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Remediating Free Chlorine from Aqueous Solution Using Hydrous Zirconium Oxide Impregnated Carbons

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Abstract

In this study, a commercially activated carbon was loaded with 10 and 25 wt% hydrous ZrO_2 followed by heat treatment at 393K in an attempt to improve its adsorption capacity towards the removal of free chlorine from water. The tested carbons were characterized by SEM, N_2-adsorption –desorption, iodine number, FTIR and pH_{PZC} techniques. The effects of adsorbent dose, contact time, initial free chlorine concentration and pH on the removal performance of free chlorine from water were studied. Loading the original carbon with 10 and 25 wt% hydrous ZrO_2 led to reduce its S_{BET} area as well as its iodine number. The same trend was also found for the measured values of pH_{PZC}. The removal performance of free chlorine was found to increase with decrease the initial solution pH. The equilibrium data fit well the Langmuir isotherm. Loading with hydrous ZrO_2 increased to a great extent the removal of free chlorine from water. The monolayer adsorption capacities of the two loaded carbons are 32.7 and 49.5 mg/g which were 133.6 and 253% than that obtained by the original carbon. The surface chemistry of the carbons and solution pH were found to play a decisive role in the removal performance of free chlorine rather than the carbon texture characteristics.

Keywords: Commercially activated carbon; Hydrous ZrO_2 loading; Surface properties; Free chlorine removal

Introduction

Chlorination is the process of adding the element chlorine to water as a method of water purification. Chlorine gas and chlorine compounds such as sodium hypochlorite, chlorine dioxide and calcium hypochlorite are commonly used for this purpose. In water, they hydrolyze instaneously to hypochlorous acid:

$$Cl_2+H_2O \rightarrow HOCl+HCl$$

$$NaOCl+H_2O \rightarrow HOCl+NaOH$$

$$Ca\ (OCl)_2+2H_2O \rightarrow 2HOCl+Ca(OH)_2$$

Hypochlorous acid dissociates in water to hydrogen ions and hypochlorite ions:

$$HOCl \leftrightarrow H^+ +OCl^-$$

Which is referred as free available chlorine (FAC) or free residual chlorine (FRC)? Chlorine is a powerful oxidizing agent, able to penetrate cells and act on vital cellular substance, killing microorganisms, thereby preventing waterborne diseases. The chlorine that is not used is called free residual chlorine. There are many health concerns regarding residual chlorine in water. This is mainly because chlorine is not naturally needed by the body and tends to inactivate enzymes [1]. Furthermore residual chlorine reacts with ammonia, amine, amino acid, etc. forming chloramines, which alters characteristics of the final product such as taste and odor. Moreover chlorinated water contains trihalomethanes which led to increase risk of cancer as well as damage to heart, lung, kidney, liver and central nervous system.

In the same context, the majority of water desalination plants currently in operation employ membrane in reverse osmosis processes [2]. These membranes undergo degradation processes due the presence of free chlorine released from hypochlorite ions and hypochlorous acid. This topic is of significant interest to researchers in the field of water treatment as polyamids based membranes becomes irreversible damaged by the presence of the excess of free chlorine decreasing thus their performance [3-7]. These concerns inform the need for an effective means of water dechlorination after disinfection at low cost. In many water purifiers, the most common means of decomposing the residual chlorine is the use an oxidation-reduction processes with calcium sulphate or ascorbic acid. Furthermore the removal of residual chlorine by a metal, such as copper, zinc, lead, and iron has also been reported [8-10]. Dechlorination by activated carbon is also extremely effective and area reliable [11-13]. The performance of activated carbon is indicates by its adsorptive characteristics which is derived from the well-developed porous structure and large specific surface area of the carbon [14-17]. Another important factor is the surface chemistry of the carbons, particularly in case of removal of specific adsorbate. Dechlorination capacity of the carbon is determined not only by normal adsorption parameters that occur for organic compound removal but also by other considerations. It has been reported that the residual chlorine was removed by the oxidation-reduction reaction between the carbon surface and the residual chlorine and the pH and the temperature of solution influenced the removal performance of the free chlorine [18]. At present, many investigations are directed towards modifying the chemical nature of the carbon surface in order to develop new carbons capable of coping with new problems and recent developments [19].

In the last decade zirconium based sorbents have also received increasing attentions due to their high affinities to fluoride and relatively lower material costs. These sorbents include nanoscale zirconium-based sorbent [20], hydrous ZrO_2 [21], Fe (III)-Zr (IV) hybrid oxide [22] and zirconium phosphate [23], etc. Due to their importance and versatility, the co-existence of hydrous ZrO_2 as a loading material on the carbon surface may provide a good sorbent for the removal of some pollutants from aqueous solution. In this context

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a commercial steam activated coconut shell based carbon was loaded with hydrous zirconium oxide in order to change its surface chemistry as well as its textural properties. The adsorption performance of activated carbon before and after loading with hydrous ZrO_2 was examined. Several factors affecting this process are considered and the nature of interaction between the activated carbon surface chemistry and adsorbate species was discussed.

Experimental Methods

Adsorbents

The base adsorbent used in the present investigation was commercially available granular activated carbon made from coconut shell (Type DGF 0.5-2.5 AW, RUTGERS Carbo Tech). This carbon was repeatedly boiled with de-ionized water, dried overnight at 120°C and allowed to cool in a desiccator and kept in tightly closed bottle, this was referred to as OC in the study. Two other carbons containing 10 and 25 wt% of hydrous zirconium oxide were obtained as follows: 100 gm of the commercial carbon (OC) was suspended in a 250 ml of 0.5N HCl solution containing the appropriate amount of $ZrOCl_2.8H_2O$. An aqueous solution of 1N NH_4OH was added to the previous solution with vigorous stirring until complete precipitation (pH ≈ 10). The resulting material was separated by filtration, after 24 hr. washed for several times with 2% NH_4Cl solution and then with hot deionized water till free from chloride ions and dried overnight at 120°C. The two carbon samples were referred to as OCZI and OCZII respectively. Only samples collected between 0.5 mm to 1 mm were used in this investigation.

Characterization of the tested carbons

Surface morphology: Scanning electron microscopy (SEM) was used to visualize sample morphology using surface morphology JSM-6510LV scan electron microscope.

Textural properties: For this purpose, adsorption isotherms of N_2 at 77K were determined using an Autosorb Quanta chrome instrument (Nova 3200e). Spcific surface area (S_{BET}, m^2/g) was determined by applying the BET equation, total pore volume "V_p" (ml/g) was evaluated from liquid nitrogen held at $P/P^0=0.95$, while the average pore radius ($\bar{r}$) was obtained from the relationship, $\bar{r}=2V_p/S_{BET}$. An additional information was obtained by applying the α_s method based on the adsorption data on non-porous carbon [24]. From a plot of V_a versus α_s (at same relative pressure), it was possible to calculate total surface area (S_t^{α}) from slope of the linear section connecting to the origin; the non-micro porous surface area (S_n^{α}) was obtained from slope of the linear section connecting latter points; micro pore volume (V_{mic}^{α}) from intercept of latter line with the V_a- axis. An estimate of mesopore volume was calculated from $V^{\alpha}_{meso}=V_p-V_{mic}^{\alpha}$ assuming negligible volume due to macropores and $S^{\alpha}_{micro}=S_t^{\alpha}-S_n^{\alpha}$.

Iodine number: The iodine number "q_{iodine}" (mg/g) of activated carbon was obtained at 25 ±1°C on the basis of the Standard Test Method, ASTM designation D4607-86 [25] as following: 0.1 gm of activated carbon was placed in a dry glass flasks tightly covered with Teflon caps. The sample in the flask was fully wetted with 10 cm^3 of 5 wt% HCl. 100 ml of 0.1 mole/L iodine solution was poured into the flask and contents were vigorously shaken for 30S. After rapid filtration 50 ml of the solution was titrated with 0.01M sodium thiosulfate solution until the solution became pale yellow, then 2 ml of starch indicator solution (1 g/L) was added and the titration was continued with $Na_2S_2O_3$ until the solution became colorless. The concentration of iodine in the solution was thus calculated from the total volume of $Na_2S_2O_3$ used and the volume of dilution factor.

IR spectroscopy analysis: The surface chemical nature of the investigated carbons was studied by FTIR spectroscopy. The FTIR spectra of the tested carbons were recorded between 400 and 4000 cm^{-1} in Jasco 410 FTIR spectrometer using KBr pellet containing 0.1% of carbon sample. The pellet was dried overnight at 100°C before the spectrum was recorded.

pH_{PZC} determination: The pH_{pzc} is the pH on zero point charge, which is the point at which the net charge of the adsorbent is zero. The procedure of pH_{pzc} determination is described as follows [26]: aliquots with 50 cm^3 of 0.1M $NaNO_3$ solutions were prepared in different flask. Their pH values were adjusted to the value between 2 and 12 with the addition of 0.01M solutions of HNO_3 or NaOH. When the pH value was constant, 0.2 gm of activated carbon sample was added to each flask and it was shaken for 48 h at 25 ± 0.1°C. The final pH was measured using pH meter "Fisher 800". The pH_{pzc} value is the point where the curve pH_{final} versus pH_{intial} crosses the line $pH_{intial}=pH_{final}$.

Removal of residual chlorine by tested carbons: The test solutions were prepared from a sodium hypochlorite solutions of known concentrations. Adsorption experiments were carried out by adding a known mass of carbon sample to glass flasks containing 50 ml of test solutions. The glass flasks containing the solution and carbons were tightly covered with Teflon caps and then placed in thermostatic shaker water bath at controlled temperature of 25 ± 0.1°C. The pH was measured using a pH meter (Fisher 800). The initial and equilibrium concentrations of residual chlorine were determined using a colorimeter kit supplied by Hach company (Loveland, Co-USA). The kit based on the principle of colorimetric method [27] by oxidation of N, N-diethyl-p-phenylen-diamine (DPD). The amount of free chlorine adsorbed on the carbon sample (q_e mg/g)was determined from the following:

$$q_e=(C_o-C_e)V/m \tag{1}$$

Where C_o, C_e are the initial and equilibrium concentrations (mg/l) respectively, V, is the volume of the solution (L) and m is the mass of carbon (g).

Results and Discussion

Characteristic of adsorbents

Textural properties: The adsorption isotherms of nitrogen at 77K on OC, OCZI and OCZII carbons are shown in Figure 1. The adsorption isotherm of OC carbon, Figure 1a, presented essentially a type I shape according to the IUPAC classification with a well-developed sharp "Knee" at low relative pressure that tend to become almost parallel to the pressure axis at high pressures which indicates an essentially microporous character [28]. While the adsorption isotherms for OCZI and OCZII carbons, Figures 1b and 1c respectively showed combined characteristics between type I at very low relative pressures and type II at high p/p^o values, disclosing the simultaneous presence of micropores (<2 nm) and mesopores (2-50 nm). This was confirmed by the presence of desorption hysteresis loop (H_3/H_4 type), associated to slit-shaped pores [29]. The α_s plots (not illustrated) present two well defined linear regions, both with positive interception and a breakpoint at $\alpha_s \sim 0.8$ for all samples indicating thus the presences both types of micropores; ultra micropores (width between 0.3 and 0.72 nm) and super micropores (width between 0.72 and 2 nm) [30].

The textural parameters of the three carbon samples obtained from the interpretation of their nitrogen isotherm are summarized in Table 1. By comparing these parameters, It is clear that, the S_{BET} values are slightly

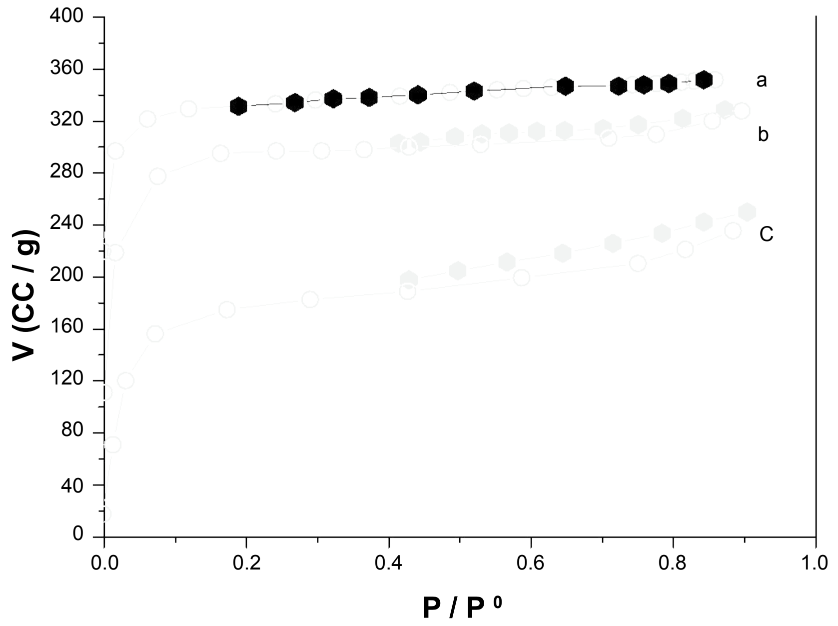

Figure 1: Adsorption – desorption isotherms of N_2 at 77 K for (a) OC, (b) OCZI and (c) OCZII carbons.

Sample	S_{BET} (m^2/g)	V_T (ml/g)	$\bar{r}$ (Å)	S_T^{α} (m^2/g)	S_{mic}^{α} (m^2/g)	S^{α}_n (m^2/g)	V_{micro} (ml/g)
OC	959	0.55	11.8	926	926	--	0.51
OCZI	840	0.49	11.5	800	754	46	0.42
OCZII	526.5	0.361	13.7	490	381	109	0.32

Table 1: Textural parameters of the Tested carbons.

higher than that estimated by the α_s- method (<5.0%). Total surface area containeously decreased by loading OC carbon with hydrous zirconium oxide, accompanied by a decrease in micropore surface area and an increase in mesopore surface area, showing that some modifications in porosity, resulting in small pore widening where mesopores are enhanced and non-microporous areas raised to around 109 m^2/g.

SEM micrographs and IR spectra: In Figure 2 shows SEM micrographs of commerically activated carbon”OC” and those loaded with 10 and 25 wt% hydrous zirconium oxide “OCZI andOCZII” respectively. In case of OC sample Figure 2a. The image indicates that the individual paticles are fractal-like shape and displayed various kinds of porosity, while that for OCZI sample Figure 2b are pitted and fragmented with the presence of fine particles of hydrous zirconium oxide deposited on the carbon surface. On the other hand SEM image of OCZII sample (Figure 2c) shows small agglomeration of hydrous zirconium oxide particles irregular in the shape and randomly distributed on the external surface of the original carbon.

In Figure 3 shows the FTIR spectra of the tested carbons. This Figure indicates that the three carbons showed abroad band in the range 3000-3500 cm^{-1}. This band together with the weak one appeared at 1620 cm^{-1} could be ascribed to stretching vibration of hydroxyl groups involved in hydrogen bonding probably participating with water adsorbed molecule on the carbon. The two bands were appeared more intense in the spectra of OCZI and OCZII carbons. Two other bands were observed in the spectrum of OC sample at 1095 and 890 cm^{-1} which can be assigned to in-plane bending of aromatic ring C-H bond and to out plane of alkene =C-H bending respectively [31]. The OC spectrum showed also strong band at 1465 cm^{-1} which can assigned to scissoring vibration of $-CH_2$ group or to in-plane of H- bonded hydroxyl group. Two new weak bands were observed in the spectra of the hydrous zirconium oxide loaded carbons, i.e., OCZI and OCZII samples at 1384 and 1565 cm^{-1}. The band located at 1384 cm^{-1} was assigned to bending vibration of Zr-OH group, while that located at 1565 cm^{-1} was assigned to Zr-OH vibration [32,33].

pH, pH_{pzc} and iodine number measurements: It has been reported that the pH_{pzc} depends on the electronic and chemical properties of the functional group located on the surface of activated carbon and also is a good indicator of these properties. In this context Faria et al. [34] established that

(i) at $pH<pH_{pzc}$, the surface global charge of the solid is mostly protonated and hence positively charged,

(ii) at $pH=pH_{pzc}$, the surface presents equal positive and negative charges, and

(iii) at $pH>pH_{pzc}$, the surface global charge of the solid is mostly deprotonated then negatively charged

The pH values of aqueous suspensions of the three carbons along with their pH_{pzc} values (as obtained from Figure 4) are listed in Table 2. It is clear that commercial activated carbon “OC” used in this work has basic character with pH and pH_{pzc} values of 9.1 and 9.4 respectively. The two values were found to decrease continuously as a result of loading “OC” carbon with two different amount of hydrous zirconium oxide, suggesting that loading OC carbon with hydrous zirconium oxide could modify the surface chemistry of activated carbon.

The Table 2 shows also the values of iodine number measured for the tested carbons. Iodine number is an indicator of the quality of an activated carbon. As can be seen from Table 2 all carbons have iodine numbers larger than 500 mg/g, the minimum iodine number recommended by the American Water Works Association (AWWA), for use of an activated

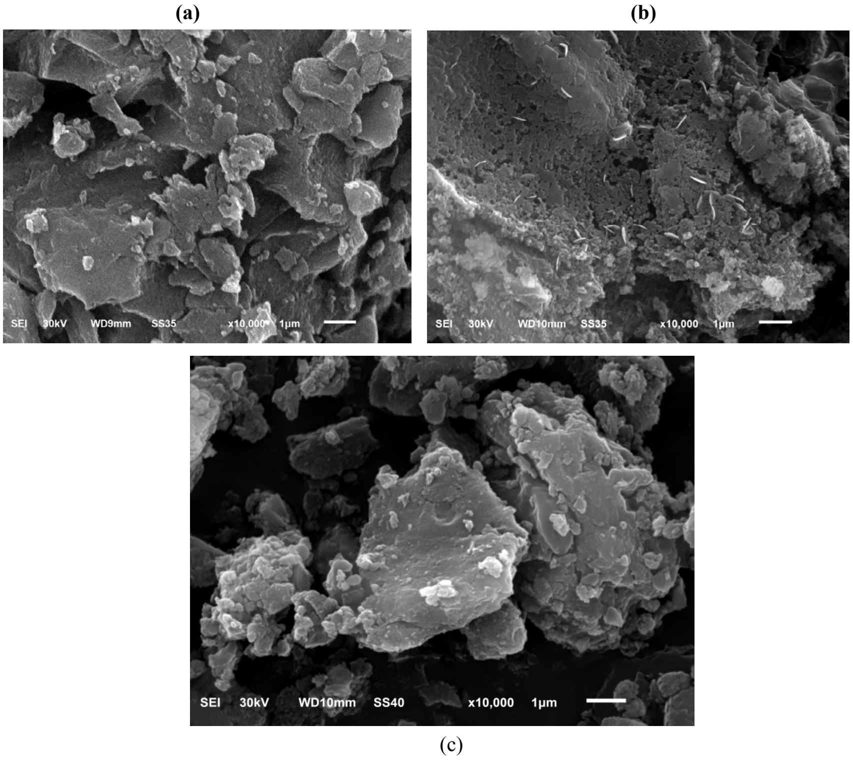

Figure 2: SEM micrographs of (a) OC, (b) OCZI and (c) OCZII carbons.

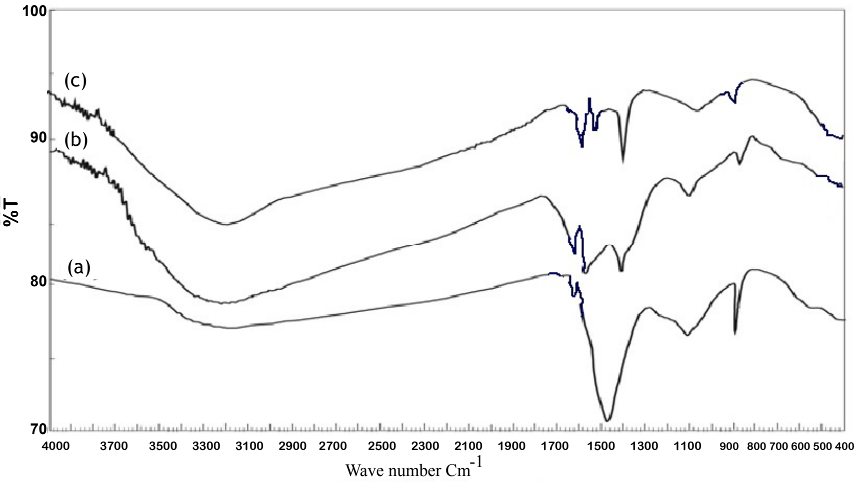

Figure 3: FTIR spectra of (a) OC, (b) OCZI and (C) OCZII carbons.

carbon in removing compounds of low molecular weight [35]. Moreover the iodine number was found to decrease with increasing the amount of hydrous zirconium oxide loaded on the carbon surface.

Removal performance of free chlorine by tested carbons

Effect of contact time: The effect of contact time in the removal of free chlorine was studied and was depicted by Figure 5. This Figure indicates that before equilibrium, there is rise in the removal efficiency with increasing contact time which is universally true for good adsorbents [36,37]. Moreover the equilibrium adsorption was attained after about 60 min. for all carbons with adsorption capacities of 37, 44 and 85% for OC, OCZI, and OCZII respectively.

Effect of adsorbent dosage: The effect of adsorbent dosage was investigated using 14 mg/l initial free chlorine concentration with adsorbent doses within 0.015 g/50 ml to 0.16 g/50 ml. The results of this study are shown in Figure 6. The percentage of removal of free chlorine for each carbon sample increase as the adsorbent dose was increased from 0.4 to 2.4 g/l and then remained almost constant. The increased removal at high dosage is expected, because of the increased of a sorbent surface area and availability of more adsorption sites [38].

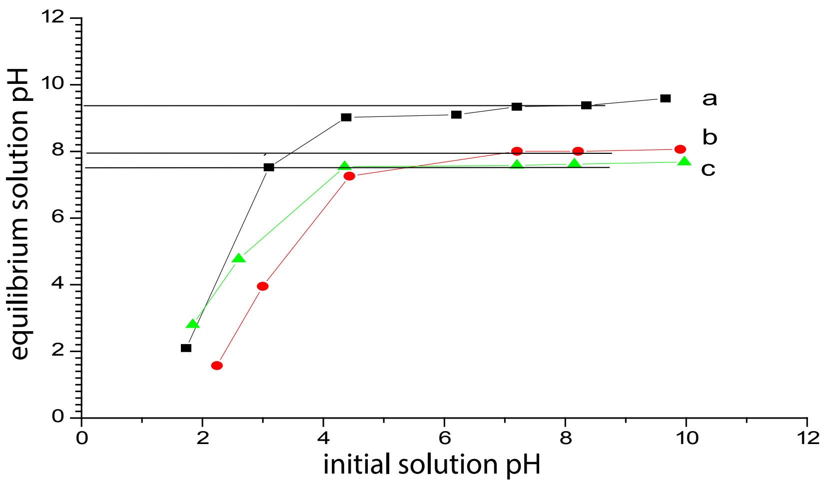

Figure 4: Relation of equilibrium solution pH and initial solution pH for (a) OC, (b) OCZI and (C) OCZII carbons.

Carbon	pH^a	pH_{PZC}	I_2 (mg g^{-1})
OC	9.1	9.4	980
OCZI	7.7	8.1	806
OCZII	6.9	7.5	620

a, pH; measured for 0.1 g carbon in 50 ml deionized water at 25°C

Table 2: pH, pHPZC and iodine number.

Effect of initial concentration: The effect of initial concentration on free chlorine removal was studied within the range of 1-45 mg/l. Similar plots were obtained (not illustrated) for all carbons and all plots had the same general feature, the removal amount increase with an increased in initial free chlorine concentration up to limit value. The reason was that the availability of adsorption sites on the activated carbons. However as the free chlorine concentration exceedingly high, the removal efficiency declines which may be due to the saturation of the binding sites of the activated carbons.

Equilibrium adsorption isotherms: A comparative study involving the adsorption isotherms corresponding to the free chorine removal from their non-buffered solutions by tested carbon are shown in Figure 7. As can be seen, each carbon adsorption data shows isotherm of type I. The sorption data are correlated with the theoretical models of Langmuir (2a) and Freundlich (2b):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2a}$$

$$q_e = K_F C_e^{1/n} \tag{2b}$$

where C_e and q_e are the adsorbate equilibrium concentrations in liquid and solid phases, q_m is the maximum adsorption capacity according to and K_L a constant related to heat of adsorption according Langmuir model. The constant K_F and n of the Freundlich model can be related to the strength of the adsorptive bond and the bond distribution. The coefficient of determination (CD) of the data fitting to each of the above models are shown in Table 3 together with the values of the characteristics parameters for each of the two models studied. According to the values of coefficient of determination (CD), both Freundlich and Langmuir models provided good fitting for the data of free chlorine removal. A characteristic of the Langmuir isotherm is the definition of a dimensionless factor R_L defined as $R_L = \frac{1}{1 + K_L C_o}$ [39] and called separation factor, where C_o is the highest initial free chlorine concentration (mg/L). Adsorption is considered favorable when $R_L<1$ which is the case in all experiments. As for values obtained from the Freudlich model, The n value indicates a favorable adsorption when $1<n<10$, Thus the adsorption is better when smaller values are obtained [40].

It was established that the pH of the adsorbate solution effects not only the surface charge of the adsorbent, the degree of ionization of the materials and the dissociation of functional groups on the active sites of the adsorbent but also the structure of the adsorbate molecule [39]. For this reason adsorption isotherm experiments were also carried out at pH=4.5 to investigate the effect of pH on the removal performance of free chlorine from their buffered solutions (Figure 8) The optimal parameters from the fitting of Langmuir and Freundlich equations with the experimental data are also given in Table 3. It is evident from Table 3 that loading OC carbon with hydrous zirconium oxide increase to a great extent the removal performance of free chlorine and the removal capacity increase from OC<OCZI<OCZII. Furthermore for one and the same carbon sample the removal capacity increases as pH decreases.

No significant correlation was found between the textural properties and the performance removal of free chlorine. For instance for the tested carbons the adsorption capacity increased with the decrease in both S_{BET} areas and V_p as indicated from Tables 1 and 3. The successive deposition of hydrous ZrO_2 particles on the carbon surface mat block some pores resulting in a pronounced decrease in both surface area and total pore volume.

At the same time, the newly formed functional groups (C-ZrOH) in the OCZ carbons as a result of imregenation of OC carbon with ZrO_2 may represent an additional adsorption sites for the removal of free chlorine. Like the function groups (C-OH) that originally exist in fresh carbon [41], C-ZrOH groups can cause deprotonation and protonation reactions respectively according the following equations:

$$\text{C-ZrOH} \rightarrow \text{C-ZrO}^- + \text{H}^+ \tag{3}$$

$$\text{C-ZrOH} + \text{H}^+ \rightarrow \text{C-ZrOH}^+_2 \tag{4}$$

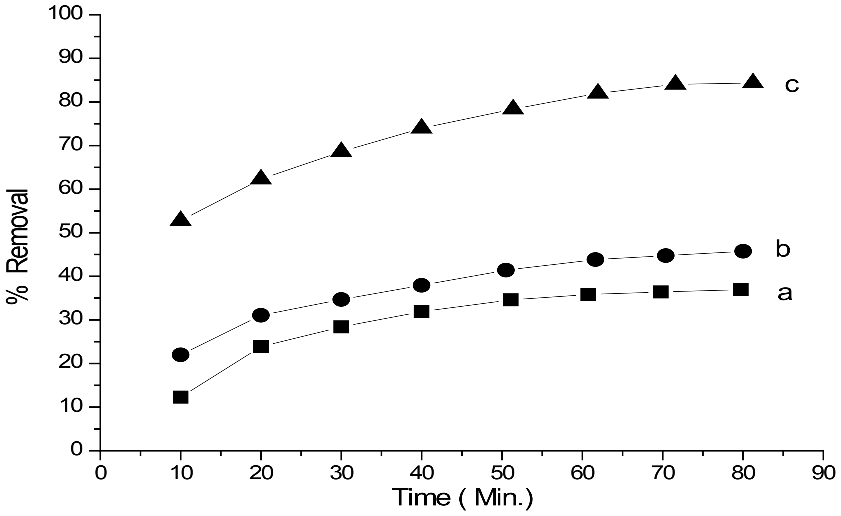

Figure 5: Effect of contact time on the % removal of free chlorine by (a) OC (b) OCZI and (C) OCZII carbons (Co=40 mg/l, carbon dosage=0.025 g/50 ml, Temperature=25+1°C, non-buffered solutions).

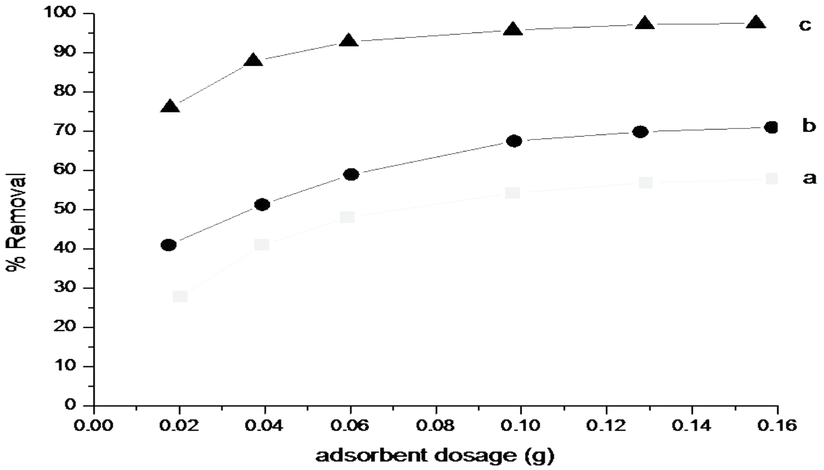

Figure 6: Effect of adsorbent dosage on the % removal of free chlorine by (a) OC, (b) OCZI and (C) OCZII carbons (C_o=14 mg/l , contact time 15 min., Temperature=25+1°C, non-buffered solutions).

Impregnation of commercially activated carbon "OC" with hydrous zirconium oxides shifts the pH at the point of zero charge (pH_{PZC}) from 9.4 to 8.1 and 7.5 for OCZI and OCZII respectively resulting in more positively charged surfaces for both OCZ carbons. With decreasing pH of the solution, the positive charges of the carbon surface increase and more positively charged sites become available.

From the above discussion it seems that the adsorption of free chlorine (HOCl and/or OCl^-) by the tested carbons involved both of non-electrostatic interactions (Van der Waals forces, and hydrogen bonding) and electrostatic interaction between charging surface and both forms of free chlorine. Howover the physical forces and the availability of surface charges are not the only factors determining the degree of free chlorine removal. Dechlorination involves also a chemical reaction of the activated carbon surface being oxidized by chlorine element, according to the following surface reactions:

$$\text{Carbon}+HOCl \rightarrow C^{*}O+H^{+}+Cl^{-} \quad (5)$$

$$\text{Carbon}+OCl^{-} \rightarrow C^{*}O+Cl^{-} \quad (6)$$

Where $C^{*}O$ represents the oxidized site of activated carbon after reacting with free chlorine. The two reactions were reported to occur very quickly [15]. It seems that the adsorption of free chlorine on the carbon surface facilitate the two reactions to occur.

It is well known that the pH of the solution influences the ratio of both forms of free chlorine. The ratios of HOCl form was found to increase sharply with decreasing the value of pH and the removal performance is especially effective at low pH values [42]. The result obtained in this study agrees will with this foundation, decreasing the pH to 4.5 considerably increase the removal performance of free chlorine by the carbons under investigation. Thus one can concluded that the removal performance is especially effective at low pH values and the form of HOCl tended to be more adsorbed than OCl^- species.

Conclusion

Based on the experimental results, the following conclusions can be decued:

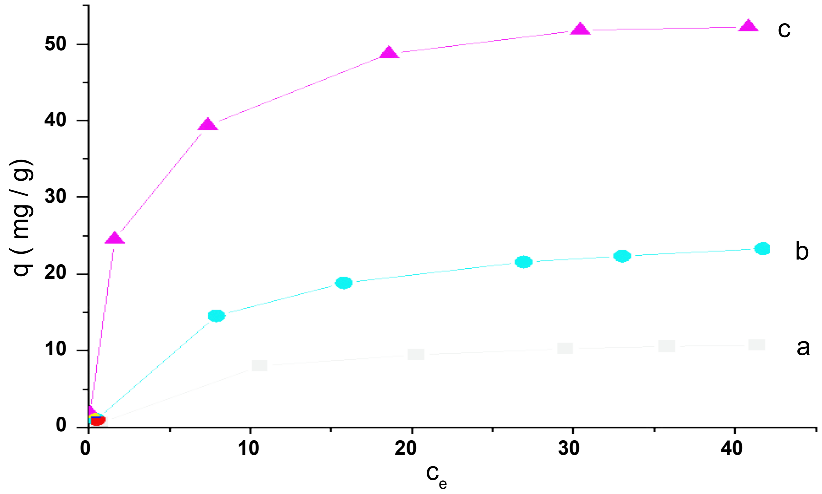

Figure 7: Adsorption isotherms of chlorine on (a) OC, (b) OCZI, and (c) OCZII carbons (C_o=1-45 mg/l, contact time 15 min., carbon dose 0.025 gm, Temperature=25+1°C, non-buffered solutions).

Adsorbent	Langmuir parameters						Freundlich parameters					
	Non buffered			pH=4.5			Non buffered			pH=4.5		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f	n	CD	K_f	n	CD
OC	13.98	0.064	0.994	27.6	0.045	0.998	0.888	1.359	0.97	1.208	1.199	0.9
OCZI	32.7	0.072	0.992	45.5	0.071	0.997	2.142	1.404	0.96	3.266	1.357	0.934
OCZII	49.5	0.50	0.986	63	0.727	0.992	10.03	1.8629	0.974	15.14	2.058	0.944

Table 3: Parameters of Langmuir and Freundlich models.

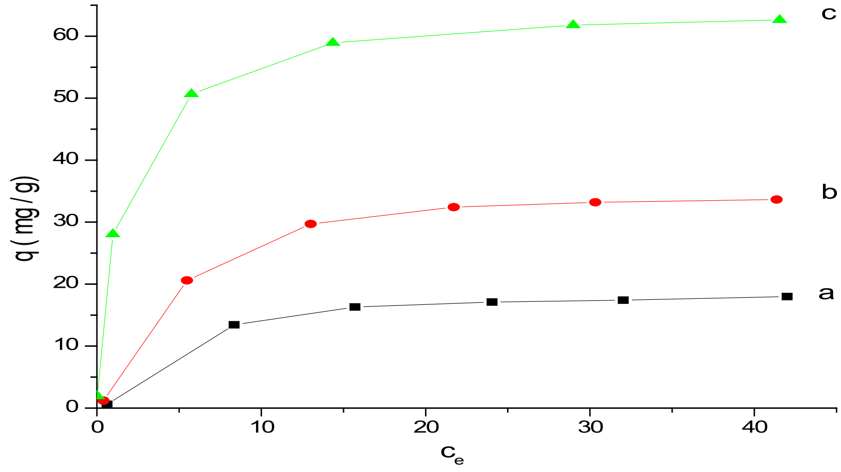

Figure 8: Adsorption isotherms of chlorine on (a) OC, (b) OCZI, and (c) OCZII carbons (C_o=1-45 mg/l, contact time 15 min., carbon dose 0.025 gm, Temperature=25+1°C, pH=4.5).

1. Loading hydrous ZrO_2 on the original carbon which is essentially microporous was associated with a significant decrease in both the surface area and the total pore volume with slight increase in mesoporosity.

2. Hydrous ZrO_2 loading reduce the point of zero charge as well as iodine number of the original carbon.

3. From batch measurements, free chlorine removal was highly dependent on some variables such as contact time, adsorbent dose and initial free chlorine concentration. Moreover, lower pH was found favorable for high removal performance.

4. The equilibrium data was presented well by the Langmuir and Freundlich models according to the measured values of K_L and n

related to the two models, the removal of free chlorine by tested carbons were found to be favorable.

5. Hydrous ZrO_2 loading significantly improves the adsorption capacity of the original carbon. Thus, the maximum adsorption capacity of free chlorine from nonbuffered solutions increased from 14 mg/g for OC carbon to 32.7 and 49.5 mg/g for OCZI and OCZII respectively.
6. It seems that the removal of free chlorine from water is related to surface chemical nature rather than the carbon texture properties.

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