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Development of Composite Adsorbent for Waste Water Treatment Using Adsorption & Electrochemical Regeneration

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***Abstract*—**A unique combination of adsorption and electrochemical regeneration with a proprietary adsorbent material called Nyex 100 was introduced at the University of Manchester for waste water treatment applications. Nyex 100 is based on graphite intercalation compound. It is non porous and electrically conducing adsorbent material. This material exhibited very small BET surface area i.e. 2.75 m^2g^{-1}, in consequence, small adsorptive capacities for the adsorption of various organic pollutants were obtained. This work aims to develop composite adsorbent material essentially capable of electrochemical regeneration coupled with improved adsorption characteristics. An organic dye, acid violet 17 was used as standard organic pollutant. The developed composite material was successfully electrochemically regenerated using a DC current of 1 A for 60 minutes. Regeneration efficiency was maintained at around 100% for five adsorption-regeneration cycles.

***Keywords*—**Adsorption, electrically conducting adsorbent material, electrochemical regeneration, waste water.

I. Introduction

ADSORPTION being the most significant separation technique has wider applications for the treatment of industrial effluents. The process of adsorption consists of placement of one or more components (adsorbates) on the surface of the adsorbent. The adsorbent may be used once and discarded or commonly it is regenerated thermally and used for many cycles. Desorption or the regenerative step is the most important step that determines the economics of the process [1]. Activated carbon has extensive applications in water treatment processes. It has high surface area and high adsorption capacity with micro porous surface morphology. Activated carbon has gained a lot of attention by the researchers and therefore has been widely studied for the removal of organic, toxic and coloured contaminations [1]-[2]. In addition to its extensive use in water or waste water treatment processes, it has not been claimed as cost effective adsorbent due to high initial cost, difficulties in regeneration, not being suitable for land-filling, off site regeneration is expensive, high material loss during regeneration. Once the activated carbon is saturated with adsorbate, it can be wasted by land-filling or incineration or it is regenerated. Regeneration is preferred as it is known to be commercially viable and environmentally acceptable method [3]. There are different methods used for the regeneration of exhausted carbon like thermal regeneration, pressure swing method and electrochemical regeneration [4]. Industrially important regeneration method has been thermal regeneration; however, it exhibits higher cost with material losses of 5 to 10% [5]. The regeneration accounts for about 75% of the total operating and maintenance costs needed for running a granular packed bed AC plant [6]. High economic factor associated with the regeneration of activated carbon led the researchers to focus on the development of low cost adsorbents for the dye house effluents, however, recovery and regeneration has been a major issue for these adsorbents and, therefore, could not be exploited for commercial use [7]. Brown developed for the treatment of waste water, contaminated with toxic or biologically non-degradable pollutants, using graphite based adsorbent called Nyex 100. Brown successfully exploited this process for the removal of phenol, crystal violet and atrazine from aqueous solutions [8]-[10]. This adsorbent was found to be non-porous and highly electrically conducting. However, it delivered a very small adsorption capacity for various organic pollutants. This study was undertaken with the aim of developing a composite adsorbent to get improved adsorption capacity and to evaluate its electrochemical regeneration capability for the removal of acid violet 17 from aqueous solution.

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II. Materials & Methods

Nyex 100 is a low cost graphite based intercalation compound comprised of greater than 98% carbon. Its average particle size was found to be 127 μm with a non porous surface. BET surface area was determined using N_2 adsorption and found to be 2.75 m^2g^{-1} [11]. The composite adsorbent was synthesized using Nyex 100 as a base material mixed with partially porous graphite based material having a BET surface area of 35 m^2g^{-1}. Due to commercial constraints of the Arvia Technology Ltd., formulation of composite adsorbent cannot be disclosed. The acid violet 17 dye was provided by Kemtex Educational Supplies with a dye content of 22 %. The Nyex 100 was supplied by Arvia Technology Ltd. Stock solutions of acid violet 17 were prepared using de-ionized water. Adsorption and electrochemical regeneration experiments were conducted in sequential batch reactor illustrated in Fig.

1. The comparative study of Nyex 100 and developed composite adsorbent comprised the following steps.

A. Adsorption Kinetics

Adsorption experiments were carried out in order to determine the time for achieving equilibrium condition. A specified mass of an adsorbent was added to samples of aqueous solution of acid violet 17. The mixing was carried out by sparging air from the bottom of the cell. At regular intervals, 10 ml samples of aqueous dye solution were collected and filtered using a Whatman GF/C filter paper. The concentration of dye solution was determined using a UV/Vis. spectrophotometer.

B. Adsorption Isotherms

Adsorption isotherms were obtained using a fixed mass of an adsorbent to 100 ml of variable concentrations of dye solution ranging 10 to 250 mg l^{-1} in a 250 ml flask. These flasks were stirred for 60 minutes using an electric shaker. Adsorption was followed by filtration and analysis was conducted using a UV/Vis spectrophotometer

C. Electrochemical Regeneration

The electrochemical regeneration of saturated adsorbents was carried out in regeneration compartment of electrochemical cell (Fig. 1). The cell comprised of anodic and cathodic compartments which were divided using a microporous Daramic 350 membrane provided by Arvia® Technology Ltd. The concentration of electrolyte was 0.3% w/w acidified sodium chloride solution. The procedure is given below:

i) ***Initial adsorption:*** A known mass of adsorbent was added to 1 L of acid violet 17 solution into the batch cell for specified time in order to achieve equilibrium conditions. Air supply was provided for mixing. After adsorption, the solid particles were allowed to settle down into the anodic compartment of the sequential batch cell. The equilibrium concentration of acid violet 17 after adsorption and thus (by mass balance) the initial adsorbent loading q_i was determined.

ii) **Electrochemical regeneration:** Once the adsorbent material settled down into the anodic compartment of an electrochemical cell, a DC current of 1 A was supplied for 60 minutes.

iii) **Re-adsorption:** Regenerated adsorbent without further treatment were allowed to retain their adsorption performance by mixing with fresh acid violet 17 solution. After adsorption the equilibrium concentration of acid violet 17 and thus (by mass balance) the adsorbent loading after regeneration q_r were determined.

For multiple adsorption / electrochemical regeneration cycles, above mentioned steps (ii) and (iii) were repeated.

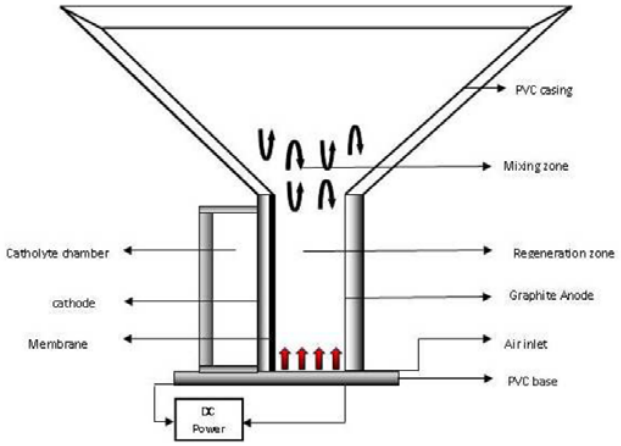

Fig. 1 Sequential batch electrochemical cell used for electrochemical regeneration of Nyex 100 and composite adsorbent

III. Results & Discussions

Adsorption on to Nyex 100 and composite adsorbent was shown to be comparatively a fast process (Fig. 2) in which 20% of the overall equilibrium was obtained within 2 minutes with initial dye concentration at around 100 mg l^{-1}. The overall adsorption equilibrium was obtained approximately within 60 minutes. The adsorption of phenol onto Nyex 100 with starting concentration of 250 mg l^{-1} provided 90 % of the equilibrium within approximately 20 minutes [8][9][10]. However, the loading of organics onto granular activated carbon has proved to be a slow process as it required 7 days to establish equilibrium using phenol as adsorbate [12]-[13]. Each type of organic pollutant may have variable affinity in order to get stuck on the surface of adsorbent material through weak Van der Waals forces. This affinity may depend on number of factors such as pore diameter, molecular size and symmetry of organic molecule and surface chemistry.

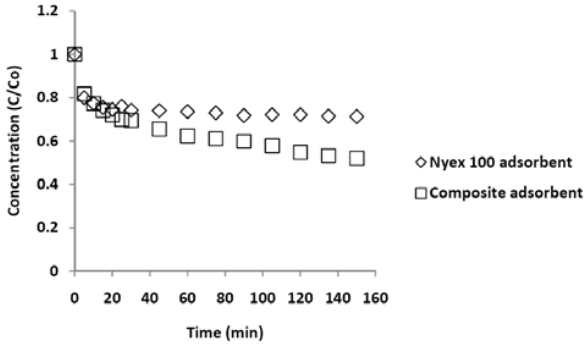

Fig. 2 Kinetic study for acid violet 17 using Nyex 100 and composite adsorbents, stirred in a 1000 ml flask

The adsorption isotherms obtained for the adsorption of organic dye onto Nyex 100 and composite adsorbents are plotted in Fig. 3 below. The loading capacity of acid violet 17 onto Nyex 100 and composite adsorbent was shown to be approximately 4.3 and 6.3 mg g^{-1} respectively. It is evident that partially porous material being one of the constituent of

the composite material significantly contributed to increase the adsorption capacity for acid violet 17 as adsorbate. The BET surface area of partially porous carbon material was found to be 35 m^2g^{-1} which is significantly higher when compared with 2.75 m^2g^{-1} for Nyex 100. Further studies using higher mass ratios of partially porous material may lead towards further improvement in adsorption capacity.

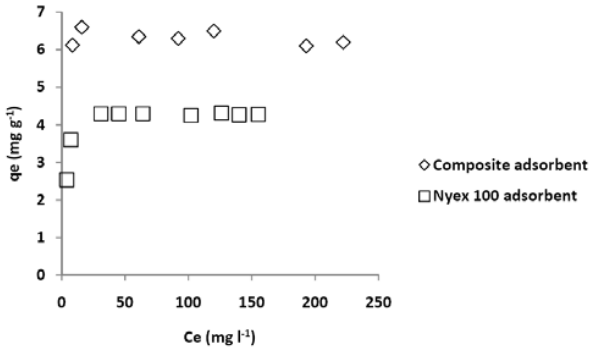

Fig. 3 Adsorption isotherms for acid violet 17 onto Nyex 100 in a 250 ml flask using a contact time of 60 minutes

The electrochemical regeneration efficiency was investigated on bench scale electrochemical cell for adsorption-regeneration cycles using acid violet 17 as adsorbate loaded onto Nyex 100 and composite adsorbents. The results are presented in Figs. 4 and 5 showing the effect of electrochemical regeneration of exhausted Nyex 100 and composite adsorbents. A regeneration efficiency of around 100 % was obtained for 5 adsorption-regeneration cylces. The same operating parameters were used in each case i.e. current density, charge passed and regeneration time. A current of 1 A for 60 minutes was passed through the cell leading towards electrochemical oxidation of adsorbed organic species. Adsorbed acid violet 17 is expected to be converted into respective mineral oxides i.e. CO2 and H2O. Gaseous analysis of mineral oxides is under investigation and will be reported later on.

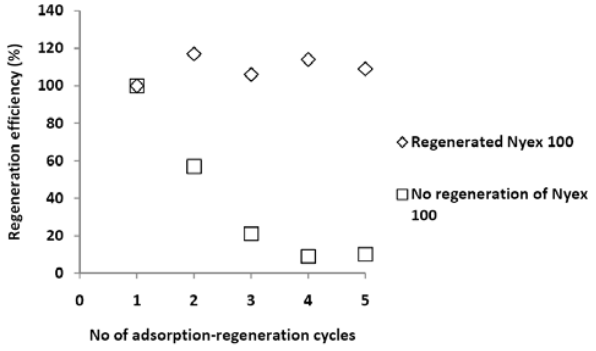

Fig. 4 Electrochemical regeneration efficiency (based on colour removal) for a number of adsorption-regeneration cycles with acid violet 17 / Nyex 100 using sequential batch cell. Operating parameters; Current 1 A and treatment time 60 min

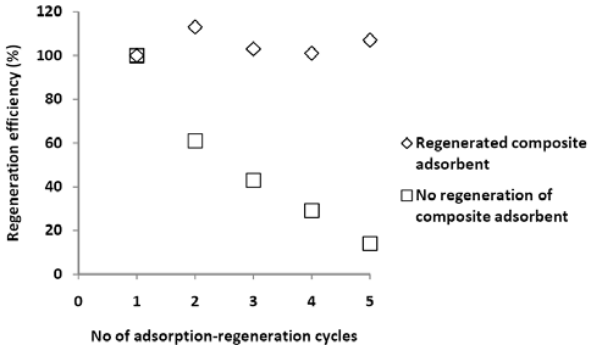

Fig. 5 Electrochemical regeneration efficiency (based on colour removal) for a number of adsorption-regeneration cycles with acid violet 17 / composite adsorbent using a sequential batch cell. Operating parameters; Current 1 A and treatment time 60 min

IV. Conclusion

Composite adsorbent material has demonstrated improved adsorption characteristics for the removal of acid violet 17 when compared with Nyex 100 adsorbent. This improved performance is attributed to the presence of partially porous carbon based material in the composite material that was blended with Nyex 100 in a specific mass ratio. The composite adsorbent material exhibited 100% regeneration efficiency similar to that of Nyex 100 using a DC current of 1 A for 60 minutes.

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