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Degradation of Aniline & Para- Chloroaniline from Water by Adsorption Coupled with Electrochemical Regeneration

Syed Muhammad Shahid Hussain [*,1]
Syed Nadir Hussain[*,1]
Hafiz Muhammad Anwaar Asghar[1]
Hamed Sattar[2]
[1] *Institute of Chemical Engineering & Technology, University of the Punjab,54590, Lahore, Pakistan*
[2] *Institute of Energy and Environmental Engineering, University of the Punjab,54590 Lahore, Pakistan*
*e-mail: shahidhussainshah24@gmail.com (S.M.S.); snhussain.icet@pu.edu.pk (S.N.H.)

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Abstract. Treatment methods for water-containing organics are gaining significant attraction in modern-day research. Amines are an important organic compound class encountered in industrial wastewater streams. The current research paper focuses on studying the adsorption behavior of aniline and parachloro-aniline using a graphite-based adsorbent, namely, Nyex-1000, and the subsequent regeneration of the adsorbent. To determine Nyex-1000's adsorption capacity, several parameters, including time, pH, and concentration, were assessed. Adsorption isotherms, kinetics, and used adsorbent regeneration were also investigated. The adsorption of aniline and parachloro-aniline was found to be quite rapid owing to its non-porous nature. Moreover, the low energy requirement makes the process quite economical due to the high electrical conductivity of the adsorbent. The adsorption data was fitted to Langmuir, Freundlich, Redlich Peterson, Sips, and Toth isotherm models. In aniline's case, Langmuir and Parachloro-aniline Sips models gave the best fitting with the highest R^2 value. A regeneration efficiency of 100% was observed in case of both aniline and parachloro-aniline by passing a charge of 5 and 10 coulombs per gram through the adsorbent bed 10 mm in thickness. Adsorption for parachloro-aniline was found to be 0.88 mg/g, and for aniline was found to be 0.40 mg/g. The reduction in adsorption capacity was minimal after several adsorption and regeneration cycles. This study found that spent adsorbent could be regenerated effectively through electrochemical regeneration.

Keywords: Adsorption, Electrochemical Regeneration, Aniline, Parachloro-aniline

INTRODUCTION

Industrialization and urbanization are leading to enormous water pollution worldwide (Mahmood et al., 2019). Different types of effluents are responsible for this problem. Organic pollutants discharged into water streams at a high level responsible for severe health problems for humans and extremely detrimental to aquatic organisms (Bhomick et al. 2017). Amines are an important class of organic compounds that are extensive applied in different industries like textile, pharmaceutical, leather, plastic paint, and petrochemical (Fishbein, 1981). These compounds are produced in bulk quantities and in effluents from various industries. These compounds are highly

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detrimental to the aquatic environment and humans, even if present in low concentration (Bhunia et al. 2003). Aniline and parachloroaniline are primary aromatic amines.

These substances can change hemoglobin into methemoglobin, lowering the blood's oxygen capacity. Humans who are exposed to such compounds may have headaches, weariness, vertigo, and respiratory problems (Bhunia et al. 2003).

Aniline $C_6H_5NH_2$ is also known as phenyl amine. In 2022 the global aniline amounted to 9.4 million tons per annum due to its extensive use in the industries.it is used in rubber accelerators, dyes and intermediates, petroleum refining, explosive manufacture, and a number of other industries. Parachloroaniline, a chlorine derivative of aniline, also finds numerous applications in dye manufacturing and the preparation of insecticides and pesticides. An effective method for removing aniline and its chlorine derivatives like parachloro-aniline from wastewater bodies is, therefore, an important issue to be addressed. It is the focus of the current paper.

A number of known techniques are available for the degradation of anilines and their derivatives. These techniques include solvent extraction, biodegradation (Campo et al., 2011), catalytic oxidation (Javaid and Qazi, 2019), membrane separation processes (Abidin, 2014), ultrasonic degradation (Liang et al., 2015), and adsorption. These techniques are, however, accompanied by many technical and economic constraints. For instance, secondary waste is produced in the solvent extraction process, , and its disposal is challenging, which may lead to more severe environmental problems (Zeitoun et al., 1966). The application of biodegradation to wastewater treatment is limited because it cannot deal with a high concentration of pollutants, and overall efficiency could be higher in some cases. Further the production of sludge during biodegradation and its disposal leads to a reduction in the overall efficiency of the process. The other methods are limited by certain factors such as cost and sensitivity, which renders them unfit for the treatment of water streams on a certain scale.

Removing organics with low concentration adsorption is an attractive technique (Bello and Raman, 2018). The various factors, such as cost, adsorption capacity, and provision for adsorbent regeneration make it a favorable choice for removing organic contaminants from water. A number of adsorbents, such as activated carbon (Saleem et al., 2019), carbon nanotubes (Ren et al., 2011), and pine saw dust (Zhou et al., 2014) have been reported in the literature for the removal of organics from wastewater. Ahmadi and Igwegbe (2018) studied the adsorption behavior of phenol on activated carbon at 30 °C. Both Langmuir and Freundlich isotherms were applied to describe the adsorption behavior of phenol on activated carbon

Although activated carbon possesses a high adsorption capacity for the targeted organic pollutants and has been found effective in removing several organics, the problem is in its regeneration. Different options like thermal and biological regeneration are available. In thermal regeneration, steam and nitrogen are used at elevated temperatures of 1100K, which requires a lot of energy input. Further during regeneration, high adsorbent losses are encountered, and the pore structure and size may change during regeneration. The offsite regeneration adds to high transportation costs and makes the regeneration process quite expensive. Large equipment cost and land requirements make the process uneconomical in biological regeneration. Further some organics cannot be removed as they are non-biodegradable (Miguel et al., 2001). For activated carbon, electrochemical regeneration is a good option as it shows high regeneration efficiencies with low adsorbent losses, but owing to the structure of activated carbon and its low electrical conductivity, high regeneration time is observed, which adds to the cost of the process (Narbaitz and Cen, 1994).

Graphite based adsorbents can effectively remove organics from water and be regenerated quite effectively, showing a regeneration efficiency of 100% by employing simple divided electrochemical cell (Brown et al., 2004). The graphite-based adsorbents have no pores and so low adsorption capacity, but due to high electrical conductivity, they can be regenerated by application of low voltages.

In a study by Muhammed et al. (2011), Nyex-1000 showed a substantial capability for adsorbing acid violet-17 and crystal violet dyes, with an efficiency of 88% in two minutes.

After the adsorbent was loaded with these compounds, 100% regeneration was done in 10 minutes by passing a charge of 25 Coulombs at a current density of 20 $mAcm^{-2}$ using a batch electrochemical cell (Mohammed et al., 2011)

A Process developed by Arvia Technology Ltd. UK, known as Arvia process, employs an electrically conducting type of Graphite based adsorbent called Nyex-1000. This adsorbent offers the adsorption of organics pollutants and a method to electrochemically regenerate the adsorbent by oxidation of organics species adsorbed. The technique has been effectively used in the removal of a number of organic compounds like phenol, atrazine (Brown et al., 2004), radioactive oily wastes (Brown et al., 2013), and volatile organic compounds (Conti-Ramsden et al., 2012).

This technique's suitable for removing aniline and its derivatives from an aqueous solution has not yet been explored. This work aims to investigate the adsorption kinetics, the adsorption capacity of adsorbent, and its subsequent regeneration, evaluate the regeneration efficiency by employing the aforementioned technique and evaluate the overall efficiency of the process.

MATERIALS AND METHODS

Materials

A GIC compound with the trade name Nyex -1000 supplied by Arvia Technology UK was used as an adsorbent. The compound was in the form of flakes and possessed a mean particle diameter of 484 μm (range 50 μm-850 μm) as can be seen from Figure 1. The BET surface area, as determined by nitrogen adsorption, was 1.0 m^2/g with a pore volume of 0.0038 cm^3/g, and bulk density 0.89g/cm^3. The particles of Nyex were nonporous, so they had no internal surface area. The iso–electric point of Nyex -1000, as reported by the supplier company, was found to be at pH 5.0. Zeta potential and XRD spectra of material are shown in Figure 2 and Figure 3.

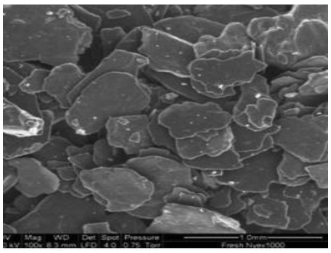

Fig. 1: Scanning electron micrograph (SEM) of Nyex -1000 flakes with smooth and flat morphology

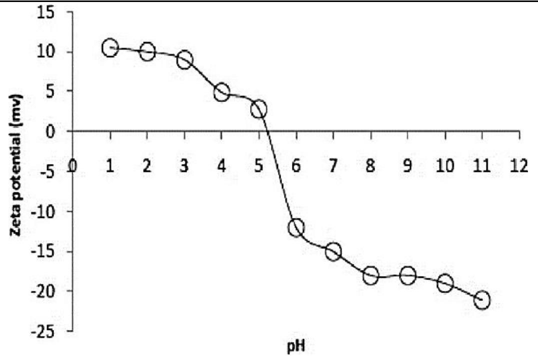

Fig. 2: Zeta potential measurement of Nyex-1000 (Asghar, 2011)

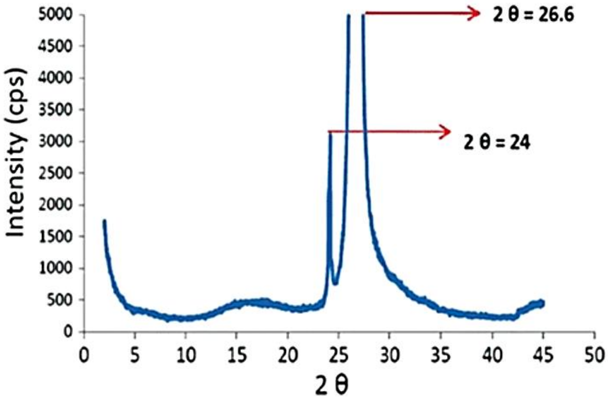

Fig. 3: XRD pattern of Nyex-1000 (adapted from Asghar, 2011)

Aniline analytical grade was purchased from Alfa Aesar Co, Germany (99.9% pure). Parachloro-aniline was purchased from Alfa Aesar Co, Germany, with 98% purity. Other chemicals, including sodium chloride, sulphuric acid, and sodium hydroxide were analytical grade.

Aniline solution Analysis

A double beam spectrophotometer measured the aniline concentration for various samples after a complex formation between acid phthalate solution, dimethyl phenylene diamine, sodium meta periodate, and the aniline solution (Kornepati and Tella, 2015). The samples were analyzed at 530 nm.

Methods

Kinetics Study

100 mgL^{-1} of aniline and parachloro-aniline solutions were taken in a 1 L flask, and 120 g of GIC was added. The mixture was stirred using a magnetic stirrer at fixed rpm, and samples were drawn at intervals of 5 minutes for the first half an hour, followed by the withdrawing samples at intervals of 10 minutes for 1.5 hours. These samples were filtered through a 0.45 μm syringe and analyzed for aniline concentration. The adsorption equilibrium time was established when no further change in aniline concentration was observed.

Adsorption Isotherms

The adsorption isotherms for aniline and parachloro-aniline were determined by mixing 10 grams of adsorbent in a 100ml flask containing 100 mg/L solution for aniline and 200 mg/L solutions for parachloro-aniline. Mixing was done at fixed rpm for 30 minutes in the case of aniline and parachloro-aniline. This was the time required for achieving equilibrium, as observed during the kinetic study of both compounds. Stock and final solution samples were obtained and analyzed for the concentration specified in the analysis section. The adsorbent loading *q* (mg/g) was determined from the initial and final concentration of the samples, as given in Eq. (1).

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

Where q_e (mg/g) is the equilibrium loading, C_0 and C_e are the initial and equilibrium concentration (mg/L) in solution, and m is the mass of adsorbent added per unit volume in grams. V is the volume in L.

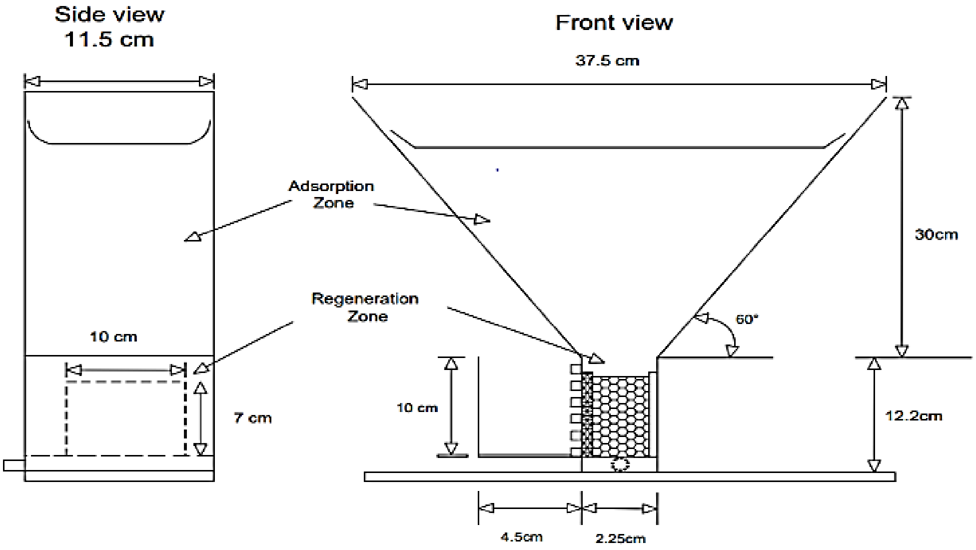

Fig. 4: Batch adsorption and regeneration cell

Effect of pH on Adsorption of Aniline and Parachloro-aniline

The effect of pH on adsorption capacity was investigated under neutral and alkaline conditions by adding 10 g of adsorbent to a 100 mL flask containing 100 (mg/L) of aniline and 200 (mg/L) of parachloro-aniline. Mixing was done at fixed rpm for 30 minutes using a magnetic stirrer. The alkaline conditions were maintained using a sodium hydroxide solution. After the adsorption, the flask's contents were filtrated and analyzed for concentration, as discussed in the Analysis section.

Batch Adsorption and Electrochemical Regeneration

The adsorption and regeneration were carried out in a Y shaped cell as shown in Figure 4. The cell is fabricated in a manner that it has compartments, an anodic and a cathodic compartment isolated by microporous polyethylene membrane Deramic-350 - At the base of the anolyte chamber, there was a provision for carrying out the mixing of adsorbent (GIC) with water containing aniline and parachloro-aniline. The dimensions of the anode were 10cm x 7cm with a 5mm thick plate of graphite. The cathode was fabricated with 316- stainless steel sheets, 1mm thick. The layout of the cycle is depicted in Figure 4.

Working of Cell

The batch mode was used for operating the cell. Solution of 0.3% concentration of NaCl was poured into the catholyte chamber to ensure complete cathode and membrane submersion. In a separate run, the anolyte chamber was filled with 1.0 liter of aniline and parachloro-aniline solutions. Solution with a concentration of 100 mg L^{-1} was used for aniline, and 200 mgL^{-1} was used for parachloro-aniline. A compressor was used to fluidize it, followed by adding 120 g of GIC. The fluidization of the mixture was carried out for 30 minutes in the case of aniline and 20 minutes in parachloro-aniline, corresponding to their adsorption equilibrium time as established in the kinetic study. After the equilibrium was established, the air supply was switched off and the adsorbent was allowed to settle down under gravity for 10 minutes. The water under test was removed from the upper portion of the cell and was subsequently analyzed for residual aniline concentration. In order to regenerate, the adsorbent currents of 0.5 A and 1.0 A for 20 minutes, respectively, were used. The treated solution was drained, and the cell was charged with another 1.0 liter of fresh aniline and parachloro-aniline solutions, in separate runs. The initial adsorption step was repeated under similar conditions. After the adsorption process had been completed with the attainment of equilibrium, the residual water was again analyzed for aniline and parachloro-aniline concentrations in separate runs. In this way, the adsorption followed by regeneration was followed for 4 cycles for both compounds in different runs.

Electrochemical Regeneration

It characterizes the degree to which the adsorbent's adsorption capacity has been restored during electrochemical regeneration. It is represented by the ratio of adsorption capacity under regeneration to that achieved under the same adsorption conditions as shown in Eq. (2).

$$\mathrm{Y_{reg}} = (\mathrm{q_{reg}}/\mathrm{q_i}) \qquad (2)$$

where q_{reg} is the adsorption capacity after regeneration and q_i represents the initial adsorption capacity.

Theoretical Charge and Current Efficiency

Assuming complete mineralization of aniline and parachloro-aniline according to Eqs. (3) and (4).

$$\mathrm{C_6H_7N + 14H_2O \rightarrow 31H^+ + 2CO_2 + NH_4{}^+ + O_2 + 32e} \qquad (3)$$

$$\mathrm{C_6H_6ClN + 12H_2O \rightarrow 26H^+ + 6CO_2 + NH_4{}^+ + }Cl^- \mathrm{+ 26e} \qquad (4)$$

The theoretical charge was estimated according to Eq (5) for aniline and parachloro-aniline, respectively,

$$Q_{\mathrm{th}} = \frac{n*(ci-cf)VF}{Mw} \qquad (5)$$

where C_i and C_f are the initial and final concentrations of adsorbate in mg/L, V is the volume of solution taken in litres and F is the Faraday constant, M_w is the molecular weight of the adsorbate in grams/mole, and n is the number of electrons involved in the complete mineralization of the adsorbate.

From the theoretical charge calculated, the current efficiency was calculated using Eq. (6).

$$current\ effeciency\% = \frac{Theoratical\ charge}{Actual\ charge}*100 \qquad (6)$$

RESULTS & DISCUSSION

Adsorption Contact Time

The adsorption equilibrium time was established by adding 120 g of Nyex 1000 in 1 L 100 ppm of amine solution (aniline and parachloro-aniline) in a flask and agitated at fixed rpm at a pH of 6.86. The samples were withdrawn from the mixture at regular intervals of 5 minutes for the first 30 minutes, followed by the withdrawal of samples after every 10 minutes for the remaining 1 hour. These samples were analyzed for aniline concentration by using an ultraviolet spectrophotometer. The initial removal rate of aniline and parachloro-aniline was fast for the first 5 minutes, and maximum aniline removal was observed in this span. This may be because a large number of vacant sites are initially available on the adsorbent's surface for the adsorbate, and eventually, with time these sites get saturated with the adsorbate. So the adsorbate uptake by the adsorbent decreases after a specific time. The concentration of aniline decreased with an increase in time until 30 minutes in the case of aniline and 20 minutes in parachloro-aniline, after which equilibrium was established which was inferred from almost no change in the absorbance values of amine samples of adsorption as depicted by Figure 5. Ahmadi and Iqwegbe (2018) has demonstrated the adsorption of aniline on modified bentonite from aqueous solution took place in 30 minutes. Zavareh et al. (2017) carried out the adsorption of aniline on Cu^{2+}–treated chitosan/alumina nano-composite and has reported an adsorption equilibrium time of 30 minutes.

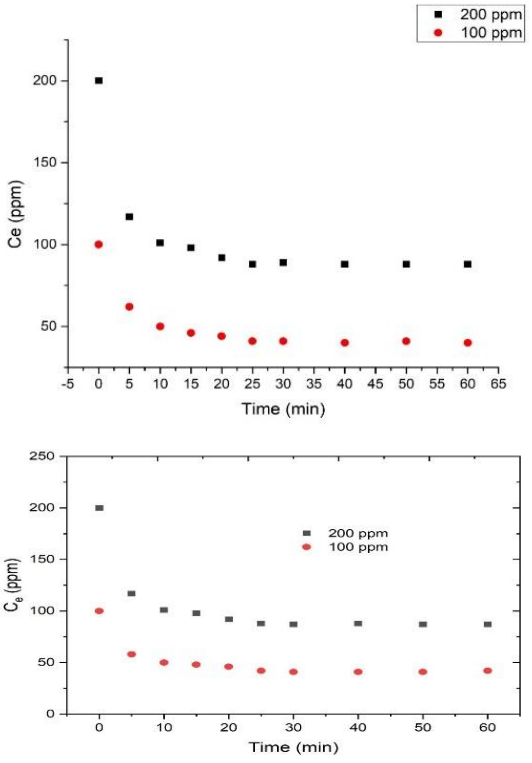

Fig. 5: Adsorption kinetics of aniline and Parachloro-aniline on GIC compound using 120 g of GIC compound in 1 L amine solution of concentration 100 ppm and 200 ppm.

Different Kinetic models are available in the literature to characterize the adsorption kinetics. The most commonly used models are pseudo 1st order and pseudo 2nd order. This Equation represents by first order model of Eq. (7).

$$\frac{dq}{dt}=k_1(q_e-q_t) \tag{7}$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t in (mg/g), and k_1 is the kinetic rate constant for the first order.

This equation represents by pseudo 2nd order model is shown in Eq. (8).

$$\frac{dq}{dt}=k_2(q_e-q_t)^2 \tag{8}$$

where q_e and q_t are the adsorption capacities at equilibrium and time t. and k_2 is the rate constant for the pseudo 2nd order model. Both models were applied to characterize the adsorption kinetics of aniline on the GIC compound.

The first order and 2nd order models were applied to the kinetic data on aniline and parachloro-aniline, as shown in Figures 6 and 7, respectively.

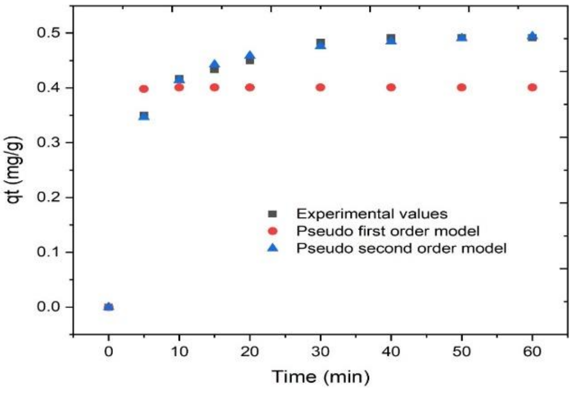

Fig. 6: Plot of pseudo 1st order and 2nd order models using non- linear squared error method for aniline loading on the GIC adsorbent.

The values of the rate constants and equilibrium adsorption capacity obtained from 1st order and 2nd order models are tabulated in Table 1.

Table 1. Kinetic constants and equilibrium loading for the adsorption of parachloro-aniline obtained through the fitting of pseudo 1st order and 2nd order models, data plotted in Figure 7)

Model compound	***Co*(mg/g)**	***qe* (mg/g)**	**k_1(min^{-1})**	**qe_1(mg/g)**	**k_2(g/mg-min)**	**qe_2(mg/g)**
Parachloro-aniline	200	0.825	0.244	0.810	0.475	0.868
Aniline	100	0.496	1	0.400	0.803	0.514

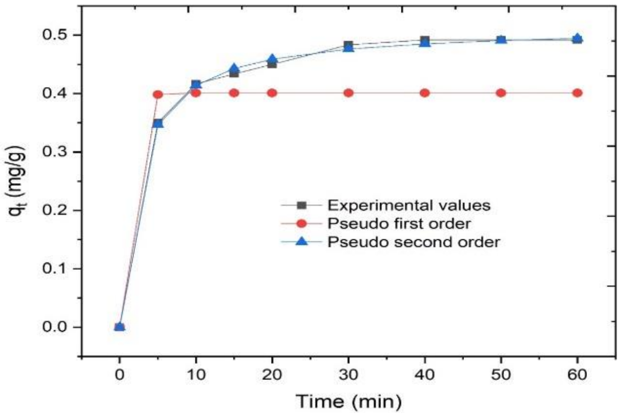

Fig. 7: Plot of pseudo 1st order and 2nd order models using non- linear squared error method for parachloro-aniline loading on the GIC adsorbent.

Adsorption Isotherms

Adsorption capacity was evaluated by adding 20 grams of Nyex 1000 to various ppm of aniline solution, as shown in Figures 6 and 7, followed by adding 10 grams of Nyex -1000 to 100 ppm solution of aniline. The samples were withdrawn after giving an equilibrium time of 30 minutes in the case of aniline and 20 minutes in parachloro-aniline. In the case of parachloro-aniline an adsorbent dosage of 5 g was selected as for a dosage instead of 10 g and 20 g as in the case of aniline a since it entirely removed the adsorbate from the solution. These samples were analyzed for aniline and parachloro-aniline concentrations. The adsorption capacity of Nyex 1000 was evaluated using Eq. (1). The adsorption capacity of Aniline was estimated to be 0.395 mg/g of adsorbent in case of aniline, while in the case of Para-chloroaniline, the adsorption capacity was evaluated to be 0.88 mg/g in the case of parachloro-aniline which was more than double of Aniline. An et al. (2016) demonstrated a greater adsorption capacity for parachloro-aniline than aniline on activated carbon based on urea formaldehyde resin. The adsorption isotherm for aniline and parachloro-aniline was obtained at 25 °C. Five different models were fitted to the isotherm data, and the details are given in the following Table 2 and fitted lines are shown in Figure 8 and 9.

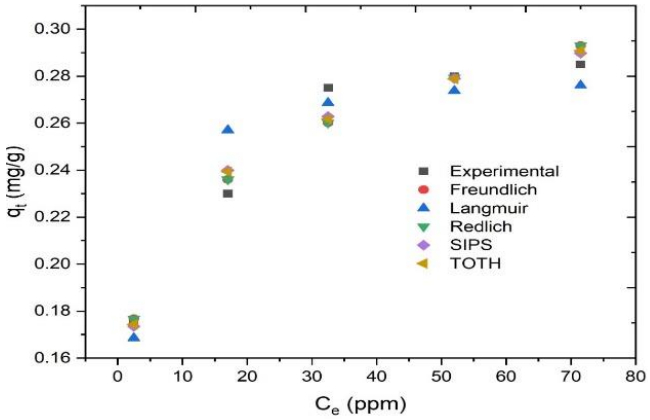

Fig. 8: Comparison of different isotherm models for adsorption of parachloro-aniline on GIC adsorbent

Table 2. Isotherm Model Parameters

Isotherm Model	Equation	Model Parameters (aniline)		Model Parameters (parachloro-aniline)	
Freundlich	$qe = K_F C_e^{1/nF}$	K_F	0.154	K_F	0.015
		n_F	6.642	n_F	0.985
		R^2	0.981	R^2	0.924
Langmuir	$qe = K_L\, Ce/(1 + bCe)$	K_L	0.283	K_L	16.230
		b	0.592	b	0.001
		R^2	0.997	R^2	0.920
Redlich Peterson	$qe = K_R Ce/(1 + a_R Ce^{b_R})$	Kr	39.996	K_r	0.076
		a_R	259.158	a_R	3.707
		b_R	0.850	b_R	0
		R^2	0.981	R2	0.691
SIPS	$qe = K_{LF}\, Ce^{n_{LF}}/(1 + a_{LF} Ce)^{n_{LF}}$	K_{LF}	0.209	K_{LF}	1.060×10^{-4}
		n_{LF}	0.302	n_{LF}	2.702
		a_{LF}	0.068	a_{LF}	0.034
		R^2	0.984	R^2	0.964
Toth	$qe = \frac{K_t Ce}{(at + Ce)^{1/t}}$	Kt	0.168	Kt	0.0166
		at	0.249	at	44.258
		t	1.148	t	140.166
		R^2	0.983	R^2	0.922

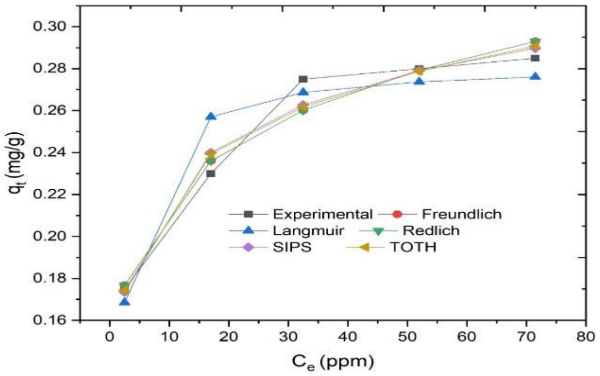

Fig. 9: Comparison of different isotherm models for adsorption of parachloro-aniline on GIC adsorbent

The application of models to the adsorption of aniline and parachloro-aniline shows that the Langmuir model fit is the best in the case of aniline and in case of Langmuir Sips model fits the experimental data more closely. In the case of aniline the favorability of models is in the order of Langmuir>SIPS>Toth>Redlich Peterson> Freundlich model. The constants evaluated in the case of Langmuir model K_L are correlated to the suitable area and porosity of the adsorbent. Its high value indicates that higher adsorption capacity can result from a greater surface area and higher pore volume. In case of parachloro-aniline the favorability of models is in the order of SIPS>Freundlich> Toth> Langmuir > Redlich Peterson model. The sips model indicates monolayer adsorption characteristics like Freundlich model, and the parameters are influenced by concentration, temperature, and pH.

Effect of pH on Adsorption Capacity

The adsorption capacity was analyzed at different pH values. The pH was increased from neutral conditions to alkaline conditions by dropwise addition of 0.1M sodium hydroxide solution. After maintaining pH at 9.4 to 9.5, various concentration solutions (i.e., 20 ppm, 40 ppm, 60 ppm, and 80 ppm) were prepared, and 20 grams of Nyex 100 was added to each of the above-mentioned solutions for an equilibrium time of 30 minutes in case of aniline and 20 minutes in case of parachloro-aniline for which the adsorbent dosage was 5 g. Samples were analyzed for residual aniline concentration adsorption capacity and were evaluated using Equation (2). After analysis of solutions, the adsorption capacity was found to be more for neutral pH conditions than alkaline conditions in both cases. This is attributed to the fact that under alkaline conditions the hydroxyl ions present in the solution start competing with the adsorbate for active sites, which is not the case under neutral conditions. The effect of pH on the adsorption capacity of aniline and para chloroaniline under acidic conditions was not investigated for two reasons. The aniline and parachloro-aniline are both basic, and there may be a chance of chemical reaction between the acid used to maintain the acidity and the anilines. Further the pKa value of aniline is 4.6 at a pH less than the pKa value of aniline is converted to anilinium ions due to protonation of amino-group present in the adsorbate and electrostatic repulsion may start between the acidic groups on the adsorbent surface (carboxylic, lactonic and phenolic) which also carry a positive charge. Zavareh et al., (2017) demonstrated that up to pH value of 7.2, the adsorption of anilines increases with an increase in pH and then starts decreasing under alkaline conditions during the adsorption of amines on Cu^{+2} – treated chitosan/alumina nanocomposite. Liu et al. (2015) conducted a similar investigation on the removal of amines from aqueous solutions by activated carbon coated with chitosan, the adsorption capacity was found to increase with increasing pH until the neutral conditions, after which a sharp decrease in pH was observed. The effect of pH on loading of both compound on GIC is shown by Figures 10 and 11.

Regeneration Efficiency

Batch adsorption experiments were conducted in a Y-cell. After each adsorption cycle, samples were analyzed for aniline concentration, and regeneration was carried out for 20 minutes by applying current 0.5 amps, and 1.0 amps. In the case of 0.5 amps, regeneration efficiency increased from 92% to 93.5% over 4 adsorption cycles. In the case of 1.0 amps, 100% regeneration of the adsorbent was observed. These results as shown in Figures 12 and 13.

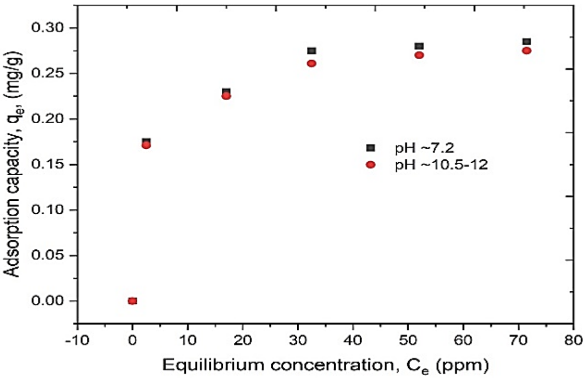

Fig. 10: Effect of pH on adsorption capacity of aniline

When a current of 0.5 A has used, the concentration of aniline adsorbed by the regenerated adsorbent was higher in the second adsorption run, which eventually reduced over a number of runs, this may be attributed to the fact that during the first regeneration, most of the aniline oxidized into subsequent products but as further regeneration cycles were carried out the adsorption sites may have been occupied by the oxidized products of anodic oxidation and the supplied charge may not have been sufficient to remove some of these oxidized species from the surface of the adsorbent. While in the case of parachloro-aniline a slight decrease in the ppm removed is observed over various adsorption followed by regeneration cycles. This may be attributed to the fact that some intermediates of oxidation have covered the vacant adsorption sites and further some surface of the adsorbent might have detoriated. The ppm of aniline removed from two compounds are tabulated in Tables 3 and 4 and Figures 14, 15 and 16.

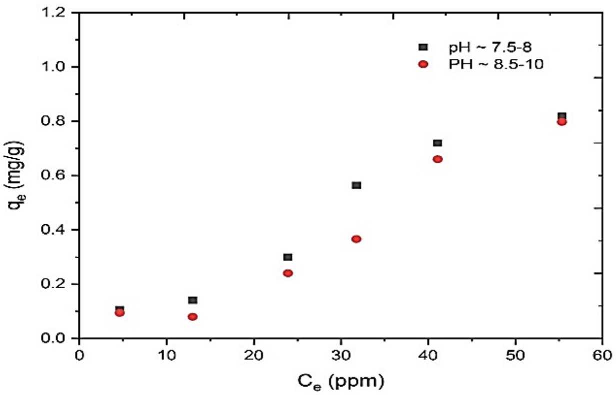

Fig. 11: Effect of pH on adsorption capacity of parachloro-aniline

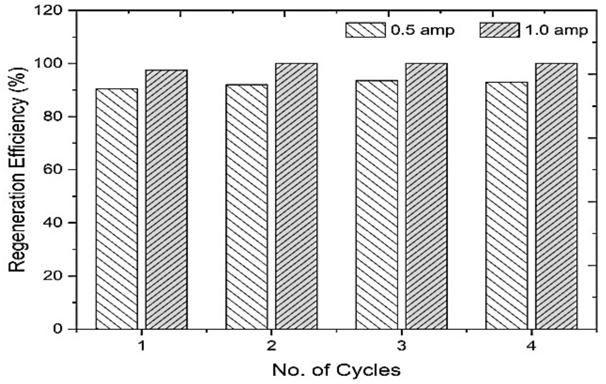

Fig. 12: Regeneration efficiency in xase of aniline

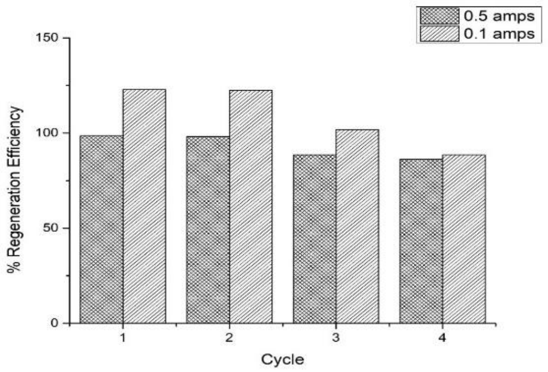

Fig. 13: Regeneration efficiency in case of parachloro-aniline.

Table 3. ppm of aniline removed

Cycle no.	Initial Concentration	ppm Removed at 0.5A	ppm Removed at 1.0A
1	100	79.3	79.6
2	100	72.0	100.0
3	100	73.0	100.0
4	100	73.5	99.8

Table 4. Ppm of parachloro-aniline removed

Cycle no.	Initial Concentration	ppm Removed at 0.5A	ppm Removed at 1.0A
1	200	98.0	103.0
2	200	91.0	125.0
3	200	89.0	120.0
4	200	90.0	118.0

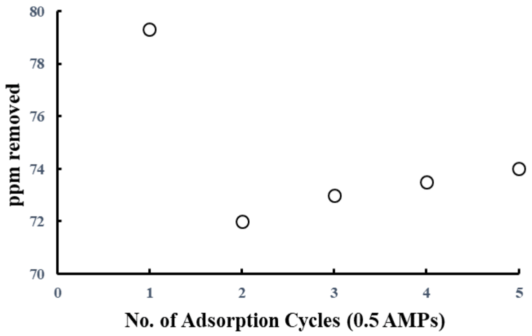

Fig. 14: ppm of aniline removed over no of adsorption cycles (0.5 A)

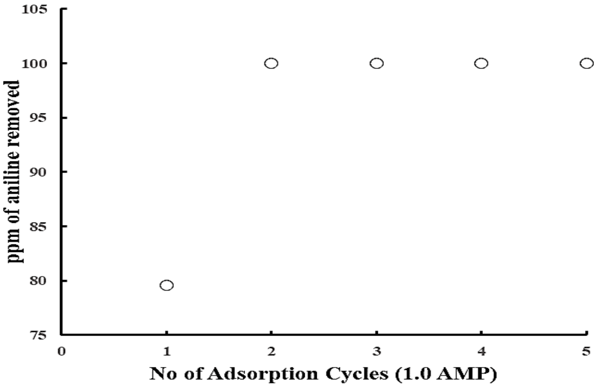

Fig. 15: ppm of aniline removed over no of adsorption cycles (1.0 A)

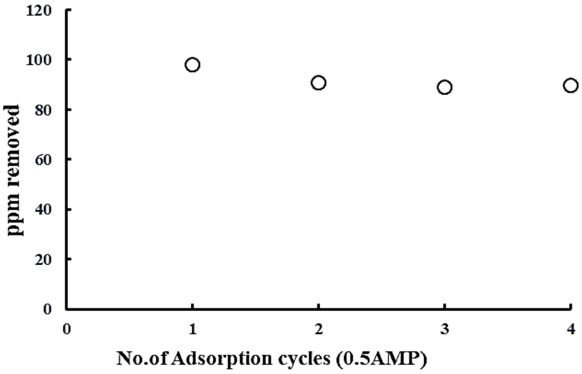

Fig. 16: ppm of parachloro-aniline removed at 0.5 A

Table 5. %-Regeneration in case of Aniline

Cycle no.	%-Regeneration in Case of Aniline		
	Initial Concentration	0.5A	1.0A
1	100	90.5	98.0
2	100	92.0	100.0
3	100	93.0	100.0
4	100	93.2	100.0

When a higher current of 1 Amp was supplied to the cell, then most of the products adsorbed over the surface of the adsorbent were oxidized into products, and hence more vacant sites may have been available for further adsorption, so an increase in the adsorption of both compounds was observed by using a higher current. The regeneration efficiencies of the two compounds are tabulated in Tables 5 and 6.

Table 6. %-Regeneration in case of parachloro-aniline

Cycle no.	%-Regeneration in case of Parachloro-Aniline		
	Initial Concentration	0.5A	1.0A
1	200	89.1	135.0
2	200	87.24	125.0
3	200	88.23	120.0
4	200	79.0	115.0

The theoretical charge required for complete mineralization of parachloro-aniline was estimated to be 3.21 coulombs per gram, whereas the actual charge applied at 0.5 amps for 20 minutes corresponds to a value of 5 coulombs per gram, and 1 amp applied for 20 minutes corresponds to 10 coulombs per gram. These values correspond to a current efficiency of 64.2% and 32.1%. The theoretical charge is estimated at 1.602 coulomb per gram in aniline case. The actual charge applied is estimated to be the same as in the case of parachloro-aniline, corresponding to current efficiencies of 32% and 16% in the case of aniline. The regeneration results shown above may give a different picture than some by products are also produced while regeneration and their identification and quantification need attention. Kirk et al. (1985) has reported the formation of maleic acid, benzoquinone, and carbon dioxide while carrying out anodic oxidation of dilute aqueous solutions of aniline on lead dioxide anodes. A current efficiency of 15-40% for the complete oxidation of aniline to carbon dioxide has also been reported in the above study. Kadar et al. (2001) carried out electrochemical oxidation of 4-chloroaniline or parachloro aniline in addition to that of 2,4-dichloroaniline and 2,4,6 trichloroaniline in acetonitrile solution and has reported 2-amino-4,5 dichloro-phenylamine and 2,4 dichloroaniline as the expected products of anodic oxidation [26]. Identifying of these products and their subsequent quantification needs attention and can help evaluate the overall efficiency of the process.

CONCLUSION

This study depicts that although the adsorption capacity of Nyex-1000 is low for aniline, it is evident that the adsorption equilibrium is attained in a very short of time. The applications of kinetic models to the kinetic data show that pseudo 2nd order model fits closely to the experimental data. The experimental isotherm data was fitted with various models and showed that Langmuir model gives a better fit in comparison to other models in the case of aniline whereas the Sips model gave a better fit in case of parachloro-aniline. Both models indicate that the adsorption is monolayer owing to non-porous nature of the adsorbent and the availability of a fixed number of vacant sites for the adsorption of aniline and parachloro-aniline. Adsorption for parachloro-aniline was found to be 0.88 mg/g and for aniline was found to be 0.40 mg/g. Furthermore, the adsorbent can be regenerated quite easily by the application of low potential and currents, so adsorption coupled with electrochemical regeneration can be effectively applied to the removal of primary aromatic amines like aniline from aqueous samples for low concentrations of aniline, and the method can prove to be quite beneficial and economical owing to low energy consumption because of higher electrical conductivity of Nyex-1000. More investigation into the adsorption of aliphatic and aromatic amines can be made using Nyex-1000 as an adsorbent and the method is a valuable addition to the current research on degradation of amines through adsorption.

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