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GIC-Based Adsorbents for Wastewater Treatment through Adsorption & Electrochemical-Regeneration

H. M. A. Asghar, S. N. Hussain, E. P. L. Roberts, N. W. Brown, and H. Sattar

***Abstract*—**Intercalation imparts interesting features to the host graphite material. Two different types of intercalated compounds called (GIC-bisulphate or Nyex 1000 and GIC-nitrate or Nyex 3000) were tested for their adsorption capacity and ability to undergo electrochemical regeneration. It was found that Nyex 3000 showed comparatively slow kinetics along with reduced adsorption capacity to one half for acid violet 17 as adsorbate. Acid violet 17 was selected as model organic pollutant for evaluating comparative performance of said adsorbents. Both adsorbent materials showed 100% regeneration efficiency as achieved by passing a charge of 36 C g^{-1} at a current density of 12 mA cm^{-2} and a treatment time of 60 min.

***Keywords*—**Intercalation compound of graphite, Adsorption, electrochemical-regeneration, waste water.

I. Introduction

WATER being a primary need for all living organisms and almost all industrial operations, has significant importance. Although two third portion of the Earth's surface is covered with water, however, quality has been a major issue rather than quantity. The development of stable and non biodegradable synthetic dyes remained as environmental threat even at very low concentration when discharged in industrial effluents [1]. The treatment methods for the removal of color imparting agents from industrial effluents can be classified into biological, chemical and physical processes. Each method has its own limitations and therefore many of these have not been widely applied at a larger scale in textile and paper industries [2]. Biological methods are preferred to reduce COD and BOD through conventional aerobic bio-degradation of various textile azo dyes [3]-[4]. The major drawback reported for this method is long residence time, batch processing and large area requirement [5]. The chemical methods for the removal of dyes are restricted due to high capital and operational cost along with sludge problem [6]-[8]. The electrochemical oxidation of adsorbed organic pollutants has been reported widely during the last decade [9]-[15]. For the adsorption of a number of organic pollutants, an electrically conducting graphite bi-sulphate intercalation based adsorbent called Nyex 1000 was developed and reported for the removal of phenol, atrazine, crystal violet, acid violet 17 and mercaptans through adsorption followed by electrochemical regeneration. Nyex 1000 adsorbent delivered comparatively a small adsorption capacity for these pollutants at around 0.1–2 mg g^{-1}. This was justified due to small specific surface area of Nyex 1000 obtained at 1 m^2g^{-1}. A modified form of Nyex 1000, called Nyex 2000 was developed and tested for the removal of acid violet 17. A significant increase in adsorption capacity of 3 folds was obtained for acid violet 17 [16]-[18]. Both adsorbent materials i.e. Nyex 1000 & 2000 were found to be capable of delivering 100% electrochemical regeneration comparatively at low current density compared with activated carbon [19]-[20]. The small energy consumption was due to high electrical conductivity of these adsorbents compared with activated carbon.

The objective of this study is to compare the adsorption and electrochemical regeneration characteristics for bisulphate intercalation based graphite compound (called Nyex 1000) and nitrate intercalation based graphite compound (called Nyex 3000). The comparative performance comprised of adsorption kinetics, isotherms and electrochemical regeneration parameters carried out for the removal of acid violet 17 selected as a model pollutant.

II. Materials & Methods

Nyex 1000 & 3000 were used as received from the Arvia Technology Ltd. UK without further treatment. Both the adsorbent materials were graphite based intercalation compounds (GIC bisulphate & GIC nitrate) containing greater than 97% carbon. The average particle size was found to be 484 μm with a flat smooth and non porous surface. BET surface area was determined using N_2 adsorption and found to be 1 m^2g^{-1} [21]. The acid violet 17 dye was provided by Kemtex Educational Supplies with a dye content of 22 %. Stock solutions of acid violet 17 were prepared using de-ionized water. Adsorption and electrochemical regeneration experiments were conducted in a sequential batch reactor as shown in Fig. 1. The comparative study of Nyex 1000 & 3000 comprised adsorption kinetics, isotherms and electrochemical regeneration for which methodology has already been reported in [22].

H. M. A. Asghar is with the University of the Punjab, Lahore, Pakistan (phone: +92-321-4771296; fax: +92-42-99231261; e-mail: engr_anwaar@yahoo.com).

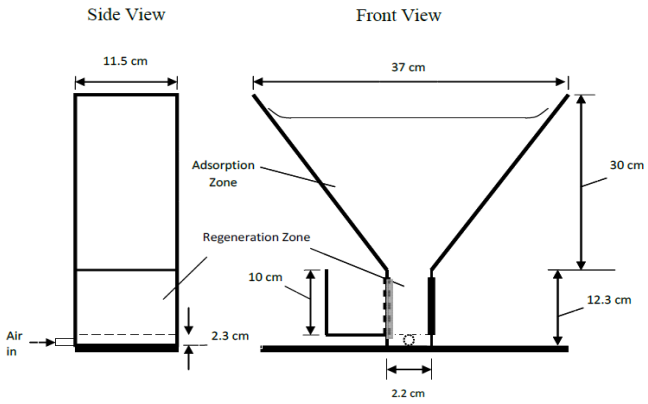

Fig. 1 Sequential batch electrochemical cell used for electrochemical regeneration of Nyex 1000 & 3000 adsorbents

III. Results & Discussions

Adsorption kinetic on to both Nyex 1000 & 3000 adsorbents was shown to be comparatively a fast process (Fig. 2) when compared with activated carbon. It is interesting to note that the adsorption onto Nyex 3000 showed comparatively a slow response to that of Nyex 1000. It can be due to variable surface chemistry responsible to develop affinity of adsorbate on the surface of adsorbent material. The starting initial dye concentration was maintained at around 100 & 70 mg l^{-1} for Nyex 1000 & 3000 respectively. The overall adsorption equilibrium was obtained approximately within 60 minutes. The adsorption kinetic study has already been published reported in [16]-[17]. These results can be compared with the kinetic study of phenol when adsorbed onto Nyex 100 with starting concentration of 250 mg l^{-1} where 90% of the equilibrium was achieved within approximately 20 minutes [12]. The adsorption of phenol onto activated carbon was found to be a slow process as it consumed 7 days to achieve equilibrium conditions [18]-[19]. It is notable that the rate of dye removal remained fast enough during the first 5 min and became almost negligible after 60 min. A time of 60 min was selected for achieving approximate equilibrium conditions.

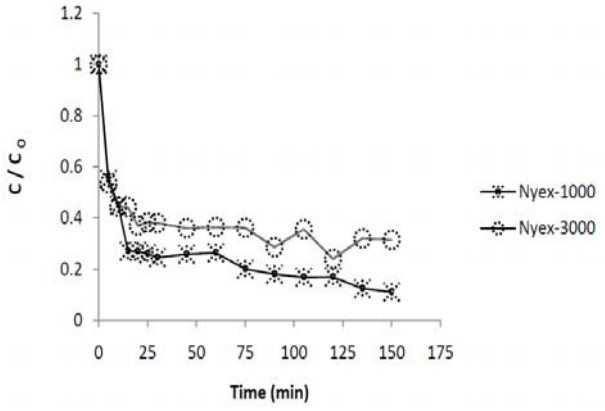

Fig. 2 Kinetic study for acid violet 17 using Nyex 1000 & 3000 adsorbents, stirred in a 1000 ml flask

The adsorption isotherm for the adsorption of acid violet 17 onto Nyex 1000 has already been reported in [17] and is provided here for the sake of quick reference / comparison with Nyex 3000. The intercalation of difference species into the gap of graphite crystal layers results the appearance of new properties. The adsorption capacity for acid violet 17 onto Nyex 1000 & 3000 was found to be approximately 3.5 and 1.5 mg g^{-1} respectively. It can be concluded that the intercalation of nitrate ions suppressed the adsorption capacity of graphite to one half. It is also consistent with kinetic study shown in Fig. 1 where comparatively a slow response was observed for the adsorption of acid violet 17. It is evident that the presence of intercalated nitrate ions could not develop similar affinity like Nyex 1000 adsorbent.

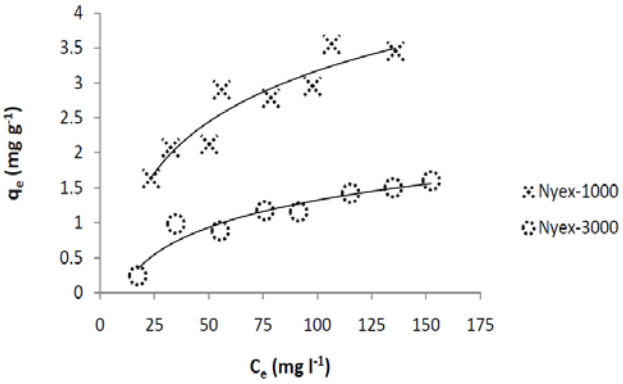

Fig. 3 Adsorption isotherms for acid violet 17 onto Nyex 1000 & 3000 in a 250 ml flask using a contact time of 60 minutes

The electrochemical regeneration of Nyed 1000 loaded with acid violet 17 has already been reported in [16]-[17].The intercalated graphite compounds i.e. GIC-bisulphate (called Nyex 1000) and GIC-nitrate (called Nyex 3000) were expected to exhibit variable electrochemical conductivity and in turns electrochemical parameters required for the regeneration of both adsorbent materials. However, it was reflected from Figs. 4 & 5 that intercalation with H_2SO_4 and HNO_3 did not significantly alter the electrical properties. Both the adsorbent materials were electrochemically regenerated using the same parameters such as current density of 12 mA cm^{-2}, charge passed of 36 C g^{-1} and treatment time of 60 min. Electrochemical regeneration leads toward oxidation of adsorbed organic species i.e. acid violet 17. Adsorbed acid violet 17 is expected to be converted into CO_2 and H_2O vapors.

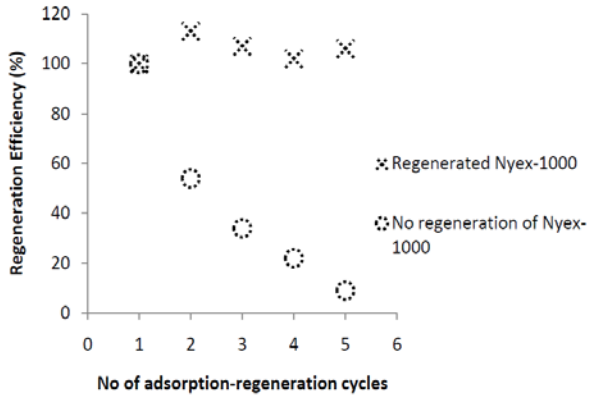

Fig. 4 Adsorption and electrochemical regeneration cycles for Nyex 1000 when loaded with acid violet 17 as adsorbate

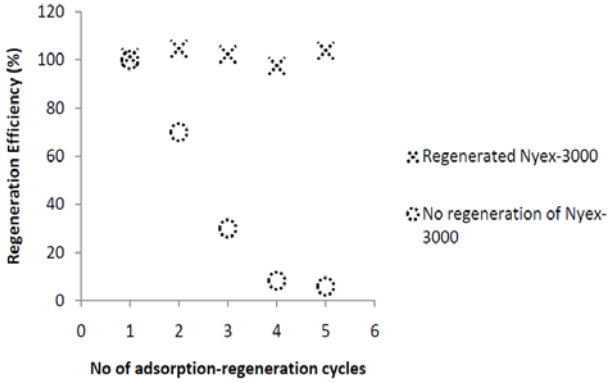

Fig. 5 Adsorption and electrochemical regeneration cycles for Nyex 3000 when loaded with acid violet 17 as adsorbate

IV. Conclusions

The study comprised of comparative performance of both adsorbent materials for the removal of acid violet 17 revealed that Nyex 1000 is a better adsorbent based on its fast kinetics and improved adsorption capacity. Nyex 1000 showed adsorption capacity of 3.5 mg g-1 which is twice to that of Nyex 3000. Both adsorbent materials are capable of passing through 100% electrochemical regeneration. A current density of 14 mA cm-2 for passing a charge of 36 C g-1 during regeneration time of 60 min was found to be sufficient for achieving 100% regeneration efficiency.

Acknowledgment

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