

Industrial Wastewater Treatment by Using Graphite Intercalation Compounds as an Adsorbent

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ABSTRACT: *Effluent, containing toxic and hazardous wastes, discharged by industries has been an eye-catching issue for researchers over the past few years. Mainly, this hazardous waste incorporates a large variety of dyes, chemicals, and traces of heavy metals. This work focuses on the treatment of industrial wastewater using the adsorption technique for Graphite Intercalation Compound (GIC) as an adsorbent. Nyex™ 1000, a commercial adsorbent with a surface area of 1.0 m²/g, offering a Bulk density of 0.88 g/cm³ and Pore diameter of 133 Å respectively, was utilized to remediate an industrial contaminant. A GIC adsorbent was found to reduce COD by about 90% i.e., 150 mg/L to 10 mg/L. The outcome of this research has revealed that Graphite intercalation compound (GIC) as an adsorbent is suitable for the reduction of COD from industrial effluent. Kinetic studies reveal adsorbent surface heterogeneity is increased and multilayer adsorption was observed. 6 cyclic adsorption studies were performed by regenerating the adsorbent 5 times consecutively. The GIC adsorbent was regenerated via an electrochemical reactor and has shown a significant regeneration efficiency of more than 99%. The electrochemical reactor was integrated with a solar energy system to make the process cost-effective.*

KEYWORDS: *Adsorption; COD reduction; Electrochemical regeneration; GIC adsorbent; Pulp and paper effluent; Wastewater treatment.*

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1021-9986/2023/11/3683-3696 14/\$/6.04

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INTRODUCTION

Water is considered vital in almost every industry, as it is a major ingredient in the industrial process; without it, an enterprise cannot run its operation. The researchers describe industrial wastewater as hazardous components released into the environment, either treated or untreated, after a particular industrial route. The release of contaminated industrial water to nearby surroundings leads to disastrous outcomes [1]. Contaminated water has been the main dilemma [2] not only for underdeveloped countries like Pakistan but also worldwide. Different countries have defined the threshold limits for the COD discharge into the environment. According to Pakistan National Environmental Quality Standards (Pak- NEQS), the maximum limit for COD discharge into inland water is 150 mg/l whereas into the sea is 400 mg/l.

Resins and fatty acids, including wood extractives, are the main contaminants found in pulp and paper effluent. The primary components of pulp and paper industry effluent also include biocides, surfactants, phenolic compounds, additives used in paper production, as well as side products created during the bleaching process, such as dioxins and furans [3].

Removal of toxic compounds, floating matters, suspended solids, colloidal particles, and the color is done by various techniques like screening, floatation, coagulation, adsorption, oxidation, sedimentation, ozonation, reverse osmosis, electrolysis, nano-filtration technologies, and ultra-filtration [4]. Dissolved air floatation (DAF) was reported to remove 65–93% of Total Suspended Solid (TSS) [5]. Another study reported more than 95% removal of TSS by Dissolved Air Floatation [6].

Many studies have been conducted on coagulants such as Horseradish Peroxide (chitosan), $Al_2(SO_4)_3$, Polyethyleneimine (PEI), and Hexamethylene diamine Epichlorohydrin polycondensate (HE) for the removal of total organic carbon (TOC), color, and absorbable halides (AOX) from paper mill effluent [7]. In another study, it was reported that using alum as a coagulant reduction of 96% COD from the waste of the paper machine, 20% COD from bleaching effluents, and 50% COD from the pulping process can be achieved [8].

Ferhan and Balcioglu et al. worked on the photocatalytic oxidation process for the treatment of bleaching wastewater from the Kraft pulp stating that the elimination immensely depends upon the concentration of COD and on chloride

reaching a specific limit [9]. *Zamora et al.* found out that using horseradish, the effluent from the Kraft mill could be decolorized by 50% in a three-hour reaction [10].

In order to benefit from the distinctive attributes of two or more methods, integrated treatment is designed. *Verenich et al.* reported 51% COD removal using a combination of wet oxidation and coagulation process [11]. *Verenich and Kallas et al.*, using the same combination, reported 83% and 75% color and lignin removal, respectively [12]. Another study reported a significant amount of COD removal using a combination of biofilm and ozone reactor [13]. *Athanasopoulos et al.* proposed electrolysis or ozonation as post-treatment procedures for lowering NH_4^+N and COD concentration to acceptable levels [14]. Ozone and activated sludge methods revealed an efficient degradation of lignin. *Jokela and Keskitalo et al.* reported that 93% suspended solids, 52% nitrogen, 92% phosphorus, 57% COD, and 50% BOD_7 can be removed from a combination of chemical precipitation and dissolved air floatation [15].

87–97% COD and 97% BOD were removed by combining ozonation and activated sludge treatment [16]. *Schnell et al.* found that the biological treatment helped in eliminating 87–95% BOD, 70–77% COD, and 80–94% resin and fatty acids. *Tardif and Hall et al.* reported that by using an SBR at 20–40 °C, 100% resin acid, 96% fatty acid, 76% dissolved COD, and 34% Total Dissolved Solids (TDS) removal can be achieved [17].

A membrane batch reactor removed 100%, 84%, and 37% of resin and fatty acids, DCOD, and TDS, respectively, at 40–50 °C. Removal of 70 to 90% of COD with the aid of biological treatment of whitewater was also reported [18,19].

The most commonly used technique to remove the contaminants from wastewater is adsorption [2,20]. Adsorption offers several merits over conventional processes, such as low energy requirement and cost-effectiveness. Adsorption posed significant potential to eliminate the effluent, making it a desirable approach for treating industrial wastewater [21]. Nevertheless, the problem with using adsorbents is that they have a specific capacity up to which they can work, and then they need to be replaced. For instance, the anode used in electroplating must be replaced after a particular duration. For this purpose, the adsorbent should be replaced or regenerated, making the process economically viable. Another option

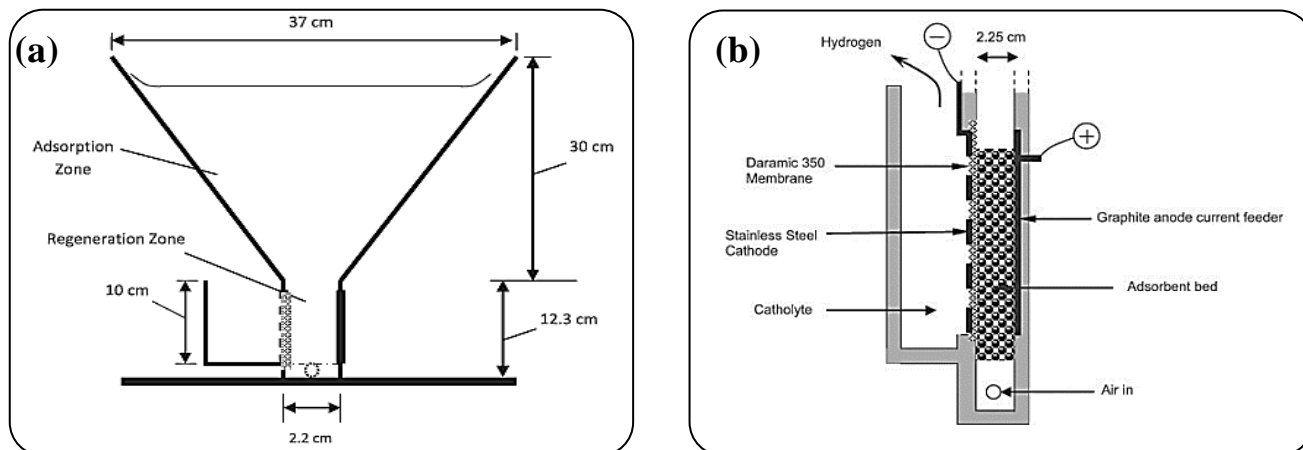


Fig. 1: (a) The sequential batch reactor (SBR) layout used to study the adsorption and electrochemical regeneration process. (b) SBR Anode Compartment

disposing of the adsorbent, which can cause many other problems [18, 19]. Studies have been performed for the adsorbent regeneration using different processes such as microbial, solvent or chemical, ultrasonic, and electrochemical regeneration [24, 25]. But, the electrochemical regeneration process offers several advantages over other regeneration processes like minimal time requirement, in situ regeneration, minimum loss of adsorbent, and maximum regeneration efficiency. Many researchers have reported granular activated carbon regeneration efficiency in the range of 70-90% with the aid of the electrochemical regeneration process [26, 27]. Removal of atrazine from wastewater was achieved by *Brown et al.*, using GIC adsorbent [28]. They reported maximum regeneration of adsorbent in 20 mins.

The present work divulges the in-depth investigation of treating pulp and paper effluent with the adsorption technique using GIC as adsorbents followed by electrochemical regeneration. This research aims to provide an effective and low-cost method for eradicating COD and regenerating the adsorbent while treating hazardous effluent. This study focuses on the adsorption performance of Nyex™ 1000, specifically to evaluate the kinetic and electrochemical regeneration of the adsorbent under different conditions. This study highlights the possible advantages of Nyex™ 1000 such as on-site regeneration of the adsorbent in a low-temperature process with prompt re-use of the adsorbent, hence lowering the amounts of adsorbent required. Moreover, the operating cost of this process is very cheap as compared to the reported studies.

EXPERIMENTAL SECTION

Adsorbent Material and Sample selection

In this work, a wastewater sample was obtained from Shaheen Paper Industry, Lahore, Pakistan. A GIC adsorbent with flake morphology was used. Arvia Technology Ltd. has supplied this adsorbent under the trade name Nyex 1000. The adsorbent is non-porous in nature, with a surface area of about $1.0 \text{ m}^2/\text{g}$. The particles have a mean particle diameter in the range of 400 to 500mm as determined by Mastersizer-2000 (Malvern Instruments, UK). N_2 adsorption method was applied to investigate the adsorbent's pore size, surface area, and other structural properties with a BET analyzer. All the chemicals employed in this research are of analytical grades.

Sequential Batch Reactor (SBR)

A sequential batch reactor (SBR), shown in Fig. 1(a), was operated in the lab to experiment with adsorption, followed by its electrochemical regeneration. An anodic section, Fig. 1(b), of SBR was used to acquire the electrochemical regeneration of sorbent. The anode current feeder consists of a 5mm thick graphite plate. In contrast, the cathode comprises perforated stainless steel (SS) 316 with 1 to 3mm thick diameter perforations.

A micro-porous polyethylene membrane, also named as Daramic 350 separator, was used to separate the electrode sections. The membrane provides low resistance to current and is known for its highly porous nature. The area of both electrodes was measured as 70 cm^2 . Water and the adsorbent were fused during the adsorption process by air sparging through a number of orifices at the bottom

Table 1: Details of Solar Panel

Panel components	Qty.
120 W/12 VDC PV panel	8.0
100 AH-12 VDC Batteries	8.0
120 V/12 VDC PV frame	4.0
100 AH-12 VDX Battery rack	1.0
ELECTRICAL Assembly Kit	1.0
Assembly Kit	1.0
120 W/24 V DX PV Panel	2.0

of the Y-cell. A proper airflow was maintained to avoid water splashing from the top of the cell and efficiently mix the wastewater and the adsorbent [22–24].

EXPERIMENTAL SECTION

Batch Adsorption and its Electrochemical Regeneration

The sample of wastewater to be treated was first analyzed to determine the COD. The process of investigating the COD is explained in sections 3.2-3.4. A known amount of GIC adsorbent was added to the SBR along with the 1L effluvia sample. Continuous air sparging was done for approximately half an hour to better mix the adsorbent and the water sample. The air supply was switched off when the complete adsorption was attained, and the adsorbent particles were allowed to settle in the anode section of the SBR for about 5 minutes under the gravitational force. Since the maximum pore size of the Daramic 350 membrane is 1 μm (with majority of pore sizes between 0.3 and 0.8 μm) [29], and the mean pore size of adsorbent is 485 μm (and a range of sizes between 400 and 500 μm), the difference in their relative sizes is in the magnitude of a few thousands. It is highly unlikely that any of the adsorbent had diffused through the membrane. Moreover, the said membrane is made of polyethylene and does not hold electrostatic charges. Hence, the chances of any adsorbent adhering to the membrane is minimal. Nevertheless, the cell was visually inspected after each experiment to ensure that all of the adsorbent was accounted for. The anode compartment can be seen in Fig. 1(b).

After settling of adsorbent particles, the treated water sample was collected. Before the final COD analysis, the collected sample was filtered to avoid contamination. About 350 mL of electrolyte, consisting of 0.3% NaCl and 0.125 M HCl, was added to the cathode section of the cell. The level of settled adsorbent bed and electrolyte was kept the same for the smooth conduct of experiments.

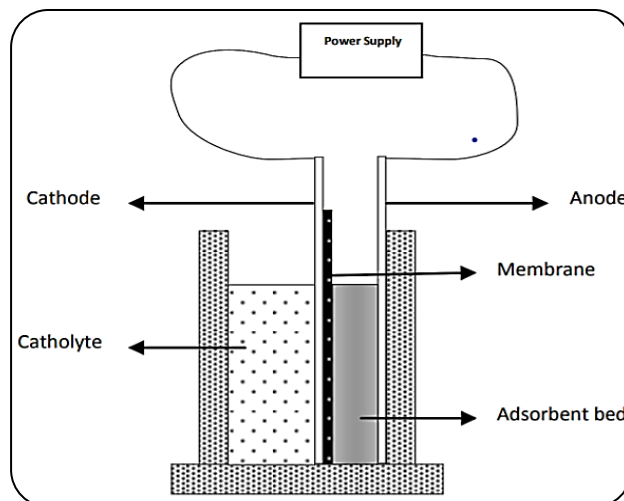


Fig. 2: Schematic representation of the cell.

For the improvement in the regeneration process, NaCl has played an important role. However, in order to maintain the separator conductivity and stability, acidic conditions are necessary [22,23,25]. For the regeneration of the GIC adsorbent, an appropriate amount of solar panel current was applied across the electrodes for a set period. During the complete regeneration process, the current was kept constant, whereas the change in voltage was monitored. The solar panel used in this process was 73.66 cm long and 137.16 cm wide. The detailed description of the solar panel is shown in Table 1.

The solar panel was found efficient because of the consumption of a renewable energy resource, i.e., Sunlight, with the production of 400 kW of electricity. The regeneration done using the solar panel was the cheapest with low maintenance cost among previously reported technologies. The schematic diagram of the electrochemical cell with power supply is shown in Fig. 2. After providing the current to the electrodes for a specific time, the electricity supply to the cell was turned off, and the water sample was taken to analyze its COD after performing the regeneration process.

The remaining water above the adsorbent bed and the electrolyte solution in the cathode section were discharged together. A fresh effluvia sample was poured into the SBR and repeated the above process to investigate the effect of GIC adsorbent on the COD of the wastewater sample. A schematic arrangement of adsorption by the selected GIC adsorbent at a laboratory scale can be seen in Fig. 3. Furthermore, to identify which types of the functional groups of the adsorbent are

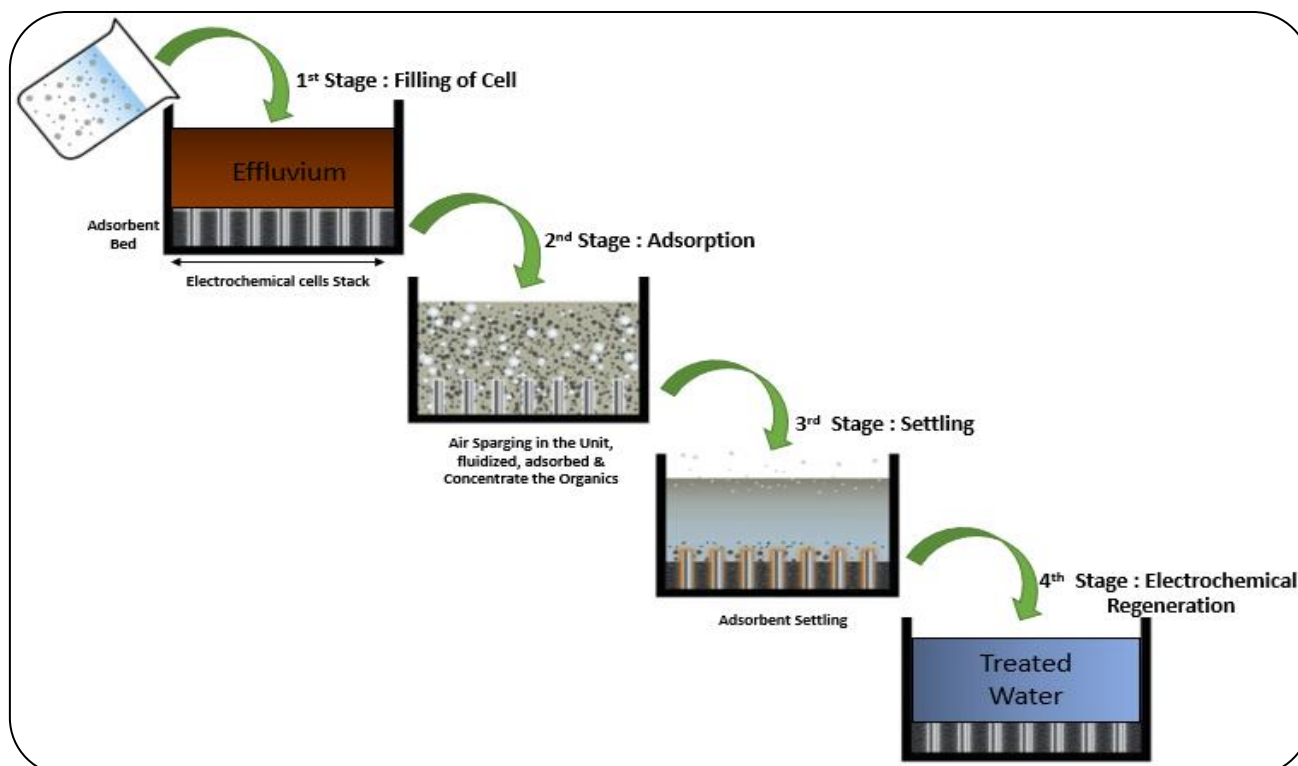


Fig. 3: A schematic representation of the Adsorption and Regeneration process

present, the concentrations of the functional groups of the adsorbent were determined using the Boehm surface titration technique [30,31].

COD investigation

Most of the organic matter was oxidized by boiling it in a mixture of sulfuric and chromic acid. A known volume of the effluent was digested for 2 hours in a strong acidic solution with an excess of potassium dichromate. The unreacted potassium dichromate was titrated with MOHR'S SALT after the 2h reflux to estimate the amount of potassium dichromate consumed during digestion and to compute the oxidizable matter in terms of the oxygen equivalent [32].

Reagents for COD measurement

A standard 0.04167 M potassium dichromate solution was prepared by dissolving 12.259 g of potassium dichromate in distilled water, drying it at a higher temperature of around 150 °C for 120 minutes, and diluting it up to 1000 mL. The endpoint of the titration was determined using a ferroin indicator solution prepared by dissolving 1.485 g 1,10-phenanthroline monohydrate and 695 mg of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in distilled water and was diluted up to 100 mL. Standard 0.25 M ferrous ammonium

sulfate (MOHR'S SALT) titrant was prepared by mixing 98 g in distilled water and was diluted up to 1000 mL.

COD Analysis

A COD digester is the standard method used to perform the COD Analysis. However, alternatives such as a hot plate or iso-mantle can also be used. The following is the process for determining the COD of effluent: With the use of a measuring cylinder, a known volume of effluent was weighed and poured into the refluxing flask. A known volume of the prepared potassium dichromate solution was added to the refluxing flask, and the condenser was carefully placed on the flask. At the open point of the condenser, acid was gradually poured into the contents of the flask, ensuring that the gradual addition of the acid should refrain from the escape of volatile matter to the environment. After the addition of acid, the flask was allowed to cool. The iso-mantle was switched on and allowed to digest the flask's contents with continuous reflux at 150 °C for 120 minutes.

When the 2h digestion was completed, the iso-mantle was switched off, and the flask's contents were allowed to cool down at ambient temperature. The contents were then transferred to a conical flask, and 2-3 drops of the indicator

Table 2: Pulp and Paper Industry effluent Properties

Parameters	Before Treatment	After Treatment
COD	150 mg/L	10 mg/L
pH	11.5	7.1
Color	Green	Colorless

Table 3: Particle size distribution and surface area of NYEX™ 1000

BET surface area (m ² /g)	Bulk Density (g/cm ³)	Pore volume (cm ³ /g)	Mean diameter (μm)	Pore diameter (Å)
1.00	0.88	0.00384	485	133

were added. The sample was titrated with the prepared solution of MOHR'S Salt until the orange color changed to red. The red color is the endpoint of the titration. The volume of Mohr's Salt used for the titration was recorded. The same procedure was repeated, but distilled water was used in place of effluent and was digested for 2h, followed by the titration and recording of the volume of Mohr's Salt used. Distilled water was used as a blank solution, and the COD was calculated by using the equation:

$$\text{COD as mg O}_2\text{/L} = (A-B) \times M \times 8000 / \text{mL of Sample} \quad (1)$$

Where; 'A' is the volume of MOHR'S SALT used to titrate distilled water. 'B' is the volume of MOHR'S SALT used for the effluent. 'M' is the molarity of MOHR'S SALT, A value of '8000' tells the milliequivalent weight of oxygen $\times 1000$ mL/L.

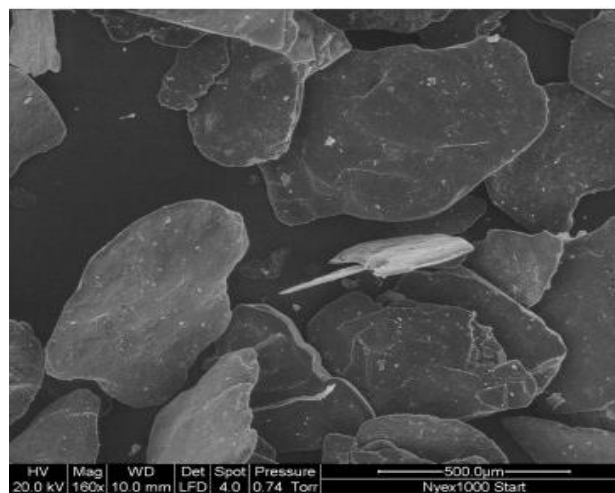
For the validation of our experiment result, a sample was also sent to the Pakistan Council of Scientific and Industrial Research (PCSIR) for testing where the initial COD was found to be around 150 mg/L. Moreover, the initial pH of the sample measured using a pH meter was found to be 11.5, which was curtailed down to 7.1 after the treatment. Table 2 shows the effluent characteristics.

Kinetic studies

To understand the effect of adsorbents on the water sample and to investigate the COD of the water sample, kinetic studies were carried out at ambient temperature. Wastewater was treated with the help of a GIC adsorbent, and the initial COD of the effluent was determined. Batch adsorption of the industrial waste was done for 120 minutes at ambient temperature. Furthermore, 1 liter of the wastewater was added into a beaker where the GIC adsorbent of known quantity was already added. The sample to be treated filtered before being mixed with

Table 4: Adsorbent elemental analysis

Oxygen wt%	Iron wt%	Carbon wt%	Sulfur wt%	Silica wt%
18.5	0.18	78	3.27	0.05

**Fig. 4: Scanning electron microscope image of NYEX™ 1000 as supplied by Arvia Technology Ltd.**

an adsorbent to remove the majority of the fibers. The adsorbent and sample were mixed by placing the beaker on a magnetic stirrer adjusted to the desired r.p.m. The water sample was stirred for two continuous hours, and the adsorbed samples were taken out at different time intervals to investigate the COD content.

RESULTS AND DISCUSSION

NYEX™ 1000 characterization and kinetic studies

Fig. 4 shows a GIC adsorbent with a flake-like structure having an irregular non-porous surface. The diameter of the particle was found to be approximately 500 micrometers and is shown in the Scanning Electron Microscopy (SEM) image taken with the help of the S50FEI SEM model.

BET analyzer incorporated with N₂ adsorption was used to calculate the BET surface area, pore diameter, and pore volume, as shown in Table 3. The surface area of NYEX™ 1000 is smaller than the surface area of the activated carbon (2000 m²/g) [33].

Moreover, Table 4 shows the elemental analysis of the adsorbent.

Results of the kinetic studies can be seen in Fig. 5 and 6, where the resulted COD after the adsorption and % age adsorption of the sample is shown. From Fig. 5, it can be observed that the GIC adsorbent is effective with

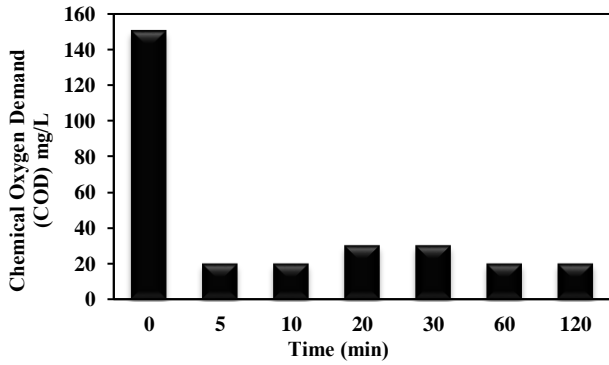


Fig. 5: COD variation with respect to time at room temperature

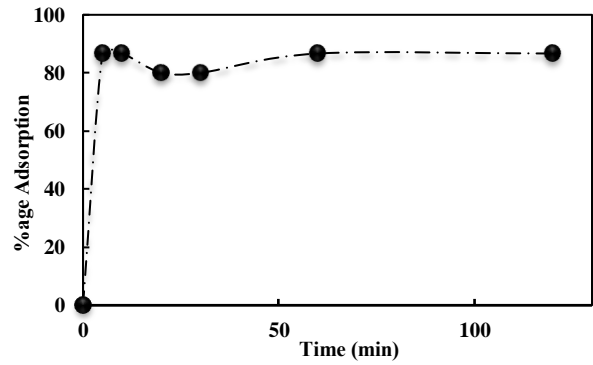


Fig. 6: Percentage Adsorption vs Time.

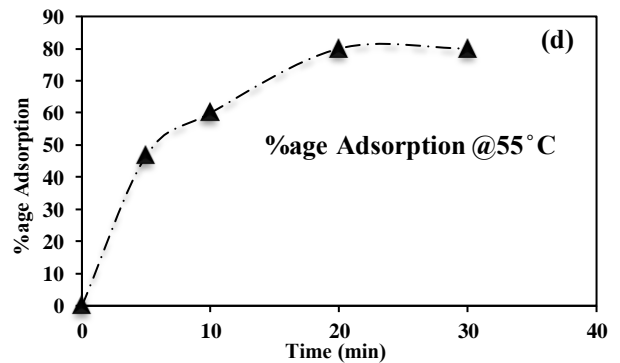
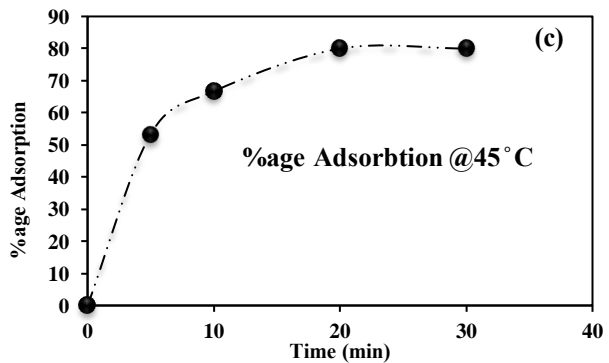
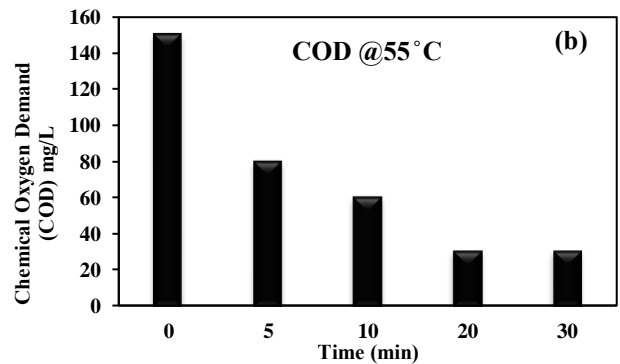
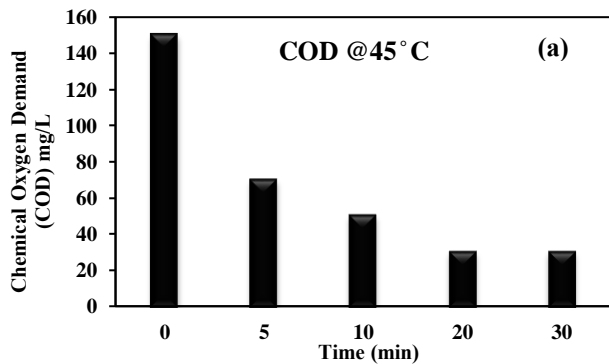


Fig. 7: Temperature effect on COD vs Time (a) @ 45 °C (b) @ 55 °C (c) %age adsorption @45 °C (d) %age adsorption @55 °C.

the effluent as it has rapidly reduced the COD of the effluent from 150 mg/L to 20 mg/L.

The considerable reduction in COD was due to the high affinity of the adsorbent towards the wastewater. The driving force for the transfer of COD from solution to adsorbent surface induces rapid mass transfer to the surface of the GIC adsorbent [34].

Compared to porous adsorbents like activated carbon, which take several days to reach equilibrium, the GIC adsorption can be considered quick [35]. Adsorption equilibrium was attained within half an hour of the adsorption process, and no further reduction in COD

was observed up to 120 minutes. Minor leaps in the COD results were observed at intervals such as $t = 20$ min and $t = 30$ min, which could be incurred due to experimental error. However, the system attains its equilibrium when the time reaches 60 minutes. The following mathematical expression was used to determine the % age adsorption:

$$\% \text{age Adsorption} = (C_0 - C_t / C_0) * 100 \quad (2)$$

C_0 represents the initial COD, and C_t represents the COD at any time interval. It can be observed in Fig. 7 that the GIC adsorbent is effective and has adsorption effectiveness of around 87%, reflecting a high affinity of adsorbent towards the wastewater.

Temperature effect on the adsorbent

In order to check the influence of temperature variation on the kinetics of the adsorbent, COD was investigated again. The batch adsorption experiments were carried out for a 30 min time interval as there was a considerable reduction in COD reported by the results of the previous investigation performed at room temperature. Two sets of experiments were performed; one at 45° C and the other at 55° C. The outcomes of these experiments can be seen in Fig. 7.

Fig. 7 (a) and (b) show that with the increase in temperature, the adsorbent functionality has reduced with a gradual decrease in the COD, which in the previous case was sudden. Though, 30 mg/L of COD was achieved in 30 min, indicating that the increase in temperature is decreasing the adsorbent efficiency, which has dropped from 90% to 87% (Fig. 7(c) and (d)). This effect of temperature was studied to understand the possible fluctuations in the process because of the seasonal variations. It was believed that the presence of organic matter in the effluent lead to a minimization of adsorption capacity at higher temperatures. Moreover, physical adsorption involves weak van der Waals forces and forces become weaker with the rise in temperature resulting in a decrease in adsorption. Another possibility could be the desorption of particles at elevated temperature.

Use of SBR for the adsorption and regeneration studies

As discussed in the previous section, the effluent sample was treated in the SBR. Two different approaches were opted to investigate the adsorption effect. Initially, the 1st cycle of six adsorptions and five regenerations was carried out using SBR, where the adsorption of the sample was done with the help of continuous air sparging for half an hour. An untreated effluent sample was taken and treated for each adsorption process in this scheme. After performing every adsorption process for half an hour, the same adsorbent had to pass through a 20 min regeneration process, after which the unwanted or excess water was discharged off, and a new effluent sample was poured into the SBR. The next cycle continued for another six adsorptions, followed by five successive regenerations. Water samples were withdrawn for COD analysis after each adsorption and regeneration process. 1.0 Amp current is used in this experiment to regenerate the GIC adsorbent as the effluent has a low COD content (150 mg/L) [36]. Since regeneration is carried out in the anodic compartment

of the cell, there are more chances for water electrolysis to occur with the production of hydrogen ions (Eq. (3)).



The results of the described approach can be seen in Fig. 8. From Fig. 8(a), it can be observed that for every 30 min adsorption, the attained COD of the effluent water was as low as 30 mg/L indicating high percentage adsorption of about 80% as shown in Fig. 8(b). High adsorption percentages are being achieved because after every adsorption process, the adsorbent is simultaneously regenerated, and the results of the regeneration are shown in Fig.s 8(c) and (d) [25,36]. Fig. 8(c) is a plot of the No. of Regenerations (x-axis) against COD/mg/L⁻¹ (y-axis), showing that after certain regenerations, the equilibrium COD of around 50 mg/L was attained, making the process effective as it is carried out at a low current of 1.0A for a small interval of time [37]. Fig. 8(d) depicts that the equilibrium percentage of adsorption is about 80%, and the regeneration efficiency is 83%; that's why an untreated effluent sample was used in every adsorption and regeneration process.

The adsorption fitting curve was plotted using the Freundlich isotherm approach, as shown in Fig. 9. The least-square error technique was applied for this isotherm. The following mathematical expression (Eq. (4)) represents the Freundlich isotherm:

$$q_e = kC_e^{1/n} \quad (4)$$

Where 'qe' (mg/g) signifies the adsorbate quantity after equilibrium, 'k' defines the adsorption capacity with units of mg/g L^{1/n} mg^{-1/n}, and C_e refers to the adsorbate equilibrium concentration (mg/L), and 'n' means the adsorption intensity.[22, 25]. Many adsorption models may be used to study the mechanism and adsorption kinetics of any process. Often employed models for analysing the adsorption isotherm include the Freundlich and Langmuir types [38]. Adsorption of the adsorbate monolayer happens at homogenous surfaces with equal-affinity binding sites in the Langmuir model [39]. Another type of sorption isotherm model for heterogeneous surfaces is the Freundlich model. In this case, adsorbent surface heterogeneity is increased and multilayer adsorption is taken into account [40,25].

In the second approach used in this research work, one liter of the same effluent sample was used to study the adsorption and regeneration mechanism in SBR. After performing the cycle of adsorption and regeneration

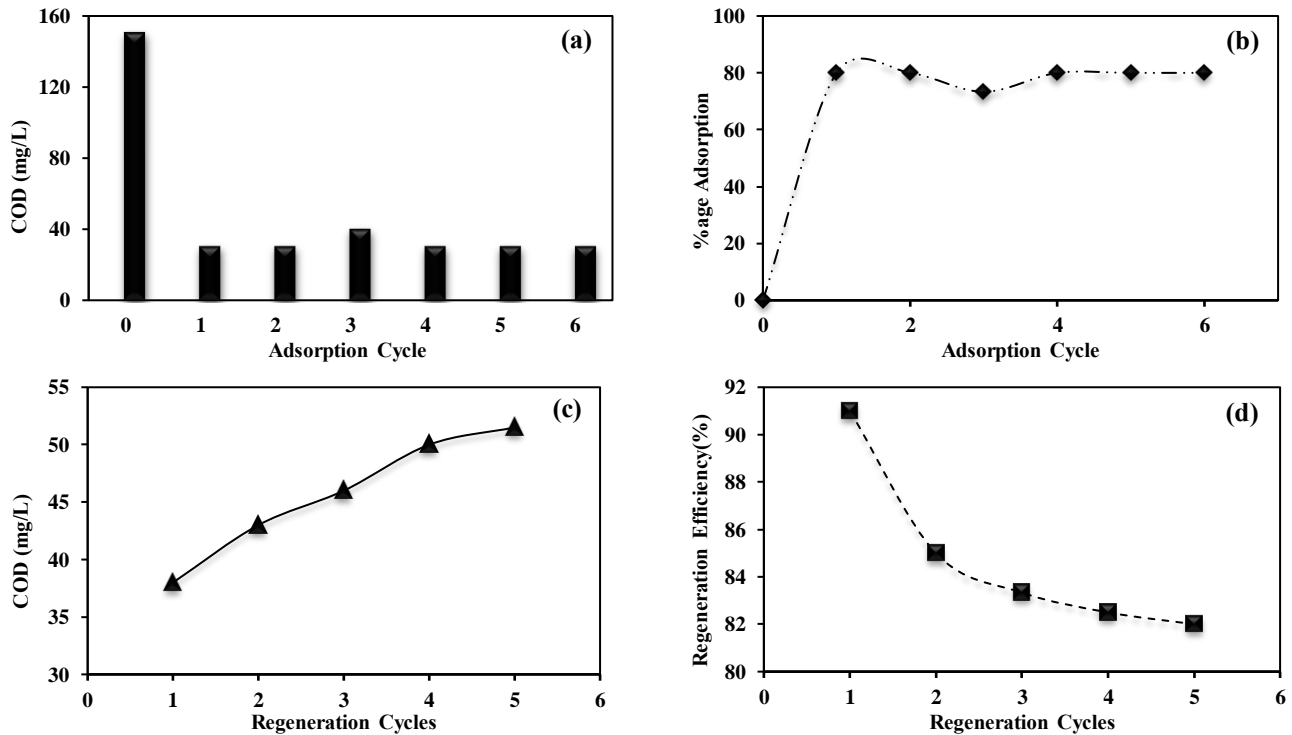


Fig. 8: (a) 30min Adsorption Using SBR (Y-Cell) (b) Variation in Percentage Adsorption using SBR (c) 20min Regeneration Using SBR (Y-Cell) (d) Variation in Regeneration Efficiency using SBR

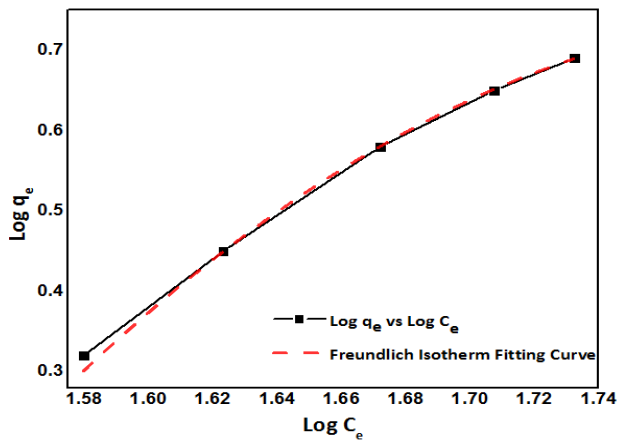


Fig. 9: Freundlich Adsorption Isotherm Fitting Curve

experiments, as mentioned above, different wastewater samples were withdrawn to analyze the adsorbent effect on the COD content of the water sample. Results of this experiment can be seen in Fig. 10 and 11.

The results from the second approach depict a similar kind of trend observed in the first approach. However, the curtailment in the COD was significantly high, reducing the COD of the sample to 10mg/L (Fig. 10(a)) with high adsorption effectiveness approaching 93% (Fig. 10(b)).

Comparing this study results with other findings has revealed that Nyxet 1000 has promising removal efficiency as compared to the reported studies (Table 5).

Fig. 11 shows high regeneration efficiencies approaching 97 percent. The reason could be due to the withdrawal of a particular volume of effluent from the system for COD analysis, resulting in a decrease in overall sample volume and a change in water and adsorbent ratio as the adsorbent quantity remains nearly the same.

Effect of charge pass and current density on regeneration of adsorbent

Fig. 12. shows the change in regeneration efficiency of the adsorbent upon passing the different quantities of charge. Regeneration efficiency is directly proportional to the electric charge passed but up to a certain level as it was noticed that after passing the electric charge of 95 coulombs per gram, the regeneration efficiency did not increase from 99.5%.

This study has revealed that renewable energy can also be used for a cost-effective regeneration process. Moreover, the electric charge used for this adsorbent is less than 15,000 coulombs per gram reported for granular activated carbon to achieve 95% regeneration efficiency [25].

Table 5: Comparison of different adsorbents used for Pulp & Paper Industry wastewater

Sr. No.	Adsorbents	Removal Efficiency (%)	References
1	Activated Carbon	>86	[41]
2	Wood Chips	87	[42]
3	Fly Ash	83.3	[43]
5	NYEX 1000	>90	This Study

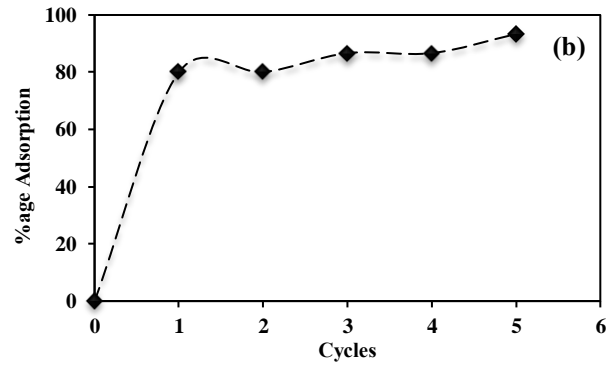
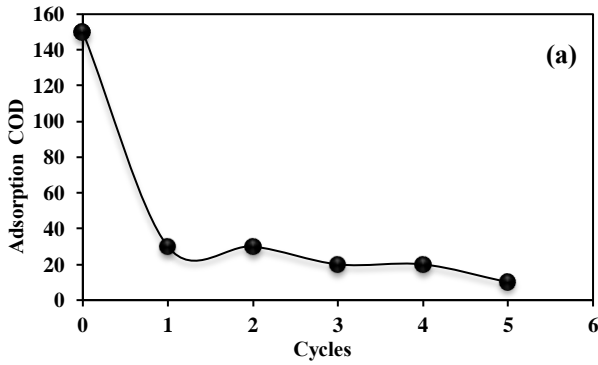


Fig. 10: Adsorption Stats (a) Adsorption COD (b) %age Adsorption COD

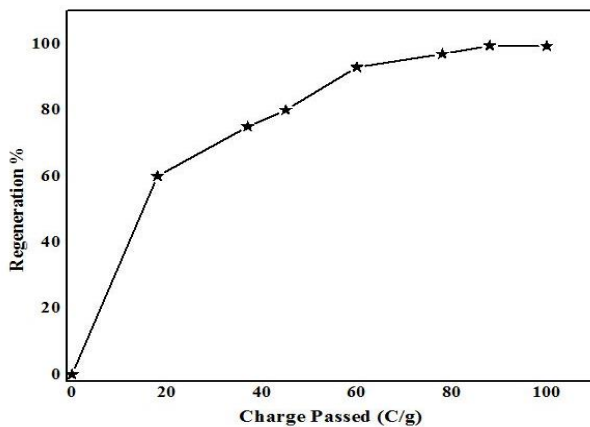


Fig. 11: Regeneration efficiency using the same water sample

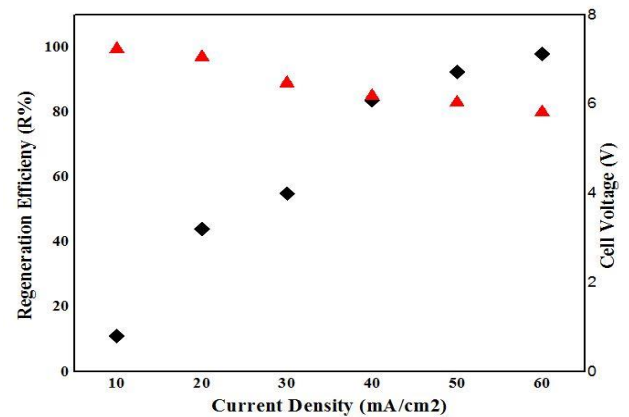


Fig. 13: Relationship between Current Density and regeneration efficiency (R %) at constant charge passed

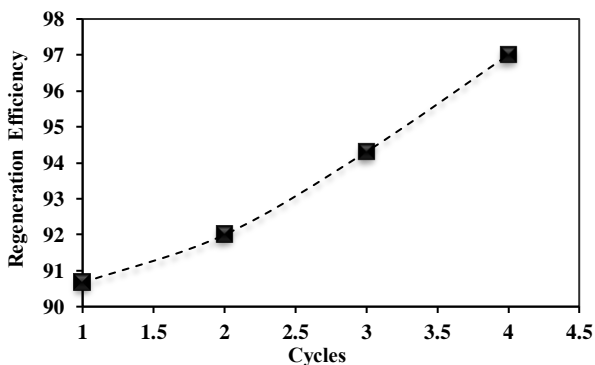


Fig. 12: Effect of Charge passed on adsorbent regeneration efficiency

Fig. 13. shows the effect of increasing current density at constant charge passed (95 C/g) on the regeneration

efficiency. However, the treatment time decreased with the increase in current density. The cell voltage of 4 to 6 V was applied for this regeneration process. As shown in Fig. 13, the regeneration efficiency decreases with the increase in the current density. The reason for this decrease can be the side reactions occurring due to the increasing cell voltage. Another drawback of higher voltage is higher power consumption.

The reusability of the said adsorbent as a sustainable option is questionable. From the result of various experiments, we observed that the adsorbent loses its performance as the number of cycles increase. It is either caused by the weak physical forces that help COD materials

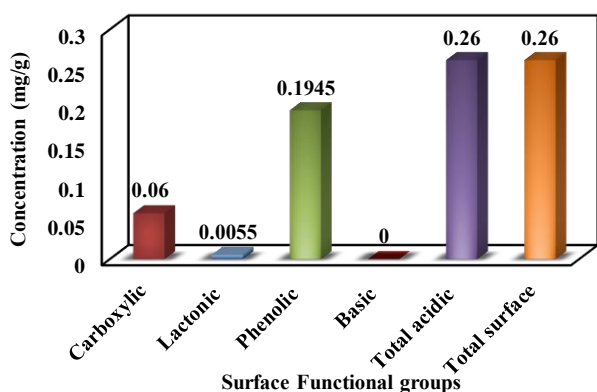


Fig. 14: NYEX 1000 Functional Groups concentrations determined using Boehm titration

to restrict its interaction with the adsorbent surface or the chemical adsorption of the COD particles on the adsorbent surface [31]. In either case, we understand that the adsorbent can either be revived by applying a higher voltage/current or increasing the adsorbent amount for adsorption stage. Both of the options mandate further study.

Adsorption Mechanism

Boehm titration studies demonstrated that the surface of Nyex 1000 adsorbent possesses high amounts of acidic functional groups but no measurable basic functional group which can be seen in Fig. 14.

The fraction of phenolic groups was found to be dominating. *K. Nkrumah-Amoako et al.* also observed that the more the adsorbent was regenerated, the more the phenol group was considerably reduced. Furthermore, a reduction in the concentration of phenol group following regeneration will eventually increase the concentration of carboxylic groups on the adsorbent surface [31,44].

Most likely water molecules as well as organic contaminants are predicted to interact electrostatically with oxygen-containing functional groups, which were noted to be prevalent on the surface of Nyex 1000 [45]. Since the polarity of hydrogen bonding in water molecules is significantly greater than that of other organic molecules, strong polar substances will generate affinity for electrostatic contact with surface functional groups of Nyex1000. Furthermore, GIC has also found to be more hydrophilic which enhances its adsorption ability. *D. Liu et al.* have also reported that regeneration taking place at the anode will also facilitate the oxidation of the adsorbates on the surface of the adsorbent [46]. A possible mechanism

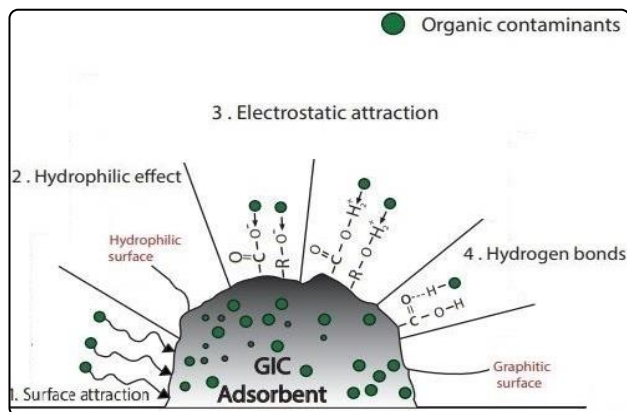


Fig. 15: Possible Mechanism showing the adsorbent-organic molecules interaction

representing the organic molecules interaction with the adsorbent can be seen in Fig. 15.

In Fig. 15, it can be clearly observed that oxygen-containing functional groups are dominantly participating in the adsorption process. Moreover, hydrogen bonding and hydrophilicity of the adsorbent are other factors leading to enhanced adsorption.

CONCLUSIONS

This work proposed a method to investigate COD removal in wastewater collected from the pulp and paper industry. The present study aimed at the NyexTM1000, a Graphite Intercalation Compound (GIC), and found it significantly feasible to reduce the COD from the pulp and paper industry effluent. The percentage adsorption achieved was more than 80% within the first 30 minutes. COD was reduced from 150 mg/L to 10mg/L using SBR's adsorption and electrochemical regeneration method. The adsorbent regeneration in the electrochemical cell achieved a maximum efficiency of almost 97%. No noticeable adsorbent capacity loss was reported after repeated adsorption and regeneration processes. While studying the effect of charge pass and current density on adsorbent efficiency, it was noticed that after passing the charge of 95 coulombs per gram, the regeneration efficiency did not increase from 99.5%. Moreover, the electric charge passed through the GIC adsorbent was less than the charge reported for granular activated carbon.

Acknowledgments

University of the Punjab, Lahore, and Arvia Technology Ltd., UK, jointly funded this project.

Nomenclature

Chemical Oxygen Demand (mg/L)	COD
Biological Oxygen Demand (mg/L)	BOD
Total Dissolved Solids (mg/L)	TDS
Total Suspended Solids (mg/L)	TSS
Graphite intercalation compounds	GIC
Sequential Batch Reactor	SBR
Initial COD (mg/L)	C_o
COD at any time (mg/L)	C_t
COD at equilibrium (mg/L)	C_e
Quantity of adsorbate (mg/g)	q_e
Adsorption Capacity (mg.L ^{1/n})	k
Adsorption Intensity	n
Temperature	°C
Molarity	M
Angstrom	Å

Received: Mar. 16, 2023; Accepted: Jun. 26, 2023

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