Blue-Green Systems

Reduction of chlorate and regeneration of activated carbon used for chlorate adsorption

Shyam Lakshmanan* and Yen Li Yung

IOI Edible Oils Sdn Bhd, Km 12, Sg Mowtas, 90000 Sandakan, Sabah, Malaysia

*Corresponding author. E-mail: lakshmanan.shyam@gmail.com

Abstract

Activated carbon (AC) from coal, coconut and palm kernel shell was regenerated after adsorbing chlorate from chlor-alkali plant brine solutions. Hydrochloric acid (HCl) of 17% w/w concentration showed the ability to regenerate AC, with some chlorine gas being released. Regeneration with HCl yielded enhanced adsorption of chlorate. AC from coconut shell adsorbed chlorate better than coal and palm kernel shell AC. Higher chlorate concentration in the influent and lower influent pH resulted in better adsorption. Regeneration of the AC with 17% w/w HCl reduced chlorate to chlorine derivatives. The AC released 107 mg/g of chlorine during the first regeneration and 160–178 mg/g after the second regeneration. During regeneration, coal AC released the highest amount of chlorine at 0.51–0.59 mg/g of chlorate adsorbed followed by palm kernel shell with 0.34–0.36 mg/g, while coconut shell AC released 0.18 mg/g. Scanning electron micrograph of the coconut shell AC carried out after each regeneration showed the structure of AC remained intact, with active sites surfacing on the regenerated AC. Using AC for chlorate adsorption followed by regeneration with 17% w/w HCl may reduce the release of brine and chlorate to the environment from chlor-alkali plants.

Key words: activated carbon, adsorption, chlor-alkali, chlorate, hydrochloric acid, regeneration

INTRODUCTION

Chlorates are released to the environment by industries such as chlor-alkali and pulp and paper mills. Studies show that chlorates are not readily decomposed in the environment (Sorlini & Collivignarelli 2005), and that they are toxic to certain strains of algae (van Wijk *et al.* 1998). There have also been cases of chlorate poisoning reported (Gil *et al.* 2016). Reports on the sources of release of chlorate to the environment (Gil *et al.* 2016) normally refer to pulp and paper mill effluent and generally do not report on their release from chlor-alkali plants (i.e., chlorine, Cl_2 and caustic soda, NaOH producing plants). Chlorine and caustic soda are used in industries ranging from food, petrochemicals and power plants to soap and water treatment chemicals, with many chlor-alkali plants as their source of supply. In petrochemical plants, the chlor-alkali plant may be a part of the industrial complex, e.g., ethylene dichloride and polyvinyl chloride. There are many sources of potential release of brine and chlorate to the environment.

The authors identified that chlorates are released to the environment by membrane cell chlor-alkali plants. The membrane cell is the best current available technology for producing caustic soda and

chlorine (Brinkmann *et al.* 2014). However, the disadvantage of this process is that it requires high quality brine. In order to maintain the quality of the brine being fed to the electrolyser, some brine is purged to the environment. Chlorate is released to the environment when plant operators purge their brine. This affects the quality of the receiving water bodies. With the call for sustainability, and greener processes, these releases must be reduced. The researchers looked for methods to reuse these streams so that there is reduced effluent released from such plants. There are legislations in some countries that limit the release of chlorate from pulp and paper mills, however there is a lack of legislation limiting their release from chlor-alkali plants. Many plant operators may be unaware of the harm caused by the release of chlorate to the environment from their plants. In work done previously, the authors studied the adsorption of chlorate from the brine stream of chlor-alkali plants using activated carbon (AC) (Lakshmanan & Murugesan 2016). ACs are used in pollution mitigation studies as they exhibit the ability to remove substances and pollutants from aqueous solutions (Arena *et al.* 2016). The present research studies how AC that is used for chlorate adsorption from a multi-component effluent stream and achieves selective adsorption of one component (Yang *et al.* 2016) can be effectively regenerated and minimise environmental pollution.

Three types of commonly available AC, namely, coal, coconut shell and palm kernel shell, were tested in the present research to study their amenability to chemical regeneration. These three types of AC were selected due to their differences in pore size, to determine which would achieve the greatest chlorate adsorption. AC made from coconut and palm kernel shell is mainly composed of micro pores, while those from coal have pores ranging from 2 to 50 nanometres. Wood- and peat-based materials predominantly include meso and macro pores. Wood- and peat-based AC is suitable for removing larger molecules, coconut- and palm kernel shell-based materials are suitable for removal of small molecules and coal-based for medium-sized molecules.

The heat activation method for different types of AC results in the formation of various surface active groups, which give the AC its adsorptive capacity. In some of the adsorptions, the surface active groups react with some component in the liquid and are converted (chemisorbed). These sites are difficult to regenerate and such ACs lose their adsorptive capacity upon regeneration. The types of surface active groups on the AC also play a part in the adsorption characteristics of the AC. The carbon-oxygen surface group affects properties of the AC such as acidity and chemical reactivity (Bansal & Goyal 2005). Also, the adsorption by AC is affected by parameters such as temperature, pH and concentration (Payne & Abdel-Fattah 2005; Yoon *et al.* 2009).

Many adsorbates are physically adsorbed onto the AC surfaces by Van der Waals forces while some adsorbates may be adsorbed by a chemical reaction with the surface active groups on the AC. Chemisorption occurs on a single layer only (Bansal & Goyal 2005). These bonds formed from chemisorption are generally stronger than physisorption and are more difficult to break. The AC contains elements such as hydrogen, oxygen, sulphur, nitrogen and chlorine on the surface. They affect the adsorption by the AC, e.g., nitrogen surface active groups give the AC the ability to adsorb more anions. Some of the common active groups found on AC include carboxyl, carbonyl, phenol, quinone, lactone, anhydride and ether (Figueiredo *et al.* 1999; Menéndez Díaz 2018). Surface active groups containing oxygen such as carboxyl, lactone and phenol are acidic, while pyrones, chromenes, ethers and carbonyls are reported to be basic (Lopez-Ramon *et al.* 1999; Menéndez Díaz 2018). Since the AC can have different combinations of surface active groups, it can have both acidic and basic groups at the same time. The adsorption of metal ions onto AC is affected by the solution pH and surface active groups.

AC exhibits an amphoteric nature due to the presence of various surface active groups. If the number of acidic sites equals the number of basic sites, this state is the point of zero proton charge, pH_{zpc} (also called the zero point charge). When the pH of the solution is lower than pH_{zpc}, the AC is protonated and the net surface charge is positive. When the pH is higher than

pH_{zpc}, then the surface becomes negatively charged and attracts cations (Cardenas-Peña *et al.* 2012; Menéndez Díaz 2018). When the AC has a surface charge, the opposite charged particle is attracted to its surface. This gives an oppositely charged cloud at a distance from the particle as per Gouy–Chapman–Stern's diffuse double layer theory (Henderson & Boda 2009). This charged cloud will then attract further but oppositely charged clouds of particles around it.

For the AC, the surface charge can be altered by adjusting the pH of the solution (Bansal & Goyal 2005). When pH of the solution changes, due to its amphoteric nature, the charge on the surface of the AC also changes, and the cloud around it is less strongly attracted to its surface. Although chloride and chlorate are negatively charged ions and present in this study, the focus of the present study is on the adsorption of chlorate.

In the chlor-alkali process (Figure 1), the reaction for the electrolysis of salt and water (H_2O) is shown in Equation (1) with production of hydrogen (H_2) and chlorine (Cl_2).

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 \tag{1}$$

Chlorates are produced through a side reaction that occurs in the electrolysers of chlor-alkali plants. The reaction route is shown below. Chlorates are formed in the brine solution and are not easily decomposed (O'Brien *et al.* 2007).

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2 \tag{2}$$

Reaction (2) is undesirable as it consumes sodium chloride which is the raw material for the process. There is a chlorate reduction step incorporated in most chlor-alkali plants (see Figure 1) that uses hydrochloric acid (HCl) and steam to reduce the chlorate content in the brine to below 5 g/L. However, this step is often unable to reduce sufficient amounts of chlorate to allow complete recovery of the brine stream.

The brine stream recirculates within the chlor-alkali plant as shown in Figure 1. As it recirculates within this circuit, the chlorate concentration will keep rising if no steps are taken to remove it. In
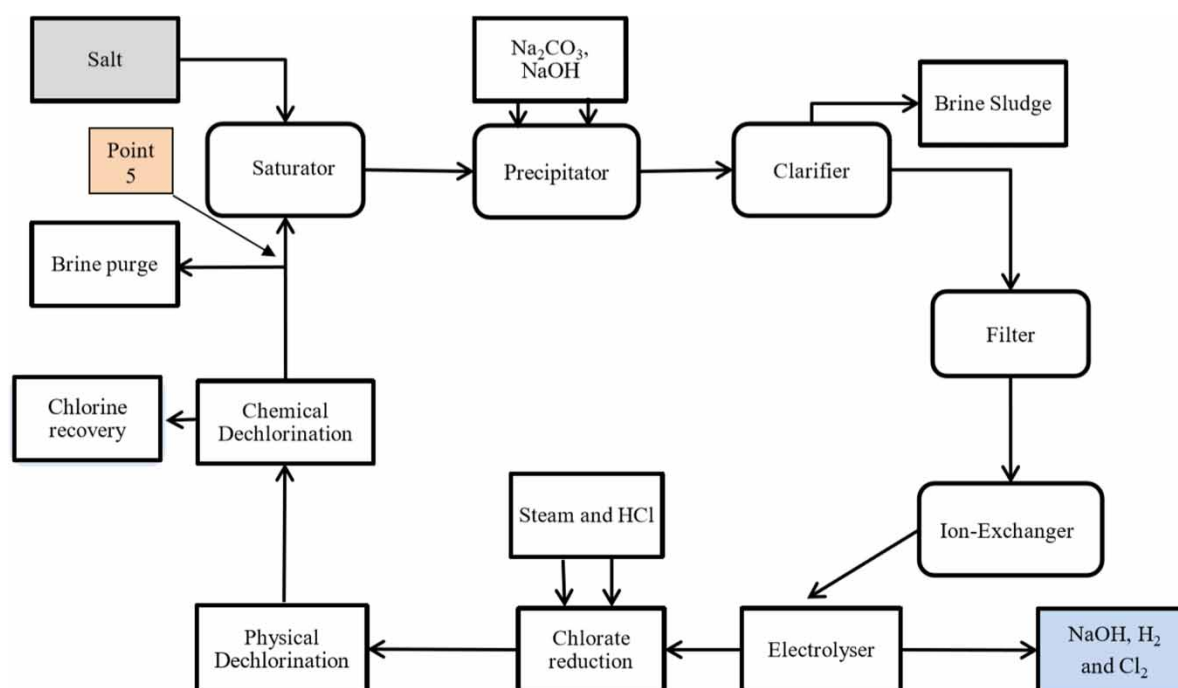
Figure 1 | Brine circuit of a chlor-alkali plant (Lakshmanan & Murugesan 2016).

order to maintain the chlorate concentration in the brine at permissible levels (<12 g/L), most chlor-alkali plants release a proportion of their brine to the environment (O'Brien *et al.* 2007).

There has not been much research done on chlorate removal, with most of the related research on polluted waterways being conducted on chlorite and perchlorate removal (Sorlini & Collivignarelli 2005; Yoon *et al.* 2009; Mahmudov & Huang 2010).

In earlier work done by the authors with AC for the chlor-alkali plant brine stream, Point 5 in Figure 1 had been identified as a suitable location for chlorate adsorption (Lakshmanan & Murugesan 2016) and is used in the present research. The present research has been undertaken to study the regenerability of AC, such that the regeneration products released should not be harmful to the environment. The present research differs from other works as it studies the regeneration of the AC used for chlorate adsorption while reducing the chlorate, permitting recovery of the brine stream. HCl was selected as the regenerant as it is produced in chlor-alkali plants and is used in chlorate reduction, as shown in Figure 1. This proposed method, if proven to be feasible, will provide a method for the brine to be recovered, giving better salt conversion efficiency and lower pollution to the environment from chlor-alkali plants. In our present research, we pursue a method that regenerates the AC and one that would not result in a new disposal problem.

METHODS

Chlor-alkali plant brine solution from an operating chlor-alkali plant was used for these experiments. Analytical reagent grade 5% w/w potassium iodide (KI) solution, 1:1 glacial acetic acid (CH_3COOH) and 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solution were used for titration and neutralisation. In addition, lab prepared distilled water and sodium chlorate ($NaClO_3$) (Merck), starch solution and small scale column assembly, as shown in Figure 2, and chlorine gas test assembly, as in Figure 3,
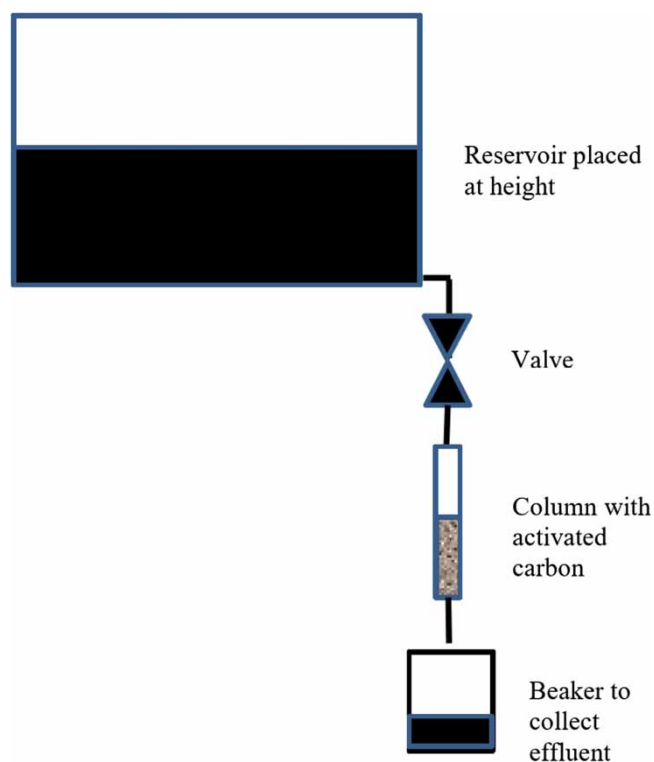
Figure 2 | Equipment assembly to saturate activated carbon with chlorate (Lakshmanan & Murugesan 2016).
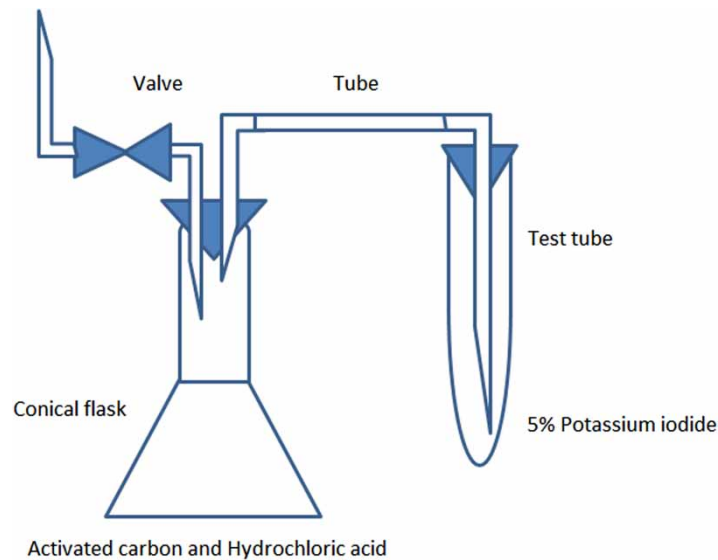
Figure 3 | Equipment assembly for reducing chlorate and absorbing chlorine.

were used. ACs used were AVOX830 (coal), AVOPSM830 (palm kernel shell) and AVOCO1,000 (coconut shell) from AVO filtration. The regenerant tested was 17% w/w HCl solution.

Coconut shell, palm kernel shell and coal AC, as received, were initially saturated with chlorate. Coconut and palm kernel shell AC were selected as they consist mainly of micro pores and are more suitable to adsorb smaller molecules. AC was placed in a column as shown in Figure 2, and chlorate containing brine solution was flowed through it at a controlled flow rate. The methods for saturating the AC and gas testing are explained below. The experiments were conducted in duplicate to confirm repeatability. Details of the company have been kept confidential.

Saturating activated carbon for regeneration experiments

These experiments were designed to regenerate AC that had been used for adsorption. The initial step was to produce AC that had adsorbed chlorate. The column assembly shown in Figure 2 was used to saturate AC with chlorate. First, 1,200 mL of brine of 20% w/w sodium chloride was collected from the location marked Point 5 in the brine circuit before the saturator (see Figure 1). This was the location where brine was being purged from the chlor-alkali plant. This brine of around 4 g/L chlorate concentration was used for the present study. The initial chlorate and sodium chloride content were tested as shown by Lakshmanan (Lakshmanan & Murugesan 2016).

Then, 100 g of coconut shell AC was placed in the column. The AC was rinsed with 250 mL of distilled water. The reservoir was placed at 1 m height to give sufficient pressure for the fluid to flow through the column.

(a) Next, 1,200 mL of the brine was placed in the reservoir and flowed through the column of AC at a flowrate of 1 mL/s and the discharge was collected. Flowrate was controlled by throttling the valve shown in Figure 2. Quality of the discharge was tested to determine the chlorate content after brine had drained out from the column. Step (a) was repeated each time after the AC had been regenerated as in step (b) below.

The amount of chlorate adsorbed in mg chlorate/g AC was determined from the inlet and outlet chlorate concentration difference. The spent AC was then placed in a 250 mL conical flask as shown in Figure 3. This assembly was used to regenerate the AC and to collect the gas being released during the regeneration step.

(b) Regeneration for 30 min using 17% w/w HCl solution was carried out by adding 100 mL of the acid to the spent AC in the closed conical flask (Figure 3) to collect the evolved gas. The gas was collected and tested as shown below. The regenerated AC was drained of acid, rinsed with 6,000 mL of water and filtered and reinstalled in the column for readsorption. Step b) was repeated each time after the AC had been saturated with chlorate.

A further 1,200 mL of dechlorinated brine from Point 5 of Figure 1 was used, and its initial chlorate and chloride concentrations were tested. Step (a) was repeated, followed by step (b).

The regenerated AC was then drained of HCl, rinsed with 6,000 mL of distilled water and placed back in the column for further adsorption. Next, a lab prepared brine solution containing 12 g/L of chlorate was placed in the reservoir, as shown in Figure 2, and step (a) was followed. The discharge was collected and the pH tested using a pH Meter (Mettler Toledo, Model number FE20). The AC was regenerated as per step (b) and the gas released was tested as explained below.

The pH_{zpc} of the three types of AC was tested previously as received. The pH_{zpc} for the AC was determined by placing 1 g of the AC in 100 mL of distilled water that was adjusted to various pH. The AC was stirred and left overnight at 24 °C. The pH of the solution was tested after 24 hours.

The effect of presoaking the AC with acid was also studied, to examine the effect of acidification of the AC on its adsorption of chlorate. The AC soaked with 17% w/w HCl for 30 min was washed with 6,000 mL of water before being used for adsorption studies.

In addition, brine solution containing around 7.6 g/L chlorate was used to compare the chlorate adsorption performance between virgin AC and acid soaked AC. The AC was soaked in 17% w/w HCl for 30 min, then rinsed with distilled water to wash away excess HCl, followed by $NaClO_3$ adsorption.

Scanning electron micrographs (SEM) are often conducted to study the surfaces of AC to better understand the surface phenomenon after adsorption and regeneration of the AC. These scans were conducted to look for any surface changes on the coconut shell AC after repeated chlorate adsorption and repeated regeneration with 17% w/w HCl. A Hitachi Variable Pressure Scanning Electron Microscope, Model SU1510, was used to perform these scans. Scans were conducted at a magnification of 10,000 times for coconut shell AC.

Collection and testing of the gas released

An experimental set-up as shown in Figure 3 was used to regenerate AC, while the gas released was collected and quantified. Experiments were conducted at 30 °C and at atmospheric pressure. In the test tube, 10 mL of 5% w/w KI solution was added along with 15 mL of 1:1 CH_3COOH and a few drops of starch solution. The starch was used as an indicator. The test tube was equipped with a rubber stopper and had a tube inserted through it such that the glass tube dipped into the solution in the test tube. This was done so that the chlorine gas (along with any other gas) generated in the conical flask would bubble into the KI solution and be readily adsorbed.

The spent coconut shell AC from Figure 2 was placed in the conical flask in Figure 3 and the magnetic stirrer was turned on. The valve on the tubing was kept closed.

Then, 100 mL of 17% w/w HCl solution was added into the flask through the tubing and the valve was rapidly shut so that any gases being generated would bubble into the KI solution in the test tube. The test tube was shaken from time to time to mix the gas and liquid streams.

After 30 min, the valve was opened and water was added into the conical flask until the flask was full. This was done in order to displace all the air and chlorine from the flask into the test tube.

The contents of the test tube were titrated with 0.1 N $Na_2S_2O_3$ solution. Titration was continued until the dark blue colour disappeared. The volume was recorded as V. The chlorine content was calculated using $V \times N \times 710 =$ chlorine in mg/L, where N is the normality of the $Na_2S_2O_3$ solution.

Next, the contents of the conical flask were filtered to collect the AC. The regenerated AC was placed back into the column seen in Figure 2. It was rinsed out with 6,000 mL of distilled water to reduce its acidity. The above procedures were repeated for the subsequent runs and for the different types of AC.

RESULTS AND DISCUSSION

Prior regeneration experiments conducted on AC with HCl of low concentration (<5% w/w) showed varying levels of regenerability, but declining adsorption of chlorate after each regeneration. This points towards some chemisorption and inactivation of some sites. The decline in adsorptive capacity in each successive step seen in those experiments indicates that some of the chlorate may be more strongly held than by mere Van der Waals forces. This could support the argument that the chlorate is chemisorbed onto the surface of AC or chlorate is reduced and inactivates the site and more energy may be needed to dislodge it, i.e., the chlorate reduction could quite possibly be forming compounds that inactivate the sites.

An observation made from these experiments was the release of a pungent gas during some of these regeneration experiments. The present experiments were designed to study whether stronger HCl concentrations would effectively regenerate the AC and reduce the chlorate, as the pungent gas was an indication of reduction of the chlorate, by producing chlorine or chlorine dioxide gas.

Point of zero charge of activated carbon, pH_{zpc}

The pH_{zpc} of the ACs were determined previously and are shown in Table 1. The coconut shell AC was found to have a pH_{zpc} of 9.9. Hence, at solution pH below 9.9, the coconut shell AC's surface would be positively charged and would attract negatively charged chlorate ions to it. Above a pH of 9.9, the coconut shell AC would have a negative charge, and would repel chlorate ions. The pH_{zpc} of the various ACs were determined by testing five initial pH and recording the final pH (after 24 hours).

For palm kernel shell and coal, the AC was tested and found to have pH_{zpc} of 9.80 and 8.30, respectively. Hence, at solution pH below 9.80 and 8.30, the respective AC's surface would be positively charged and would attract negatively charged chlorate ions to it.

The pH_{zpc} of the AC may be used to explain the improved adsorption exhibited by the AC. Table 2 shows the amount of chlorate adsorbed by the three types of AC. The acidification of the AC resulted in enhanced chlorate adsorption. Compared with the other ACs, the highest adsorption in the first run was achieved using coconut shell AC which adsorbed 6 mg/g, followed by 9.5 mg/g in the second run and 36 mg/g in the third run. The solutions became most acidic in the third run, which also contributed to the high adsorption achieved in the third run. The acid regeneration resulted in the formation

Table 1 | Point of zero charges of various activated carbons (Lakshmanan & Murugesan 2017)

Coconut shell AC		Palm kernel shell AC		Coal AC	
Initial pH	After 24 hr	Initial pH	After 24 hr	Initial pH	After 24 hr
5.78	9.16	6.04	9.14	5.83	8.01
7.21	8.69	7.21	8.90	7.23	8.01
9.50	9.92	9.50	9.66	8.50	8.28
10.00	9.93	10.00	9.88	9.00	8.51
10.50	9.98	10.50	9.85	9.50	8.80
$pH_{zpc} =$	9.90	$pH_{zpc} =$	9.80	$pH_{zpc} =$	8.30

Table 2 | Chlorate adsorption and chlorine gas release

AC type	Sample	pH		NaClO$_3$ (g/L)		NaClO$_3$ adsorbed (mg/g)	Cl$_2$ collected (mg)	Cl$_2$/ NaClO$_3$ (mg/mg)
		Before	After	Before	After			
Coconut shell	Run 1	10.6	10.4	3.0	2.5	6.0	107	0.18
	Run 2	10.7	7.1	3.6	2.8	9.5	160	0.17
	Run 3	6.6	5.6	13.2	10.2	36.0	1,075	0.30
Palm kernel shell	Run 1	10.2	10.0	2.9	2.7	3.0	107	0.36
	Run 2	10.3	6.8	2.9	2.4	5.2	178	0.34
	Run 3	6.8	6.0	12.0	9.5	30.0	1,793	0.60
Coal	Run 1	10.4	10.2	2.5	2.4	1.8	107	0.59
	Run 2	10.1	6.6	2.6	2.3	3.5	178	0.51
	Run 3	6.7	5.9	11.8	9.7	24.8	2,151	0.87

of more acidic surface active groups on the AC (Li *et al.* 2016), which would have strongly attracted the negatively charged chlorate molecules to its surface. A pungent gas was again detected during the regeneration step using HCl. The set-up in Figure 3 was used to capture and determine as well as quantify the gas being released. The gas was tested and confirmed to contain chlorine (O'Brien *et al.* 2007), with the possible reaction as shown in Equation (3).

17% W/W hydrochloric acid as regenerant

Since the use of HCl showed potential, further experiments were conducted using a stronger acid solution (17% w/w HCl) to reduce chlorate. The experimental set-up used was as in Figure 2 for adsorption and Figure 3 for regeneration and gas collection. The results obtained are shown in Table 2. Tests were conducted with coconut shell, palm kernel shell and coal AC.

Run 1 refers to the first run using virgin AC. Run 2 was after the AC had been regenerated with 17% w/w HCl. Run 3 was after the AC had been regenerated again with 17% w/w HCl. For Run 3, the solution fed to the column was a lab prepared brine solution with higher chlorate concentration (~12 g/L) to evaluate the influence of infeed concentration and pH towards chlorate adsorption. For the three types of AC tested, it was observed that there was greater chlorate adsorption after regeneration with 17% w/w HCl. The influent pH was suspected to play an important role in the adsorption. To test this, a lab prepared brine solution with lower pH and higher chlorate concentration was fed to the column. The higher chlorate concentration was used to study the ability of the AC to remove higher levels of chlorate in the event there are sudden spikes in chlorate levels coming from the chlor-alkali plant.

The results from Table 2 show that chlorate was adsorbed by the three types of AC tested. In Run 2, upon regeneration using HCl, all three types of AC exhibited enhanced adsorption of chlorate. Enhanced adsorption was also noted by other researchers in their regeneration of AC using sodium hydroxide and sulphuric acid (Li *et al.* 2015). The regeneration of the AC with HCl produced acidic surface active groups effectively regenerating it, and this provided greater attraction towards the negatively charged chlorate ions, thus resulting in greater removal of chlorate by the acid regenerated carbon.

From stoichiometric calculations, 1 mole of NaClO$_3$ will produce 3 moles of chlorine gas if reacted with HCl in excess, as shown in the equation below (Sharma & Agarwal 2014):

$$NaClO_3 + 6HCl \rightarrow NaCl + 3Cl_2 + 3H_2O \tag{3}$$

Thus, 1 mg of NaClO$_3$ should yield 2 mg of chlorine. The quantity of chlorine (mg) released in the first two runs was very similar for all three types of AC. Table 2 shows that although coconut shell

exhibited the highest amount of chlorate adsorbed, the chlorine recovery was best with coal AC. This indicates that other reactions may be occurring in addition to Equation (3). This is an area for further work to be done to optimise the amount of chlorine recovered.

Table 2 shows that not all of the chlorate is converted to chlorine. This indicates that some of the chlorates may be irreversibly bound to surface active sites on the AC, or that they may have been reduced to other chlorine products such as chlorine dioxide.

For the third run using lab prepared brine solution, the pH of the influent was lower than that of the plant brine solution. This may have contributed to the high adsorption of negatively charged chlorate onto the AC, due to the high positive charge on the surface of the AC. The three ACs tested showed a drop in pH of the discharge when compared with the influent, indicating that the pH of the AC was reduced by the regeneration using HCl. The coconut AC was initially used as received with a pH_{zpc} of 9.9. This is close to the solution pH and hence no reduction was seen on the solution pH. Upon regenerating the AC with HCl, the pH of the AC was reduced significantly. This caused the subsequent sample for adsorption to record a drop in its pH upon flowing through the acidified (regenerated with 17% w/w HCl) AC. The subsequent run with a more acidic solution resulted in increased adsorption, showing that the solution pH plays an important role in the adsorption of chlorate onto the AC. Further work has to be done to study the effect of pH, chlorate concentration and type of AC, on adsorption of chlorate.

The experiments conducted on the three types of AC recorded enhanced adsorptions of chlorate when the incoming chlorate content in the brine solution was higher. Testing at 12 g/L chlorate levels was conducted to study the response of the AC to sudden spikes in chlorate concentration. The results obtained here show that the AC is able to adsorb chlorate at higher concentrations. This is an indication that the AC has more active sites able to adsorb chlorate, and that the AC would be able to respond to fluctuations in incoming chlorate concentration. The improvement in coal AC's chlorate adsorption was the most significant, bringing it close to that of coconut AC with elevation of brine solution concentrations from below 4 g/L to 7.6 g/L.

Effect of acidification of AC

To test the effect of acidification, experiments were conducted by initially soaking the AC in 17% w/w HCl followed by rinsing off with water. Adsorption experiments were conducted with coconut shell, palm kernel shell and coal AC. The results obtained are captured in Figure 4. The results show that acid-soaked AC yielded higher adsorption of chlorate when compared against normal (non-acid-soaked) AC. All three types of AC showed markedly higher adsorption of chlorate from brine solution. Among the three types of pre-acidified AC tested, coconut shell showed the highest amount of chlorate adsorbed at 35.0 mg/g and the lowest adsorption was by palm kernel shell of only 27.5 mg/g. However, the greatest adsorption improvement was observed in coal AC, when compared with non-acidified AC, as shown in Figure 4. These studies show that acidification of the AC improves its chlorate adsorption capacity.

Effect of higher influent chlorate concentration

The coconut shell AC showed the highest amount of chlorate adsorbed at all the chlorate concentrations tested, rising from 6 mg/g to 25.4 mg/g, as shown in Figure 5. Similar increasing trends can be observed for the palm kernel shell and coal. Both palm kernel shell and coal AC showed greater adsorptions of 84.3% and 89.6%, respectively, at higher chlorate concentration (7.6 g/L) compared with coconut shell (76.4%).

The high chlorate removal rate in the third run and high volume of chlorine released during the regeneration indicate greater physisorption by the low pH of the AC attracting the negatively charged

	Coconut shell	Palm kernel shell	Coal
■ Normal AC	25.4	19.1	17.3
■ Acidified AC	35.0	27.5	32.2
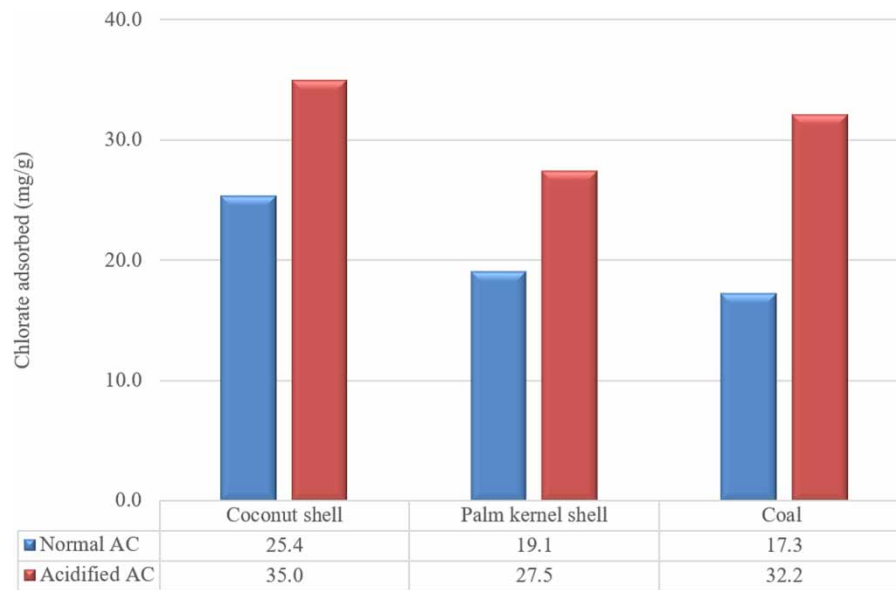
Figure 4 | Comparison of chlorate adsorbed between normal and acidified activated carbon.

	Coconut shell	Palm kernel shell	Coal
■ Brine < 4 g/L	6.0	3.0	1.8
■ Brine 7.6 g/L	25.4	19.1	17.3
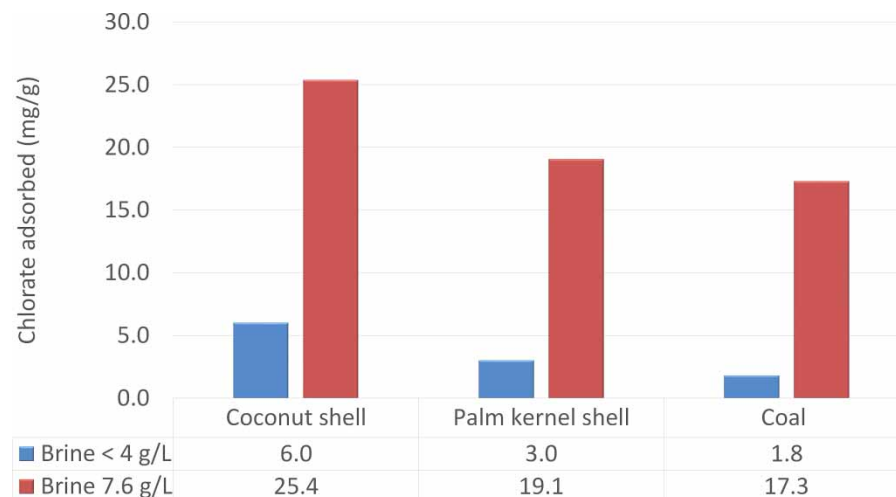
Figure 5 | Chlorate adsorbed by activated carbon at varying chlorate concentrations.

chlorate to its surface. The wash water was tested and found to be free of chlorate, but contained high chloride levels due to the brine solution and the HCl used for regeneration. This dilute HCl can be utilised by the chlor-alkali plant in other parts of its process and would not generate further effluent for the plant.

Scanning electron micrograph analysis of the activated carbon

The coconut shell and coal AC samples were investigated using SEM to better understand the adsorption taking place. Similar observations were obtained from both coconut shell and coal. Only coconut shell scans are discussed further here. The coconut shell AC samples were prepared and labelled as follows:

(a) K1 – virgin coconut shell AC.
(b) K2 – after the AC was saturated with chlorate.
(c) K3 – after the AC was regenerated with 17% w/w HCl (first regeneration).

(d) K4 – after the AC was resaturated with chlorate a second time.

(e) K5 – after the AC was regenerated with 17% w/w HCl (second regeneration).

(f) K6 – after the AC was resaturated with chlorate a third time.

The scan for the virgin AC, K1 in Figure 6, showed fairly uniform pores. The structure of the AC could be seen as thin flakes, which provides a large area for adsorption (Borah *et al*. 2017) of irregular distribution and various sizes of pore.

The majority of the visible pores on the surface were in the 5 micrometre range, which were consistent with that expected for coconut shell AC, whereas the smaller pores of less than 1 micrometre could be seen within these 5 micrometre pores. K2 in Figure 6 shows changes to the surface of the AC upon adsorption of chlorate onto the surface active sites. There are signs of changes to these pores as some of them adsorb chlorate and other pores are blocked by the chlorate and chloride molecules. At 10,000 times magnification, deposition can be observed around the small pores and at the entrance to the larger pores, as the surface active groups are expected to be situated in abundance at these areas.

K3, which is after the AC had been regenerated with 17% w/w HCl, showed changes on the surface with the pores being cleared of deposition and the visual appearance of additional pores. Changes were also seen on the surface of the AC, probably indicating formation of surface active groups by the action of HCl on the AC resulting in chemical changes to the AC's surface.

This explains the enhanced adsorption after regeneration of the AC. During regeneration, the release of chlorine was detected. This results in an improved surface adsorption by the AC due to creation of more adsorption sites. The process of adsorption and regeneration was repeated several times to better understand the surface reactions occurring. For K4, the regenerated carbon was resaturated. The images show that some surface changes have occurred that possibly resulted in an enhanced number of active sites on the AC upon regeneration. There are more surface contours and possible adsorption sites for chlorate, which could result in greater adsorption of chlorate.

The scan for K5 was carried out after the saturated AC was regenerated, again with 17% w/w HCl. A large area can be observed on the surface of the AC which has potential for adsorption of chlorate.
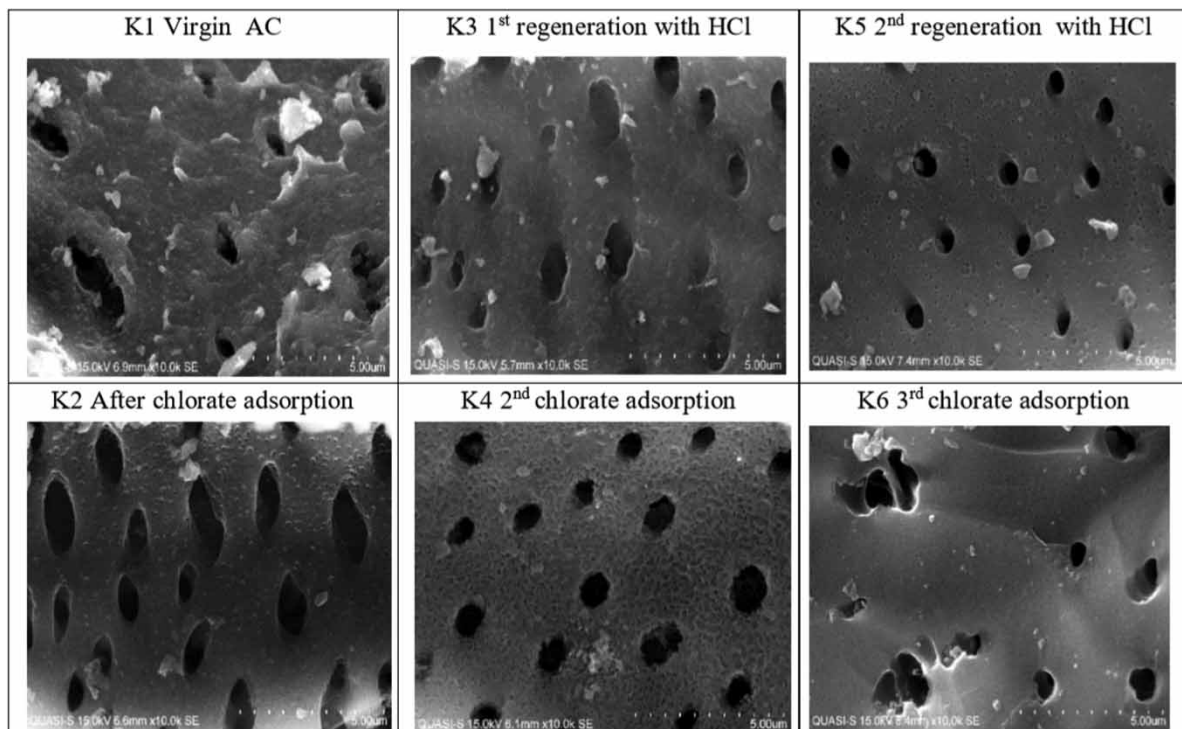
Figure 6 | Scanning electron micrography of coconut AC after adsorption and regeneration.

The surface of K5 looks very similar to that of K1, but with the pores seen to be considerably smaller. The AC had been effectively regenerated without any obvious signs of deterioration. This gradual decline in the pore sizes probably indicates declining adsorption of chlorate if the regeneration is repeated.

The acidic regeneration of the AC has quite possibly formed surface active sites that enhance the ability of the AC to adsorb greater amounts of chlorate.

The image for K6 shows the pores on the AC. These have generally remained intact, indicating the possibility for repeated regeneration of the carbon. There were no visual signs of physical deterioration in the AC from these repeated adsorption and regeneration steps. There were no signs of any cracks to indicate deterioration in the mechanical properties of the AC. This indicates that the AC may be repeatedly reusable and regenerated in this manner, up to a point yet to be determined.

CONCLUSION

The earlier research work done with AC showed its ability to remove sufficient amounts of chlorate from the brine stream of a chlor-alkali plant such that all the brine may be recovered without the need for brine purge (Lakshmanan & Murugesan 2016). The present research was embarked upon with the intention of identifying a suitable method for regenerating the AC in order to make the AC reusable for chlorate adsorption. HCl was seen to enhance the adsorption of chlorate by the regenerated AC. The use of 17% w/w HCl also made this regeneration step an acid activation for the AC. During the regeneration step, the HCl reduced some of the adsorbed chlorate to products such as chloride, chlorine dioxide and chlorine gas, while also regenerating the AC.

This current research presents a method for regenerating AC, using materials available in a chlor-alkali plant. The regeneration of the AC using 17% w/w HCl makes the AC reusable up to at least three times as investigated here. The release of chlorine as a by-product during regeneration makes this method attractive to chlor-alkali plants, as chlorine is one of the co-products of the chlor-alkali plant. The experiments showed that not all of the chlorate is converted to chlorine, that some of the chlorates may be irreversibly attached to some surface active groups. And, or alternatively, these chlorates may have been reduced to other chlorine products, e.g., chloride or chlorine dioxide, ClO_2, as shown in Equation (4) (O'Brien *et al.* 2007):

$$2NaClO_3 + 4HCl \rightarrow 2NaCl + Cl_2 + 2ClO_2 + 2H_2O \tag{4}$$
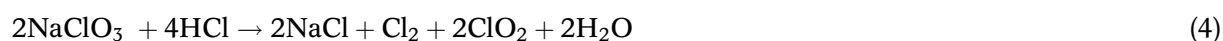
The ratio of chlorine produced to chlorate did not in all cases follow the above equation. There are several other reaction mechanisms with different ratios of reduction products to chlorate (House & House 2010). Under varying acidic conditions and with various types of AC, different reactions or combinations of reactions may occur, resulting in varying amounts of chlorine gas being produced. This suggests the possibility of optimising the regeneration step to produce the desired reduction product, i.e., chlorine, chlorine dioxide or chloride.

This research shows a method that allows more brine to be recovered, reducing the amount of brine purged by chlor-alkali plants. This helps prevent the release of chlorate into the environment. Treatment of the virgin AC with HCl enhanced chlorate adsorption.

The experiments done here confirm that higher chlorate influent concentrations result in greater adsorption by the AC. The use of HCl (which is one of the products from a chlor-alkali plant) as the regenerating agent, and the recovery of chlorine during regeneration, makes this proposed chlorate removal process reproducible at chlor-alkali plants. The recovered HCl after regenerating the AC can be used for the chlorate reduction step after the electrolyser (Figure 1), further reducing waste released from chlor-alkali plants.

The wash water, which is mildly acidic, can be recovered and used in other parts of the chlor-alkali process including the production of HCl, which also further minimises water pollution from this industry. The proposed method, if developed further and used, can reduce the release of pollutants from chlor-alkali plants.

Further areas to study are the effect of solution pH, influent chlorate concentration and type of AC on adsorption and the impact of the HCl concentration and type of AC on the chlorate reduction products formed during regeneration.

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