



## ABATEMENT OF FREE CHLORINE FROM WATER USING KAOLINITE CLAY

Mahmoud M. Kamel and Ahmed M. Ismael

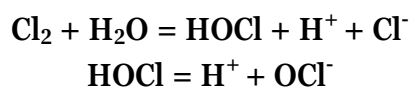
Chemistry Department, Faculty of Science, Al-Azhar University (Assiut)

### ABSTRACT :

Solid sheets of kaolinite clay exhibit a good affinity towards deduction of free chlorine and hence rectifying water. Initially, results of chlorine abatement by inactivated kaolinite sheets show a lower uptake percent. As far as the samples are activated the uptake percent of chlorine increases given high values according to the initial concentration of free chlorine. Dipping time of the sample on water as well as the firing temperatures used for preparing the kaolinite samples are significant factors for the chlorine uptake percent. Through the entire results, the uptake mechanism of free aqueous chlorine by kaolinite clay is based on sorption. The sorption includes physical adsorption (Freundlich isotherm) and absorption due to the pores in sample surface. As far as sorption takes place, the surface plays an outstanding effect for decomposition of HOCl either by catalytic effect of some cations already present in kaolinite structure or by redox effect.

### INTRODUCTION:

Chlorine is mostly used in the disinfection of drinking water supplies, sewage, and swimming pool water. It readily combines with chemicals dissolved in water, microorganisms, small animals, plant material, tastes, odors, and colors. However, disinfection of water with chlorine leads to the formation of trihalomethanes (THMs)<sup>[1,2]</sup> which are associated with adverse health effects. The chlorine that does not combine with other components in the water is free (residual) chlorine which is available for continuous disinfection. Free chlorine is defined as the concentration of residual chlorine in water present as dissolved gas (Cl<sub>2</sub>), hypochlorous acid (HOCl), and/or hypochlorite ion (OCl<sup>-</sup>). The three forms of free chlorine exist together in equilibrium<sup>[3,4]</sup>.



Their relative proportions are determined by the pH value and temperature. At 25°C when the pH is between 2 and 7, the equilibrium is in favor of HOCl. As the pH falls below 2, the predominant form of the chlorine is Cl<sub>2</sub>. At a pH of 7.5, HOCl and OCl<sup>-</sup> are about equal, and as the pH goes above 7.5, increasing proportions of OCl<sup>-</sup> are present<sup>[5]</sup>. The excess amount of free chlorine in drinking water causes a risk of adverse health effects, in addition to the unpleasant taste of water.

Ion exchange and adsorption are such methods that can be so far used for elimination of several water pollutants. Clay is a natural material for good adsorption as well as an ion exchanger. The ion exchange properties of clays have been intensively studied<sup>[6]</sup>. The mechanism

by which the adsorption process that takes place by clay is concerned mainly with the nature of forces acting between the adsorbed material and the adsorbent. According to the forces involved, three basic kinds of adsorption can be distinguished as; physical adsorption, chemisorption<sup>[7]</sup> and electrostatic adsorption<sup>[8,9]</sup>. Our concern is mainly reducing the economical cost of adsorption process and using cheaper adsorbents having no effect on physical and chemical characteristics of the solution. Since kaolinite clay has been previously chosen for adsorption of some pollutants [Pb(II), Cu(II), Fe(III), Mn(II) and Zn(II)]<sup>[10]</sup>, it is concerned for an abatement of chlorine from water.

## EXPERIMENT:

The typical kaolinite clay sample which was previously used for adsorption of some heavy metals pollutants<sup>[10]</sup> was concerned for preparation of two solid sheet samples. The specifications of sample are 4cm. length, 4cm width and 1cm thickness for the first sample whose weight is 50 g while the second one is 8cm. length, 8cm. width and 1cm thickness and weights about 100g.

Investigation of free chlorine concentration was carried out using spectrophotometer type of DR/2010, Hach company, USA. Alkalinity was carried out using EPA's sampling and analysis methods, method 310<sup>[11]</sup>. The total hardness of water was determined by the procedure of method Who/M/26.R1<sup>[12]</sup>.

Bi-distilled water is used for the analytical purposes.

## RESULTS AND DISCUSSION:

Basically, the association between a gas and a solid surface can be either physical or chemical in character. Physical or Van der

Waals adsorption occurs to some extent whenever a gas in contact with a solid. However, the type of adsorption (chemisorption) is substantial when the gas and the solid can react chemically.

Physical adsorption is characterized by low heat of adsorption ( $\leq 5$  Kcal/mol). Moreover, the obtained equilibrium between solid and gas is reversible and considerably varies with temperature and pressure changes. This adsorption is solely more significant for gasses that boil above 200 K, hence large amounts would be adsorbed at normal temperatures and they persist on solid surfaces. Virtually, the boiling point ( $T_b$ ) of chlorine at 1atm equals to -34.6°C which is below of the environmental temperatures<sup>[5]</sup>. Thus we would expect that the uptake of an aqueous free chlorine by the fired solid kaolinite clay is achieved mainly by physical or Van der Waals adsorption. The availability of free chlorine uptake by the fired kaolinite clay and all influencing factors are examined.

### Effect of dipping time on the uptake of free chlorine by fired kaolinite clay:

Table (1) shows the effect of dipping time on the uptake of free chlorine by the two different areas or weights inactivated solid kaolinite sheets [sample one; 4cmx4cmx1cm, 50g, and sample two; 8cmx8cmx1cm; 100g]. It is obvious that the uptake percent of chlorine increases as increasing time. The data in Table (1) also clearly indicate that the uptake increases markedly through the first 5 and 10 minutes regarding the sample two and sample one respectively. Although, the uptake value becomes a maximum (48%) after one hour for both samples, through the first 5 minutes, the sample two exhibits nearly the double response of chlorine uptake in comparing with that of the

sample one. Exceeding that time (5 min), the double uptake response of the sample two diminishes until to become the same value of that of the sample one. Moreover, the rate of the

uptake by samples one and two becomes low after 10 and 5 minutes respectively.

Table (1): Values of free chlorine uptake by solid kaolinite clay at different dipping times

Time	C <sub>0</sub> mg/l	C <sub>c</sub> mg/l	X mg/g	Uptake %
<b>Sample one</b>				
5 sec.	2.5	2.44	0.06	2.4
15 sec.	2.5	2.41	0.09	3.6
1 min.	2.5	2.39	0.11	4.4
5 min.	2.5	2.13	0.37	14.8
10 min.	2.5	1.93	0.57	22.8
15 min.	2.5	1.82	0.68	27.2
30 min.	2.5	1.47	1.03	41.2
60 min.	2.5	1.3	1.2	48
<b>Sample two</b>				
5 sec.	2.5	2.37	0.13	5.2
15 sec.	2.5	2.31	0.19	7.6
1 min.	2.5	2.25	0.25	10
5 min.	2.5	1.7	0.80	32
10 min.	2.5	1.59	0.91	36.4
15 min.	2.5	1.5	1.0	40
30 min.	2.5	1.4	1.1	44
60 min.	2.5	1.3	1.2	48

Where:

C<sub>0</sub>=Initial concentration of free chlorine

C<sub>c</sub>=Final concentration of free chlorine .

Sample one is 50g (4cmx 4 cmx1cm), sample two is 100g (8cmx8cmx1cm).

pH = 7.4

Volume of water = 1liter of tap water.

The fired temperature of sample = 200°C.

The quantity of free chlorine in one liter of water as a blank experiment is estimated after one hour for each opened and closed vessels without kaolinite samples.

Results show that the percentage of the free chlorine elimination are 27% and 24% for opened and closed vessels respectively. This observation assures that the highly uptake of free chlorine (48%) is currently due to the influence of kolinite clay.

Besides, the important effect of the current kaolinite samples for deduction of the free chlorine quantity, it is crucial to investigate the specifications of water before and after using

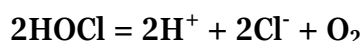
the sample two (8cmx8cmx1cm; 100g). Table (2) illustrates the observed changes in water specifications after dipping the sample two for 15 and 60 minutes in one liter of water.

Table (2): Variation of water specifications after 15 and 60 minutes dipping times

Specifications	Raw water	After dipping sample for	
		15 min.	60 min.
Chlorides( mg/l)	16	30	60
Alkalinity (mg/l)	100	112	120
Total Hardness (mg/l)	96	110	120
Conductivity( $\mu$ s)	290	330	380
pH	7.4	7.25	7.1

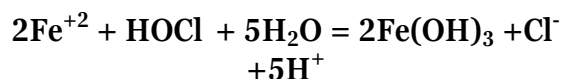
The observable relative minor changes regarding total hardness may be due to

releasing of some calcium and/or magnesium cations from sample. The chloride values of distilled water after dipping the same sample for 5 and 15 minutes are estimated. Results show that no change concerning chloride values of distilled water, this absolutely prove that the observable increase of chloride values is attributed to presence of free aqueous chlorine. As mentioned previously, aqueous chloride first reacts to form hypochlorous acid, which then dissociates to form hypochlorite ion. The formed hypochlorous acid is removed from solution in several ways. It may volatilize directly and it is decomposed by energy of light especially ultra violet light<sup>[13]</sup>.



The acid is also consumed through redox reactions. It rapidly oxidizes various reduced inorganic species such as S(-II), Mn(II), Fe(II), and (NO<sub>2</sub>)<sup>[13]</sup>.

The oxidation of Fe<sup>+2</sup>, for example, occurs as follows:



Through the results of blank experiments, we certainly ignore the effect of direct volatilization of HOCl<sup>0</sup> as a responsible factor for the high uptake results. An increase of chloride ions as shown in Table (2) is practically due to the decomposition of aqueous HOCl.

Hence, we emphasis that the high uptake of aqueous free chlorine is essentially due to the effect of the solid sheets of the kaolinite clay.

Similarly; the uptake of SO<sub>2</sub> and NO<sub>2</sub> by soil and clay is also enhanced by the presence of moisture<sup>[5]</sup>, as these gases are quite soluble and react with water. A slightly decreased of pH is due to the formation of protons and chloride ions that are extremely weak conjugate bases of strong HCl (pK<sub>a</sub> = -3)<sup>[13]</sup>.



### Effect of firing temperature of kaolinite clay on the uptake process:

Several samples (8cmx8cmx1cm, 100g) have been prepared and fired at four different temperatures(100, 200,300 and 400°C) then the corresponding values of chlorine uptake are examined. Table (3) and Fig.(1) show that the best firing temperature of kaolinite clay is 200°C.

Table (3): Variation of free chlorine uptake with samples obtained by different firing temperatures

Firing temp. (°C)	C <sub>0</sub> mg/l	C <sub>e</sub> mg/l	X mg/g	Uptake %
100	2.07	1.17	0.9	43.48
200	2.07	1.07	0.99	47.82
300	2.07	1.21	0.86	41.55
400	2.07	1.31	0.76	36.71

Where:

C<sub>0</sub>=Initial concentration of free chlorine

C<sub>e</sub>= Final concentration of free chlorine. Sample is 100g, (8cmx8cmx1cm).

pH = 7.4

Volume of water = 1liter of tap water.

**Effect of concentration on the uptake of free chlorine by fired kaolinite clay:**

The relationship between the uptake amount of free chlorine per gram, (X/m) against the equilibrium concentration [C] on a log-log scale is examined according to the following general equation<sup>[14]</sup>:

The amount sorbed per gram clay

$$(X/m) = (C_0 - C_e) \times V/m$$

where:

C<sub>0</sub> : is the initial concentration of free chlorine (mg/l)

C<sub>e</sub> : is the final concentration of free chlorine (mg/l)

V : is the volume of the aqueous phase (ml),

m : is the weight of the clay sample (g).

Hence, X/m = K C<sup>1/n</sup>

$$\log (X/m) = \log (K) + 1/n \log (C)$$

Where K and 1/n are empirical constant depending on the nature of the aqueous and the solid phase used at constant temperature.

Table (4) and Fig. (2) show a straight linear relationship suggesting that the uptake process can be described by a Freundlich type of adsorption isotherm. Results are quite consistent to the fact that equilibrium has established between the free chlorine and the solid sample and that only monomolecular layer of gas molecules has been adsorbed. This result is generally applicable when environmental temperatures are above the normal boiling point of gases and vapours<sup>[5]</sup>.

Ultimately, it can be seen from Table (4) that the uptake values [48%, 50.2%, 55.55%, 59%, 65.55%] increases as the initial concentration becomes more [2.5, 3.6, 4.5, 6.1 and 9 mg/l].

Table(4): Variation of logarithmic concentration of free chlorine with the amount of chlorine adsorbed per gram of fired kaolinite clay

C <sub>0</sub>	C <sub>e</sub>	X	Log (C)	X/m = (c <sub>0</sub> -c <sub>e</sub> )*V/m	Log (X/m)
2.5	1.3	1.2	0.114	2.5-1.3*1000/100 =12	1.079
3.6	1.8	1.8	0.255	3.6-1.9*1000/100 =18	1.255
4.5	2.0	2.5	0.301	4.5-2.0*1000/100 =25	1.398
6.1	2.5	3.6	0.398	5.6-2.5*1000/100 =36	1.550
9.0	3.1	5.9	0.491	9.0-3.1*1000/100 =59	1.771

**Rinsing and reusability of the fired kaolinite clay:**

The used sample is rinsed three times as well as immersed for one hour using distilled

water. Table (5) shows the variation of distilled water specifications after rinsing and dipping the used sample.

Table (5): Variation of distilled water specifications after rinsing the used sample

Specification	Pure distilled water	After 1 <sup>st</sup> wash	After 2 <sup>nd</sup> wash	After 3 <sup>rd</sup> wash	After 1 hr. dipping time
Chlorides	4	6	8	12	28
Alkalinity	4	6	6	8	12
Total hardness	2	4	6	6	48
Conductivity	4	8	14	20	100
pH	6.89	7.3	7.35	7.4	7.4

Results imply that beside cleaning of external surface of sample the process involves rinsing the interior parts releasing the decomposition product of HOCl.

The clean wet sample is further used for illustration of its reusability. Table (6) surely

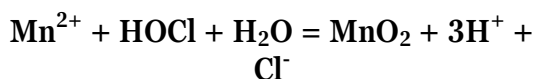
testify the reusability of sample for chlorine uptake. The uptake value for the cleaned sample after one hour (47%) is nearly close top that (49.33%) obtained for the first use sample, at initial chlorine concentration of 3mg/l.

**Table (6): Free chlorine uptake by rinsed sample of kaolinite clay**

Time	C <sub>0</sub> (mg/l)	C <sub>e</sub> (mg/l)	X (mg/g)	Uptake %
Sample two				
5 sec.	3	2.87	0.13	4.3
15 sec.	3	2.81	0.19	6.3
1 min.	3	2.71	0.29	9.6
5 min.	3	2.1	0.90	30.0
10 min.	3	1.97	1.03	34.33
15 min.	3	1.86	1.14	38.0
30 min.	3	1.74	1.26	42.0
60 min.	3	1.50	1.40	47.0

### Activation of Fired Kaolinite sample:

Activation process of the clay is very important since it may affect the uptake process. Activation of fired kaolinite clay has been occurred by mixing and packing the appropriate weight of clay powder with solution of manganese sulphate (8 M)<sup>[10]</sup>. After drying and firing the sample at 200°C, the free chlorine uptake value is studied. Sample shows a high uptake percent about 86.2% after one hour in comparing to that (48%) of in activated one, in case of initial chlorine concentration of 4.2g/l . This high value of uptake as expected is presumably due to some redox reaction between HOCl and Mn(II)<sup>[13]</sup>. The rate of Mn(II) oxidation increases with increasing pH. Since the pH of water is slightly alkaline (7.4) and HOCl is a strong oxidizing agent the following reaction may be run<sup>[15]</sup>:



The other possible suggestion based on (1) Mn(II) is a good catalyst for decomposition of HOCl.



Through the entire results, the uptake mechanism of free aqueous chlorine by kaolinite clay is based on sorption. The sorption includes physical adsorption and absorption due to the pores in sample surface. As far as sorption takes place, the surface plays an outstanding effect for

decomposition of HOCl either by catalytic effect of some cations already present in kaolinite structure or by redox effect. This conclusion is absolutely evidenced by the idea of the commercial KDF filter which is comprised of 50% copper and 50% zinc. It removes free chlorine by reversing the electrochemical process that originally separated the chlorine from sodium in a brine solution. This is how it works: Copper and zinc are dissimilar metals. The tension between these metals generates between 900 and 1100 millivolts of electricity as water passes through it. This is enough electricity to generate a galvanic charge which re-establishes the original electrolytic environment that created the free chlorine. The chlorine is able to recombine with a metal ion, normally zinc, to form a soluble zinc chloride which washes out of the filter and is harmless to humans<sup>[16]</sup>.

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## إنقاص الكلور الحر من المياه باستخدام طفلة الكاولينيت

محمود محمد كامل، أحمد محمد إسماعيل

قسم الكيمياء - كلية العلوم - جامعة الأزهر (أسيوط)

تظهر الشرائح الصلبة من طفلة الكاولينيت فاعلية عالية نحو إنقاص الكلور الحر ومن ثم تنقية المياه أوضحت النتائج الأولية لاستخدام العينات غير النشطة نسبة صغيرة من إنقاص الكلور الحر. ولقد ازدادت نسبة إنقاص الكلور معطية قيم عالية معتمدة على التركيز الابتدائي في حالة العينات المنشطة. وقد أظهرت الدراسة أن عملية الإنقاص تعتمد على كلا من زمن الغط، وكذلك حرارة الحرق للعينات. ومن خلال النتائج الكلية وجد أن عملية إنقاص الكلور الحر تعتمد على الامتزاز الفيزيقي الذي يتبع نظام (Freundlich isotherm)، وكذلك الامتصاص خلال الثقوب السطحية للعينات، ويتبع ذلك عملية تحلل لحمض (HOCl) خلال التأثير الحفزي لبعض الأيونات المعدنية المتواجدة في تركيب العينة أو قد يتم ذلك التحلل من خلال تفاعل الأكسدة والاختزال .