

A Chemical study on the dark colored filters sand  
and its effect on filtration process

دراسه كيميائيه علي رمل المرشحات الداكن اللون واثره في  
عملية الترشيح

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شركة مياه الشرب بالاسكندريه

محطة ك٠٤

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## ملخص البحث باللغة العربية

### ( دراسة كيميائية على رمل المرشحات الداكن اللون واثره في عملية الترشيح )

تحول لون رمال الترشيح من اللون الطبيعي الاصفر الي اللون المتدرج من البني الفاتح الي الاسمر اثار مؤخرًا جدلا حول سبب هذا اللون و أثره حتي ان البعض قد حاول ازالته بغسيل الرمال بحامض الهيدروكليك.

و قد دفعني هذا الي عمل دراسته علي الرمال للتعرف علي سبب هذا اللون و اثره علي عملية الترشيح وهل هو ضار ام نافع ؟

وكان نتيجة الدراسة ان سبب اللون هو امتزاز اكاسيد الحديد و المنجنيز ذات اللون الغامق علي السطح الخارجي لحبيبات الرمال والتي نتجت من اكسدة ايونات الحديد و المنجنيز الذائبة بواسطة الكلور و الاكسجين الذائب في الماء و تحويلهم الي صورة الاكاسيد الغير ذائبة التي امتزت علي سطح حبيبات الرمال و اعطت للرمال لونها الغامق.

و قادني هذا الي الدراسة الثانية وهي دراسة قدرة هذه الاكاسيد علي انتزاع المعادن الثقيلة من المياه و كانت النتائج مدهشه بحيث تبين ان هذه الاكاسيد لها مساحة سطحيه قادره علي امتزاز المعادن الثقيله علي سطحها الخارجي مما يؤدي الي زيادة كفاءة الترشيح بنزع المعادن الثقيله من المياه .

وكان هذا سببا في الدراسة الثالثه لمعرفة مدي تاثير هذه الاكاسيد علي المواد العضويه و قد نتجت الدراسة عن ان الرمال المغطاه بالاكاسيد لها القدره علي تجميع المواد العضويه علي سطحها الخارجي .

اذا نستطيع ان نستنتج من الدراسات السابقه علي رمل المرشحات الداكن انه ذو فائده كبيره في ازالة المعادن الثقيله و المواد العضويه من المياه بواسطة الترشيح.

و لكن لتتم الاستفادة من هذه الرمال يجب عمل اعاده تنشيط لها باستخدام الغسيل بعامل مؤكسد مثل برمنجنات البوتاسيوم او الكلور و ذلك لازالة ما تم امتزازه علي سطح الرمال من معادن ثقيله و مواد عضويه ليعود سطح الاكاسيد قادر علي الامتزاز مره اخري و حتي لا تتم العمليه العكسيه وهي انتزاع المواد الممتزه اثناء الترشيح و نزولها مع المياه المرشحه.

# Qualitative and quantitative studies on the dark color of the Filters sand

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## **Absract**

*Over* along period of using sand in filtration, it has been stained with black and brown color so it was important to identify the reason of this color, this was done qualitatively by investigation for the radicals analytical groups by certain reagents which will precipitate the members of a given group if they were present then those radicals could be identified by confirmatory experiments, and quantitatively by redox and gravimetric analysis. in these work it was proposed that ferrous ions in water were oxidized by the oxidants such as chlorine or dissolved oxygen into ferric ions which were hydrolyzed into insoluble red hydrated ferric oxide also manganese ions were oxidized into the insoluble reddish-brown manganese dioxide were both of them were adsorbed on the filters sand granules surface.

## **Introduction**

The black and reddish brown colors which stained the filters sand over a long period of usage in water treatment plants evolved the necessity of studying the possibilities of adsorption the colored manganese <sup>[1]</sup> and ferric oxides on the filters sand granules. Any soluble manganese and iron in water will be in the form of  $Mn^{2+}$  and  $Fe^{2+}$

as the same as the soluble iron - max. 0.35% - in liquid alum which is used in clarification <sup>[2]</sup>, both on exposure to air or addition of oxidants will be oxidized to the more stable oxidation states of Mn<sup>4+</sup> as a black MnO<sub>2</sub> precipitate <sup>[3]</sup> and Fe<sup>3+</sup> which may hydrolyze to form insoluble red hydrated ferric oxide <sup>[4]</sup>. Elevated levels of these sediments can cause stains in plumbing, laundry, and cooking utensils <sup>[3,4]</sup>. In this work qualitative and quantitative analysis were done which confirmed that manganese and iron oxides were adsorbed on the sand granules surface.

## **Experimental**

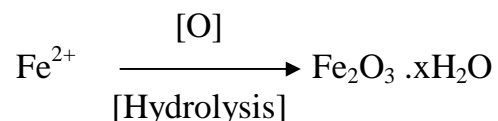
10 gm of sand was treated with conc. Hydrochloric acid which made dissolution to the dark color on it and retained the original color of sand, the concentrated Solution was diluted with distilled water and filtered then qualitative scheme for radicals investigation was done on the filtrate <sup>[5]</sup>, after that quantitative volumetric -redox- <sup>[6]</sup> and gravimetric <sup>[5,7]</sup> analysis were done.

## **Results and discussion**

### **\*Qualitative analysis**

the group 3 reagent for cations investigation NH<sub>4</sub>Cl + NH<sub>4</sub>OH gave a brown gelatinous ppt. which was dissolved in mineral acids and could not be dissolved in excess of the reagent NH<sub>4</sub>OH this indicated that the ppt. was Fe(OH)<sub>3</sub> <sup>[5]</sup>.

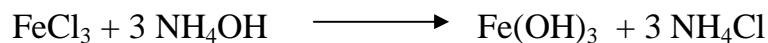
as reported previously <sup>[4]</sup>,



The formed ferric oxide reacted with the conc. HCl and gave the soluble ferric chloride

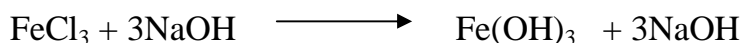


which reacted with the group 3 reagent and gave the brown gelatinous ppt.



This result was confirmed by the following confirmatory experiments <sup>[5]</sup>:

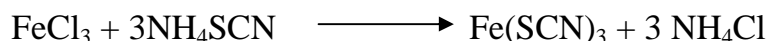
1-Sodium hydroxide: gave a reddish brown ppt.  $\text{Fe}(\text{OH})_3$  which could not be dissolve in excess of  $\text{NaOH}$



2-Sodium phosphate solution: yielded a yellowish white ppt.  $\text{FePO}_4$  which was dissolved in mineral acids but could not be dissolve in acetic acid.

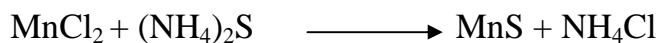
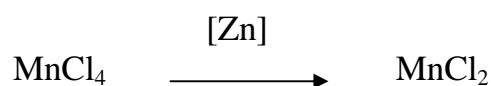
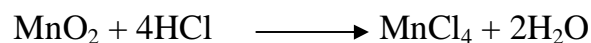


3-Ammonium thiocyanates: formed a blood red coloration due to the formation of ferric thiocyanates



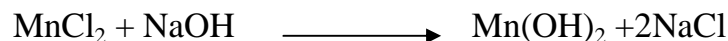
4- Ammonium molybdate : gave phosphoric yellow color indicated the presence of  $\text{Fe}^{+3}$  ions

after that the filtrate was reduced with zinc dust, the resulted solution gave with the group 4 reagent for cations investigation  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + (\text{NH}_4)_2\text{S}$  a buff ppt. which was dissolved in dil mineral acids and acetic acid, this indicated that the ppt. was manganese sulphide <sup>[5]</sup>.

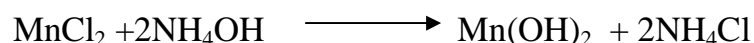


This result was confirmed by the following confirmatory experiments<sup>[5]</sup>:

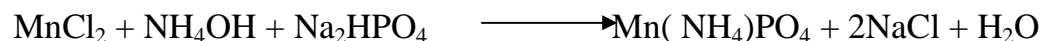
1-Sodium hydroxide: gave a white ppt. of  $\text{Mn(OH)}_2$  which could not be dissolved in excess of the hydroxide.



2- Ammonium hydroxide: formed a white ppt. of  $\text{Mn(OH)}_2$  which could not be dissolved in ammonia.



3- Sodium phosphate solution: gave in the presence of ammonia buff ppt.



The previous experiments confirmed that the filtrate contains manganese and iron ions which have been proposed to be formed from the reaction of the adsorbed ferric and manganese oxides on sand granules with hydrochloric acid.

#### \* Iron Quantitative analysis

##### -Redox analysis

The sand sample was treated with conc. Sulphuric acid then the solution was diluted and the iron ions in solution were reduced by Zn dust to  $\text{Fe}^{+2}$  ions which were oxidized by potassium permanganate in the presence of sulphuric acid<sup>[6]</sup>,



##### -gravimetric analysis

$\text{Fe}^{+3}$  ions were precipitated as  $\text{Fe(OH)}_3$  by ammonium hydroxide then the ppt. was dried and weighted<sup>[7]</sup>.

### **\* Manganese Quantitative analysis**

Manganese ions were reduced by Zn dust to  $Mn^{+2}$  ions which was precipitated as  $Mn(OH)_2$  by ammonia then the ppt. was oxidized by atmospheric oxygen into  $Mn_2O_3$  [5] and dried then weighted.

As a result the detected amount of Manganese dioxid and ferric oxide was in the range of 0.1 gm to 2.2 gm and 0.007 gm to 0.05 gm respectively per 10 gm of the sand sampl.

### **Conclusion**

The qualitative and quantitative analysis for the dark color on the sand, have revealed that the color is due to the adsorption of manganese and iron oxides which were resulted from the oxidation of  $Mn^{+2}$  and  $Fe^{+2}$  ions in water and  $Fe^{+2}$  ions in the added liquid alum by chlorine and dissolved oxygen in water into  $Mn^{+4}$  and  $Fe^{+3}$  ions which were hydrolyzed into the black and reddish brown oxides which adsorbed on sand, hence sand has converted into naturally oxides coated sand.

### **References**

- [1] Mark Eley and Keith Nicholson Environmental geochemistry and health  
1993 15(2/3) page 85
- [2] The Egyptian company for liquid alum standards.
- [3] Standard methods for the examination of water and waste water 21st  
edition page 3-84.
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[6] V Alexeyev Quantitative analysis book page 348

[7] V Alexeyev Quantitative analysis book page 165

# The effect of naturally oxides coated sand on metals reduction

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## **Abstract**

Due to the danger and non economic use of hydrochloric acid in sand color recovery and the change in heavy metals concentration from the clarified to filtered water, and as reported previously that sand has been coated with iron and manganese oxides it was important to make a study on the oxides coated sand to reveal if this oxides are useful or not so a study has done to test the sand ability for metals adsorption. Manganese was tested for adsorption. Adsorption isotherm of manganese on the sand granules, heat of adsorption and the surface area of the coated sand granules have been determined which have revealed that the naturally oxides coated sand have an ability for metal adsorption.

## **Introduction**

The danger and non economic use of hydrochloric acid in sand color recovery, the change in heavy metals concentration after filtration have evolved the necessity of studying the ability of oxides coated sand on the reduction of metals concentration through filtration. Where the adsorbed oxides on sand granules formed an active sites for cations adsorption, where the strong adsorption capacity of manganese and iron oxides for cationic species arises from the electrostatic attraction between the ions and the negative charge on the oxides .

(Crerar et al., 1980) have studied the adsorption properties of manganese oxides and reported that the negative charge increases concomitantly with PH in most natural aqueous environments hence the adsorption increases with PH in the

Order  $Mg < Ca < Sr < Ba < Ni < Zn < Mn < Co < Cu$ .

(Nicholson 1988, 1989) recorded from different sites in Scotland that manganese oxides have deposited from fresh water on fluvial sediments and quaternary gravels. (Buamah, R et al., 2007 ) have studied the adsorptive removal of manganese(II) from the aqueous phase using iron oxide coated sand and reported that manganese adsorption has been increased from PH values 6 to 8 and the adsorption rate decreased after the initial phase due to the saturation of the adsorption sites on the iron oxides coated sand <sup>(1)</sup>. The adsorption properties of the naturally oxides coated sand have been determined which approved the ability of coated sand on metal adsorption.

## **Experimental**

The adsorption isotherm of a metal such as Manganese on the filtration sand was done by adding 10 g of sand into each 6 dry glass-stoppered Erlenmeyer flasks then a series of Manganese sulphate concentrations ( 0.5, 0.4, 0.3, 0.2, 0.1 ) N were prepared and each concentration was added into one flask, those flasks were swirled vigorously at room temperature and only one other flask with concentration 0.4 N was swirled at 44.5 °C, swirling was continued for an hour then the flasks were let to stand over night, after that the solutions were filtrated and their concentrations were measured.

## **Results and discussion**

The adsorption isotherm was achieved by the following data

NO.	C	Log c	x/m	log x/m	Notes
1	0.0929 5	-1.031	0.08403 525	-1.075	At 25 °C
2	0.0422 5	-1.374	0.06738 875	-1.1714	
3	0.0422 5	-1.374	0.05048 875	-1.29	
4	0.0507	-1.294	0.03354 65	-1.47	
5	0.0253 5	-1.596	0.01677 325	-1.77	
6	0.0672 62	-1.170	0.06726 2	-1.1722	At 44.5°C

The adsorption was found to follow freundlich equation with heat of adsorption equal to -0.2145.

From the relationship between the amount of adsorbed manganese sulphate (  $\log x/m$  ) which has adsorbed on sand and the concentration (  $\log c$  ) it was found that by increasing concentration adsorption increases and by calculating number of layers it was found to be more than one layer so it was followed by multilayer formation which indicated that the adsorption is physisorption. This result was insured by the relationship between (  $c$  ) and (  $x/m$  ) which indicated that by increasing concentration, adsorption increased then became constant which indicated monolayer formation then a sudden increase in the curve indicated multilayer formation by the attraction between the first layer and other molecules.

By heating it was noticed that desorption was occurred where the amount of adsorbed molecules were decreased so this physisorption is reversible to temperature.

From the negative value of the heat of enthalpy, the adsorption process is exothermic.

## **Conclusion**

Naturally oxides coated sand at K40 water treatment plant has been approved adsorption ability for metals, hence the ability for heavy metals reduction so there is no need to get rid of this oxides using hydrochloric acid instead that we have to make regeneration and activation for the oxides coated sand to avoid surface saturation and guarantee a continuous metal adsorption .

## **References**

- [1] Mark Eley and Keith Nicholson Environmental geochemistry and health  
1993 15(2/3) page 85

# The effect of naturally oxides coated sand on organic matters

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## **Abstract**

Organic matters ( OMs ) is one of the most disturbing issues in drinking water treatment plants, in this work i wish to prove and make a benefit of the naturally oxides coated sand to be an adsorption media for OMs to make reduction for disinfection by products ( DBPs ), this was done by determining the adsorption isotherm of acetic acid as an example for OMs , heat of adsorption and the surface area on the oxides coated sand granules, this study has shown that oxides coated sand can adsorb OMs from water.

## **Introduction**

OMs in raw water make many problems in water treatment process where if it present in water it makes shielding for turbid particles and surrounding it with negative charge which results in producing repulsion forces between the turbid particles making it difficult for coagulants to be able to coagulate turbidity in water, so to over come this problem -1- the dose of coagulant must be increased such as in alum dose where it must be increased over the optimum dose to decrease the PH of water to make protonation for the OMs and decrease the negative charge of OMs as reported by Davis et al <sup>(1)</sup> hence increase the coagulation performance and OMs reduction -2- using apreoxidant as prechlorination where chlorine is a strong oxidizing agent which oxidizes the negative

functions groups on OMs hence decreases the repulsion forces between turbidity particles and enhance coagulation, but using prechlorination resulted in the formation of DBPs such as haloacetic acids (HAAs) and trihalomethanes (THMs) <sup>(2)</sup> which are considered as carcinogenic compounds<sup>(3)</sup>.

Trying to make reduction for DBPs and making benefit from the charged oxides coated sand. this work studies the ability of oxides coated sand at K40 Water Treatment Plant for OMs reduction by adsorption and electrostatic attraction between different charges on the oxides and OMs.

## **Experimental**

The adsorption isotherm of acetic acid on oxides coated sand was done by adding 10 g of sand- washed and regenerated by 0.1N KMnO<sub>4</sub> - into each 6 dry glass-stoppered Erlenmeyer flasks then a series of acetic acid concentrations ( 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 ) M were prepared and each concentration was added into one flask, those flasks were swirled vigorously at room temperature and only one other flask with concentration 0.5 M was swirled at 35.5 °C, then the flasks were let to stand over night, after that the solutions were filtrated and their concentrations were measured.

## **Results and discussion**

The adsorption isotherm was achieved by the following data

NO.	C g/l	Log c	x/m	log x/m	Notes
1	87,78	1,943	0,04928	-1,307	At 25 °C
2	70,02	1,848	0,039424	-1,404	
3	62,464	1,796	0,036736	-1,430	
4	00,176	1,7	0,027686	-1,008	
5	37,632	1,070	0,020608	-1,686	
6	22,22	1,346	0,018816	-1,720	
7	12,032	1,080	0,009806	-2,006	
8	62,72	1,797	0,034944	-1,406	At 35.5 °C

The adsorption was found to follow Freundlich equation with heat of adsorption equal to -874.8 cal/mol.

From the relationship between the amount of acetic acid ( $\log x/m$ ) which was adsorbed on sand and the concentration ( $\log c$ ) it was found that by increasing concentration adsorption increased and by calculating number of layers it was found to be more than one layer so it was followed by multilayer formation. This result was insured by the relationship between ( $c$ ) and ( $x/m$ ) which showed that by increasing concentration, adsorption has increased then became constant which indicated monolayer formation then another increases have occurred in the curve which indicated multilayer formation by the attraction between the first layer and other molecules this attraction may be due to hydrogen bond formation between the acetic acid molecules of the first layer and the other molecules in the solution.

By heating it was noticed that desorption was slightly occurred in very little amount which indicated that the attraction between molecules is quietly strong which indicated hydrogen bond formation in our case.

From the negative value of the heat of enthalpy, the adsorption process is exothermic.

## **Conclusion**

Oxides coated sand can adsorb OMs from water so we have to make benefit from it and make regeneration for it to be ready for continuous adsorption.

## **References**

- [1] J.A. Davis, R. Gloor, Environ. Sci. Technol. 15 (1981)1223.
- [2] G.L. Amy, M.R. Collins, C.J. Kuo, P.H. King, J. Am. Water Works Assoc. 79 (1987) 43.
- [3] D.A. Okun, J. Environ. Eng. 122 (1996) 453.



## Conclusion and Recommendations

From the previous work we can conclude that filters sand at K40 Water Treatment Plant has been coated with Manganese and iron oxides with average surface area  $57.3 \text{ m}^2/\text{g}$  which generated the ability for Organic matters and metals removal from water.

So the sand became quite similar to the green sand which is artificially manganese or iron oxides coated sand, which is used in removal of iron and manganese from ground water.

But the capacity of adsorption is limited and saturation could occur as reported by (Buamah, R et al., 2007 ) who have studied the adsorptive removal of manganese(II) from the aqueous phase using iron oxide coated sand and reported that manganese adsorption has been increased from PH values 6 to 8 and the adsorption rate decreased after the initial phase due to the saturation of the adsorption sites on the iron oxides coated sand(1).

From this observation we have to make regeneration for the oxides coated sand to keep up its adsorptive power.

Because of the oxides are naturally deposited from water through long filtration term and the difference in water content of organic matters and heavy metals concentration in incoming water. Time of filter usage for adsorption before regeneration has to be determined for each plant separately according to the ability of filters for adsorption and this done by continuously determining the efficiency of filtered water.

As occurred in the new greensand regeneration done by soaking the sand in Potassium permanganate (2% - 3% ) for several hours or Intermittent Regeneration (IR) which means that after the filter has backwashed a dilute solution of Potassium permanganate

is added to the media and left in contact for several minutes then the filter is backwashed again from the excess of Potassium permanganate(2).

Potassium permanganate acts as a strong oxidizing agent which oxidizes adsorbed metals and organic matters which have been adsorbed on the oxides coated sand so we can also use chlorine in the regeneration process.

It's recommended for the purpose of this work not to use intermediate chlorine which is injected before filtration and justify by the residual chlorine from clarifiers because excess of chlorine will make desorption and leaching of adsorbed metals and organic matters into drinking water, and this may be the reason of increasing manganese, iron and disinfection by products in drinking water in the past.

Primarily and finally thanks to allaa who helped and gave me the ideas of this research and I wish for this work to be helpful and a step for improving water quality at water treatment plants.

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Virginia University