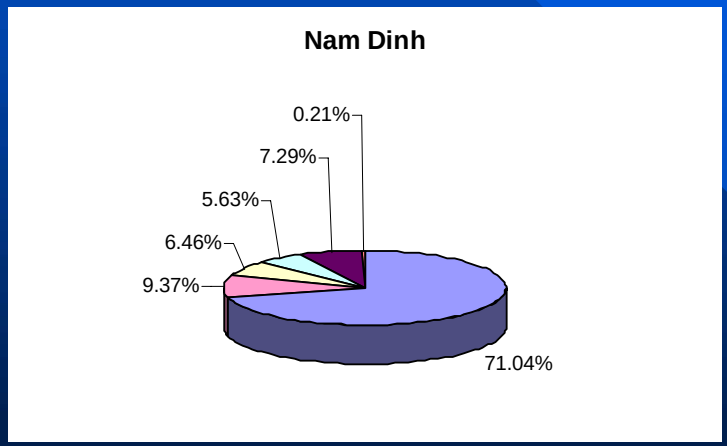
504 tube well (Hanam, Dongthap): As> 200ppb
24 tube well (Dongthap): As> 500 ppb;
1-2 tube well (Hanam): As>1000 ppb:
Source: VN-UNICEF,2004

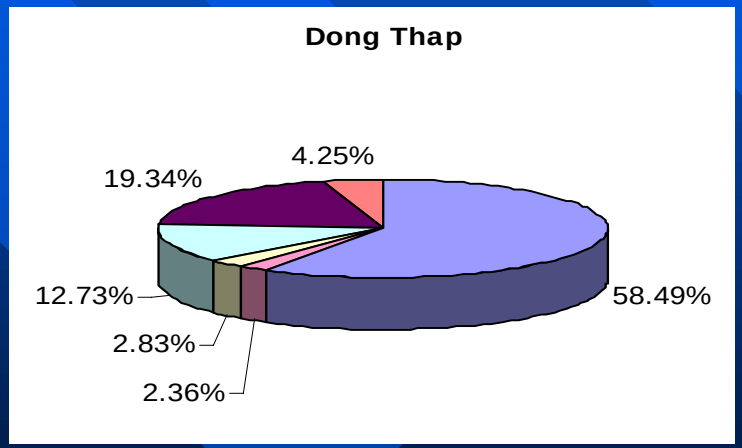
GROUND WATER QUALITY





- 0-10ppb
- 11-50ppb
- 51-100ppb
- 101-200ppb
- 201-500ppb
- >500ppb

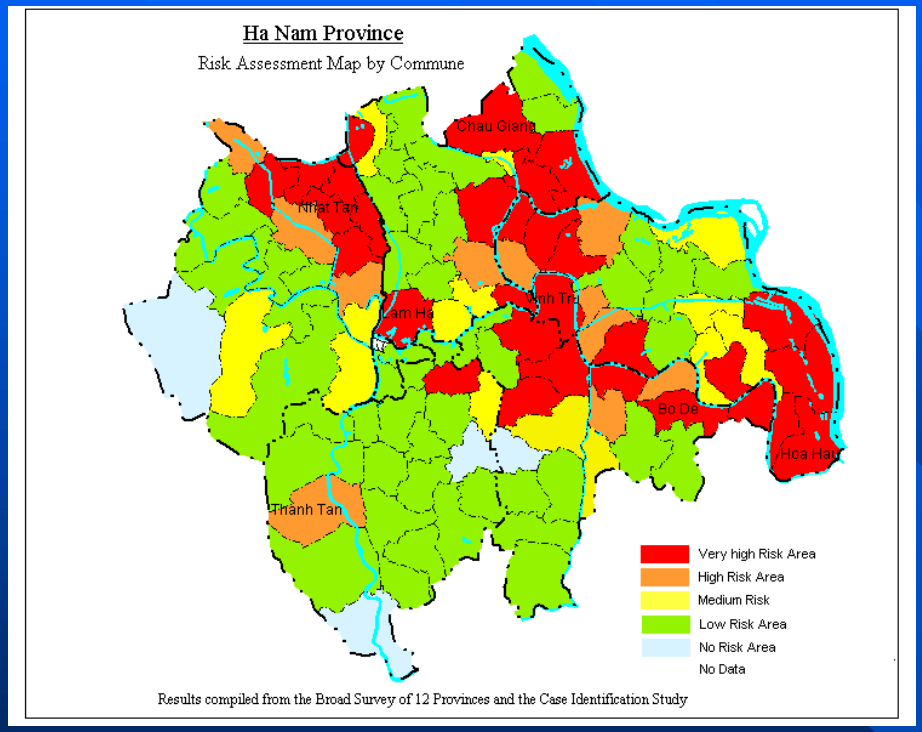


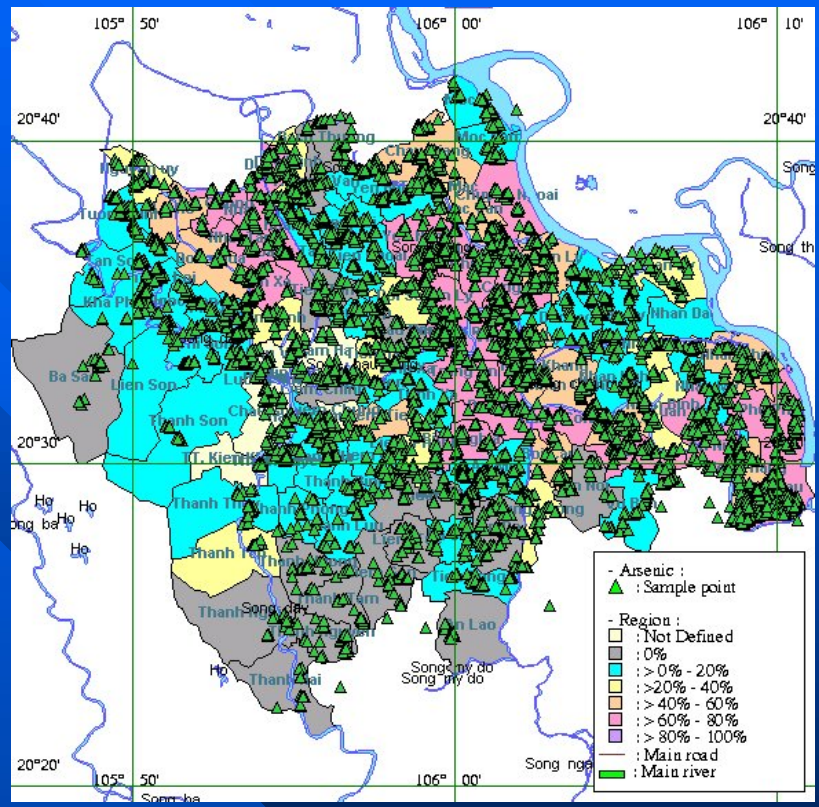


Results of As concentration analysis in 12 province

(% calculated based on the total samples tested)

GROUND WATER QUALITY





As Risk Map of Ha Nam

The delineation map of arsenic contamination risk prediction in Ha Nam province

Using As and Mn contaminated water source for a long time will cause tiredness, affect nervous system, even stomach cancer and other internal organs

To eliminate arsenic and manganese from water source, development of feasible technologies to their treatment process as well as house-hold scale is essential requirement in Vietnam

Study and assessment of the nature MnO_2 and diatomite mineral adsorptive abilities to treat Mn and As total in underground water was carried out.

The processing technologies are simple, low-priced, and easily-operated.

Utilizing mobile and statically absorptive ability is a method of assessing the As and Mn eliminating process from underground water by determining the maximum adsorption capacity into the nature MnO_2 and diatomite mineral which is investigated with hopes to contribute a part of technology and science to solve this urgent problem.

Material quality

Material	Surface area (m^2/g)	Capillary radius (A^0)
Diatomite	30	300-1600
Silicagel	500	100
MnO_2	75	--

MnO_2 ore

MnO_2 is a weak adsorptive substance but strong oxidant and catalysis.

The component of MnO_2: MnO 1,7-2; MnO_6, $Mn(O,OH)_6$, cation, anion, H_2O, ect.

MnO_2 can be divided 3 groups:

Chain structure: Pyrolusite, Ramsdellite and Nsutile minerals, b - MnO_2

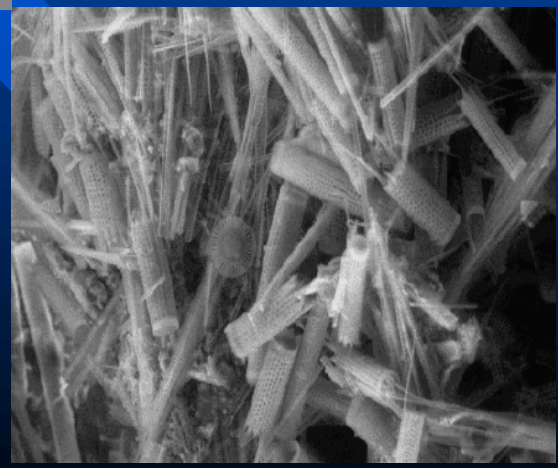
Ring structure: γ - MnO_2, Cryptomelane vμ Hollandite minerals

Layered structure: Chalcophanite, Lithiophorite (Li+, Al3+), Bernessite (Na+, Ca2+) and Vernadite minerals; O - Mn - O - Zn -H2O - Zn - O - Mn - O

Material quality

Natural diatomite

Component	Content (%)
SiO_2	72-75
Al_2O_3	6-9
FeO, Fe_2O_3	5-7
H_2O	8-10
Ignition loss	9-9,5
Other	2-3



RESULT AND DISCUSSION

1.
Investigation of the adsorptive ability of MnO_2 for removing As and Mn in under ground water by
mobile adsorptive method

2.
Investigation of the adsorptive ability of MnO_2 and diatomite ore for removing As and Mn in the under ground water by
statically adsorptive method

RESULT AND DISCUSSION

Determination of As and Mn by statically absorptive method

Determination of As and Mn by mobile absorptive method

1g of MnO_2 ;

Or diatomite mineral ,

100 mL of a mixed solution of 0.1 mg/L As , 4 mg/L Mn,

stirred gently: 3hrs

1g of MnO_2 or diatomite mineral, 0.1 mg/L As ; 1 mg/L Mn,

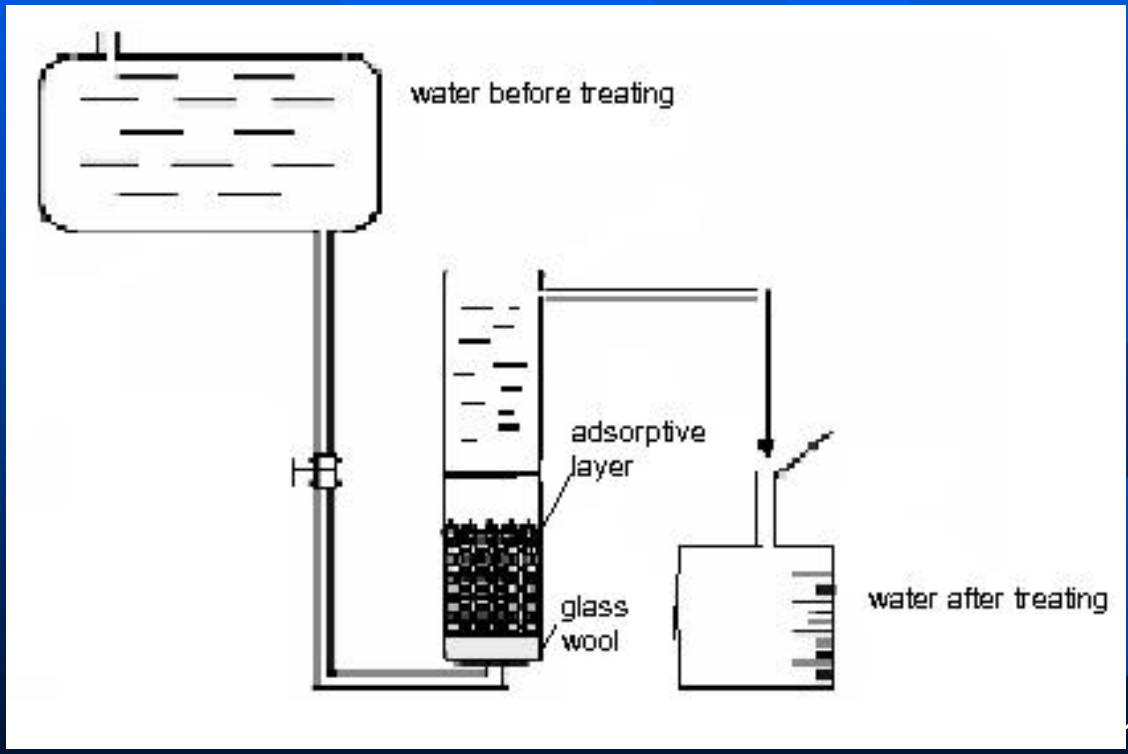
stirred gently: 72hrs

10 g materials

(7.5 cm^3)

Result and discussion

1. Investigation of the adsorptive ability of MnO_2 for removing As and Mn in under ground water by
mobile adsorptive method



Sketch of As and Mn treated system by mobile adsorptive method

1. Investigation of the adsorptive ability of MnO_2 for removing As and Mn in under ground water by
mobile adsorptive method

Determination of Mn :

10g materials; 1mg/L Mn ; flow rate=1.6 mL/min.

99% of Mn ion has been removed after 1day. Almost Mn was adsorbate into MnO_2 ore. The concentration of Mn after treatment is lower than VNese std limit. **The productivity is of 99.9%.**

Time (hour)	Sample mark	Output concentration of Mn C_1 (mg/L)
0	Mnd_1-01	1
2	Mnd_1-02	0.7
4	Mnd_1-04	0.5
8	Mnd_1-08	0.3
12	Mnd_1-12	0.1
16	Mnd_1-16	0.06
20	Mnd_1-20	0.01

Table 1. The result of treatment of Manganese by MnO_2 ore

1. Investigation of the adsorptive ability of MnO_2 for removing As and Mn in under ground water by
mobile adsorptive method

Determination of As:

As initial concentration (C_0) is 0, 1 mg/l. Asd1-01, Asd1-02 ... Asd1-240 is the sample mark, corresponding to adsorbent reduction time.

The concentration of As has not much been removed after 10 days for using MnO_2 ore.

This result indicated that **almost As was not adsorpted into MnO_2**.

Time (hour)	Sample mark	Output concentration of As C_1 (mg/L)
1	Asd1-01	0.100
2	Asd1-02	0.100
10	Asd1-10	0.093
20	Asd1-20	0.091
48	Asd1-48	0.060
120	Asd1-120	0.057
168	Asd1-168	0.058
240	Asd1-240	0.051

Table 2: The result of Arsenic treatment by MnO_2 ore

2. Investigation of the adsorptive ability of MnO_2 and diatomite ore for removing As and Mn in the under ground water by

statically adsorptive method

Determination of Mn :

1g materials into 100mL of Mn solution which has 4mg/L.

Mn was well treated by $MnO_2$and diatomite natural

MnO_2 and diatomite ores are very good at treating Mn in the water. MnO_2 is not only oxidized but also adsorbent material

Table 3: The result of statically adsorptive process for treating of Mn by some materials

Name of material	Sample symbol	Mn concentration after treating C_1 (4 mg/l)
Diatomite	Do-Mn - 03	<0.01
MnO_2 ore	M-Mn - 03	<0.01

2. Investigation of the adsorptive ability of MnO_2 and diatomite ore for removing As and Mn in the under ground water by

statically adsorptive method

Determination of As:
100mL As C= 0,1mg/L; stirred:3 hrs

97% As in sample after treatment was below VNese std.

As is well treated by diatomite due to the high As adsorption capacity of diatomite. Possibility, diatomite natural was made up of many other mineral materials like Al_2O_3, Fe_2O_3, betonies and ect.

Table 4: **The result of statically adsorptive process for treating of As by some materials (C_0 = 0,1mg/l)**

Name of material	Symbol sample	Output of As C_1 (mg/l)	Treatment productivity (%)
Diatomite	Do-As-03	0,0054	94,62
MnO_2 ore	M-As-03	0,0031	96,95

To identify the maximal adsorptive capacity of substance on materials basing on adsorbent isotherm

To make the calculation of adsorption of material, it is necessary

As treatment efficiency was high up to 80% with adsorbent capacity calculated by Longmuir formula 1, **Fig.2:**
Am=2,08mg/g (y=1,535x+0, 48) (1)

MnO_2 is oxidability and minus chargeable, it can be attracted Mn^{2+} ion and created Mn_2O_3. Maximal adsorption capacity calculated by L. 3, **Fig.4**:
Am = 12,7mg/g (y= 10,29x + 0,079) (3)

Gauge adsorbent Isotherm and determine maximal adsorption capacity of As and Mn onto some materials

The adsorptive of Fe_2O_3/Diatomite is dependent on ·OH group, which adhesion onto diatomite surface, can be replaced As.
The adsorbent ability of As into diatomite is higher than that intoMnO_2.**(Fig.3)**
Am = 2, 5 mg/g (y= 20,03x + 0,406) (2)

Diatomite/Mn $(OH)_4$ which was created through oxidization process which played an important part for Mn oxidization process.
Adsorbent capacity of Mn is calculated by Longmuir formula 4,**Fig.5**:
Am = 15, 15 mg/g (y= 7,508x + 0,066) (4)

Gauge adsorbent isotherm and determine maximal adsorption capacity of As and Mn onto some materials

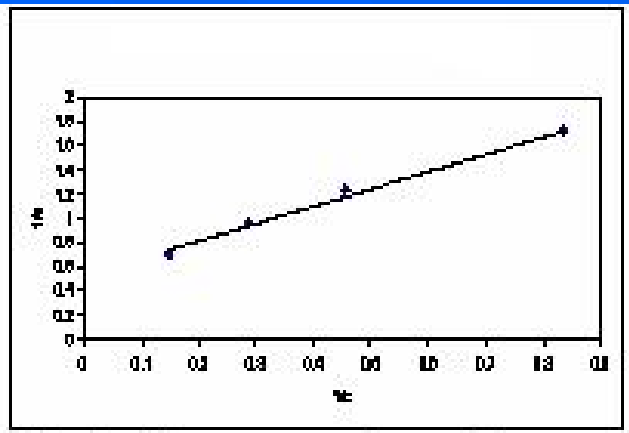


Fig.2: Adsorption isotherm of As into MnO_2

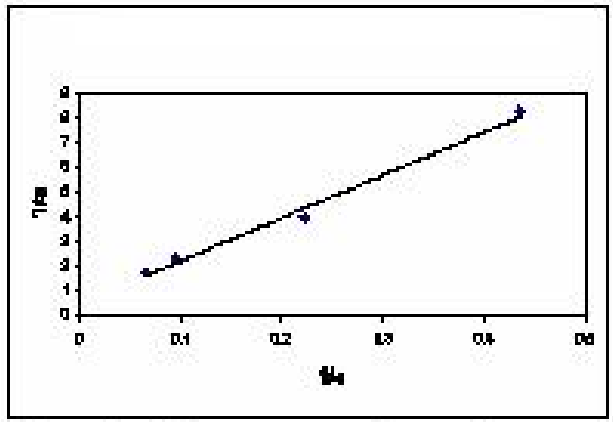


Fig. 3. Adsorption isotherm As into $1\%Fe_2O_3$ diatomite

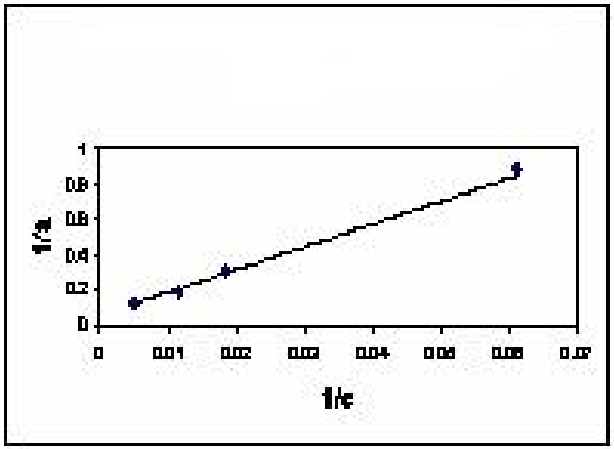


Fig. 4. Adsorption isotherm of MnO_2 for Mn

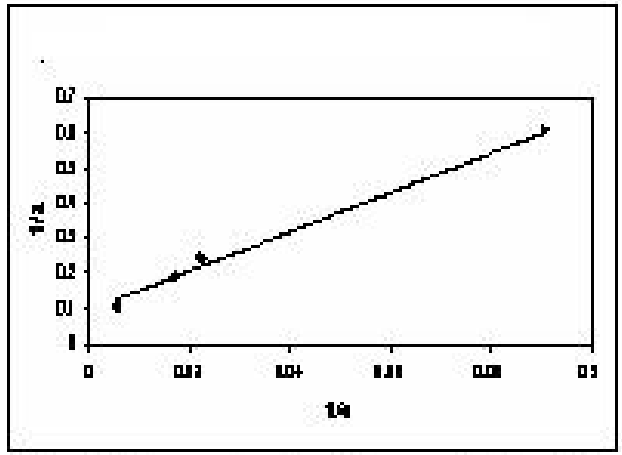


Fig. 5. Adsorption isotherm of Mn into diatomite

CONCLUSION

The adsorptive ability of MnO_2 for manganese removal in underground water by mobile adsorptive method is very good. Using 10 g material, it can treat 1mg/L Mn with the treatment productivity is of 99.9%.This method can not applied to As case

The adsorptive ability of MnO_2 and diatomite ore for arsenic and manganese removal in underground water by statically adsorptive method is excellent. It means MnO_2 and diatomite ores are very good for Mn treatment in the water. Manganese dioxide is not only oxidized but also adsorbent material. Arsenic is well treated by Diatomite due to the high As adsorption capacity of Diatomite.

Those above results proved that natural manganese dioxide, diatomite mineral were potential adsorbent materials which could be applied to treat Mn and As in water source. Using manganese dioxide and diatomite mineral would concurrently treat both Mn and As in the supply water.


Thank you for your attention!