Adsorption of Rhodamine B from Aqueous Effluents on Graphite from Spent Lithium-Ion Battery Anode

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Abstract: *The purpose of this study was to investigate the possibility of the utilization of Graphite from Spent Lithium-Ion Batteries (LIBs) anode as adsorbent for removal of rhodamine B (RB) from aqueous solutions. The effect of different parameters (such as pH of the medium, sorbate concentration, adsorbent dosage and contact time) were investigated. The sorption process was relatively fast and equilibrium was reached for Rodhamine B after 60 min. Equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 2.905 mg/g RB (at 25ºC). Removal efficiency even reached 96% within 25 min at 1 mg/L initial RB concentration. The procedure developed was successfully applied for the removal of rhodamine B in aqueous solutions.*
Keywords: *Rhodamine B,Spent Li-Ion Battery Anode,AdsorptionIsotherm, Wastewater treatment, Pollution control.*

I.   INTRODUCTION

The safe and effective disposal of industrial wastewater is thus a challenging task. Among the industries whose activities can cause contamination of water, it can highlight the textile sector that generates large volumes of wastewater and whose main characteristic is the color, as in the dyeing process, the part not fixed dyes on the fabric fiber. Thus, when an untreated effluent is released into water bodies, besides affecting the color of the water, the dyes can be absorbed by aquatic organisms, altering the natural balance and causing serious problems to the ecosystem because many of these dyes are toxic and some have even carcinogenic and mutagenic effects [1].

Rhodamine B, in addition to high levels of toxicity, cause visual pollution, has a resistance to destruction and not readily degraded by conventional methods for the treatment of effluents [2]. The main techniques for textile effluent color removal involving precipitation, chemical degradation, electrochemistry, photochemistry, biodegradation [3-8].

However, among the most used and effective processes for the removal of color, adsorption is the one that provides the best results and can be used to remove different types of materials. It is widely used for removal of some types of water pollutants, especially those that are more difficult to biodegrade. Extensive literature has been reported regarding dyeremoval from aqueous solutions by using a myriad of adsorbentsderived from clay minerals[9], activated carbon [10-12], coal [13], wood[14], carbon xerogels[15], fly ash[16-18] and bio-materials[19, 20].

Although the activated carbon is one of the main adsorbents for the removal of color due to pores that are evenly distributed [21], the high cost makes their use restricted [22]. Thus, it is proposed as an alternative to use of the graphite from spent LIBs anode, thus adding value to the residue, producing an adsorbent material of high quality with low associated cost.

The anode is made of graphite in spherical form. The structure of pure graphite is close to the basic structural unit of activated carbon [23]. Thus, it has been hypothesized that the graphite of the spent LIBs anode may exhibit characteristics similar to the activated carbon, being possible its use as an adsorbent.

This paper describes a study of the use of graphite from spent LIBs anode as an adsorbent for removal of Rhodamine B (RB) from aqueous solutions. The effect of various important parameters on removal such as pH, RB concentrations, anode dosages and contact time is also discussed. It was found that graphite from spent LIBs anode is an excellent adsorbent for removal of RB and has several advantages over other materials.

II.   MATERIALS AND METHODS

2.1Materials

All chemicals were reagent grade. All solutions were prepared with pure water (18 MΩ/cm) obtained in a Corning Mega Purification System. All glassware were demineralized with HNO₃ 20% v/v before use. The

rhodamine B was obtained from Vetec in distilled water. 0.1 M NaOH and HNO_3 solutions were used for pH adjustment. A Quimis pH meter (Model Q400ISE) was used for pH measurements.

2.2 Preparation of Adsorbent

The spent LIBs was collected by donation campaign into the university. Individualized disassemble the battery was held in the chapel as the organic solvents and lithium salts are toxic and in contact with air react and form gases that can cause explosions [24,25]. The process of opening the battery was carried out after confirming that they were fully discharged. At this stage, we used a resistor connected in series with a current meter and a voltmeter in parallel, which simulated a load on the battery poles. Only when they showed values close to zero was given continuity to the opening of the battery. The Li-ion batteries (LIBs) were separated into their parts: anode, cathode, steel separators and current collectors. The anode was obtained by manually scraping of the material deposited over the cupper sheets. The spent LIBs anode was dried in a laboratory oven at 105°C for 24h to complete electrolyte evaporation.

2.3 Characterization

The physical–chemical characterization of graphite from spent LIBs anode and/or spent LIBs anode-RB was performed by Powder X-Ray Diffraction (XRD) with a diffractometerRigaku (DMAX) using CuKα1 radiation (1.5818 Å), operating at 40kV and 20mA. Scans were performed from 10 to 60° (2θ) at a step size of 0.02° with a scan speed of 2°/min. Qualitative phase analysis was carried out by using the Joint Committee on Powder Diffraction–International Center for Diffraction Data (JCPDS–ICDD) databases.

Thermal analysis of the samples was performed by determining the behavior thermogravimetric (TGA) and the differential thermal analysis (DTA) using equipment Netzsch (409C). The heating rate was 10 K/min, the purge gas was nitrogen with a flow rate of 50 ml/min, and the reference used was an alumina empty crucible. These analyses were performed to find out the physicochemical properties, aiming specifically at the application of graphite from spent lithium-ion batteries anode for the removal of rhodamine.

The morphological characteristics were evaluated by using a Zeiss (EVO LS 15), Scanning Electron Microscope (SEM-EDX). The samples were covered with a thin layer of gold and an electron acceleration voltage of 20 kV was applied.

Fourier Transform-Infra-Red Spectroscopy (FT-IR) was used to provide information regarding the surface properties. The spectra were recorded between 4000 and 500 cm^{-1} on a Nicolet 6700 IR – ATR mode with 36 scans at a resolution of 4 cm^{-1} by placing a small amount of the sample on the diamond crystal.

The surface area and adsorption average pore width of the selected fraction of nano alumina was determined by the N_2 gas Brunauer-Emmett-Teller (BET) method of analysis using a Micromeritics Chemisorption (ASAP 2420).

2.4 Batch Adsorption Experiments

Batch adsorption experiments were carried out by mechanically stirring a series of bottles containing 0.10 g of graphite from spent LIBs anode sample with 25 ml of an aqueous solution of Rhodamine B (RB) of the desired concentration and pH in different properly cleaned beaker of 100 ml on a stirring hot plate with a constant speed of 100 rpm. The beaker were agitated for pre-determinate times until equilibrium was attained. At the end of the agitation period, the mixture was centrifuged at 4000 rpm for 20 min.

The percent removal of RB from aqueous solution was calculated by the following equation:

$$\% \ Removal = \frac{C_i - C_f}{C_i} \ x \ 100 \qquad (1)$$

Where C_i and C_f are the initial and equilibrium concentrations of the adsorbate, respectively.

III. Results and Discussion

3.1 Characterization

3.1.1 X-Ray diffraction (XRD)

The X-ray diffraction patterns of graphite from spent LIBs anode and spent LIBs anode-RB are presented in Figure 1. As shown the strong diffraction intensity of peaks appeared at 2θ of 26.5º, in correspondence with the characteristic peaks of the hexagonal structure (PDF#25-284), indicated that the main composition of anode active materials was graphite with integrated graphite layered structure [26,27]. It can be noted in the Figure 1 that the characteristic peaks of graphite anode does not change after RB adsorption; only a

reducing on the intensity of the peaks after adsorption of RB was noted, indicating that this process does not alter the crystalline structure of the adsorbent.
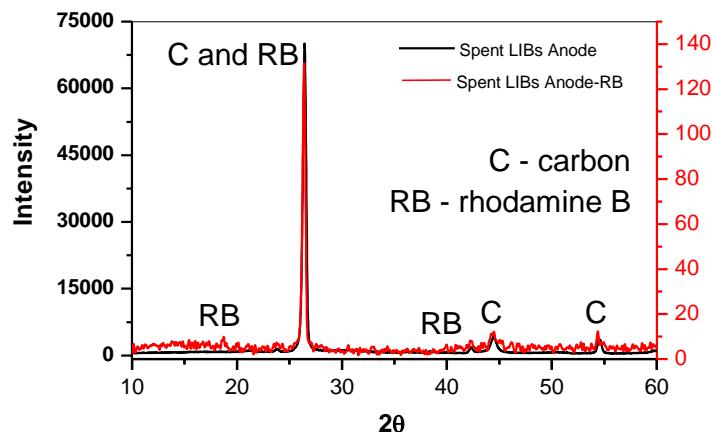

Figure 1: XRD patterns of graphite anode active materials from a spent lithium-ion batteries (LIBs) and after adsorbed by Rhodamine B.

3.1.2 Thermogravimetric Analysis

In order to decompose them effectively, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of graphite from anode were carried to determine the pyrolysis temperature range as shown in Figure 2. The decomposition due to loss of organic material that composes the electrolyte occurs in the spent LIBs at 150ºC. The endothermic peak centered at 211.6ºC in the graphite from spent LIBs anode DTA curve is attributed to the volatilization of organic material of the electrolyte, not completely removed in the drying process. The TGA curve for graphite from spent LIBs anode shows a weight of loss starting at 144 ºC until 352.3ºC, totalizing 3.88% [28].
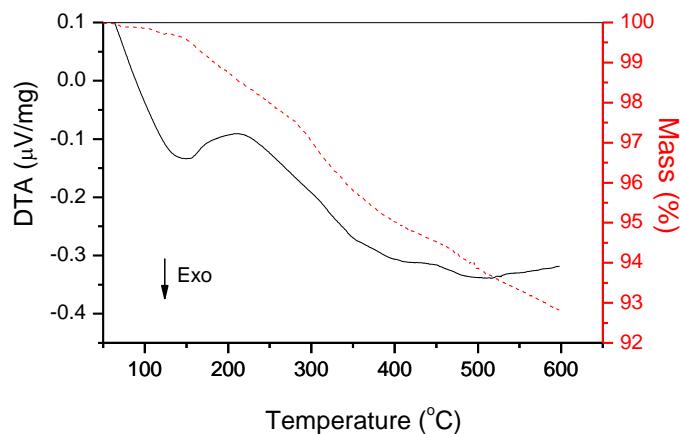

Figure 2: The thermogravimetricbehavior of the graphite from spent LIBs anode.

It is possible to note, another weight of loss after 350ºC, attributed to the carbonate (from the electrolyte) decomposition. After all, less than 7.5 % mass is loosed in the thermal treatment of graphite from spent LIBs anode. These results indicate that a washing step during the adsorbent preparation is suitable to the electrolyte removal, and let the surface more available to Rhodamine B adsorption. In addition, it was observed that the graphite anode is very thermally stable under N_2 atmosphere, similar to the active carbon.

3.1.3 Scanning Electron Microscopy (SEM)

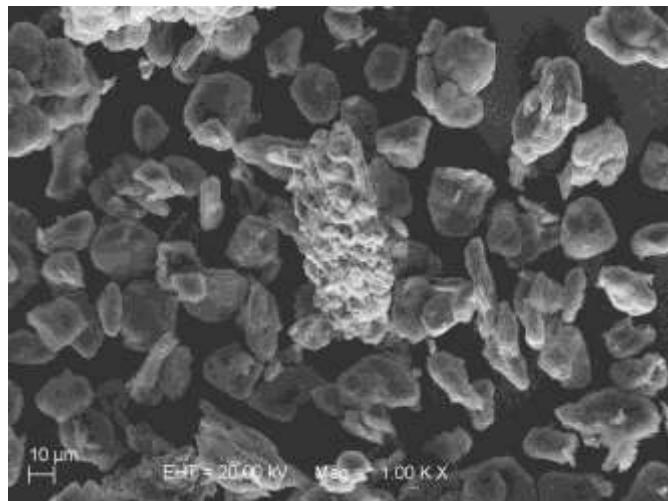Figure 3 presents the imaging of the surface of the graphite obtained from spent LIBs anode.

Figure 3: Scanning electron micrographs of graphite from spent lithium-ion batteries (LIBs) anode.

Analysis by energy dispersion x-ray (EDX) is presented in the Figure 4. It is possible to identify the presence of carbon (anode). In the meantime, is not possible to observe the presence of cupper (residual of sheets).
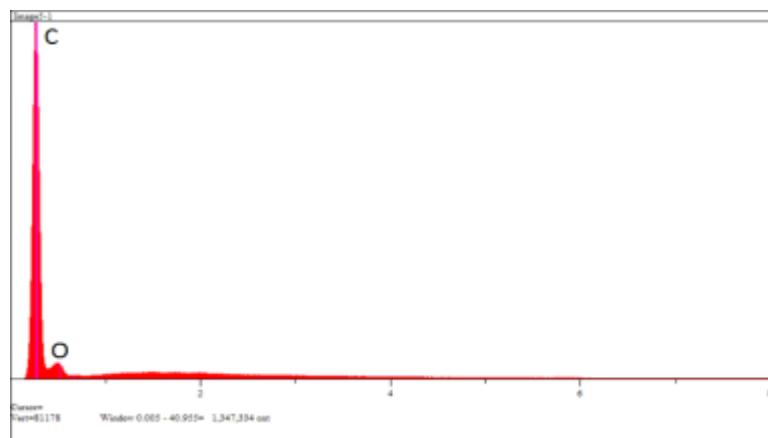

Figure 4: Energy Dispersion X-ray (EDX) spectrum of graphite from spent LIBs anode.

Figure 5 shows the deposition of Rhodamine B (RB) on the surface of the graphite from spent LIBs anode after immersion in aqueous RB solution (10 mg/L). Individual areas of RB can be seen on the surface of the graphite.
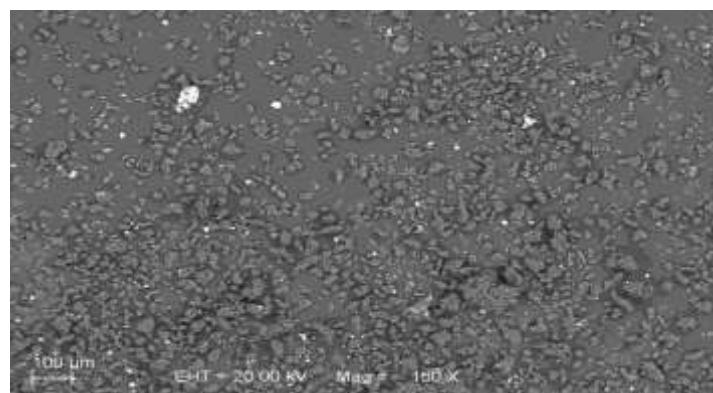

Figure 5: SEM images of Rhodamine B on the surface of the graphite from spent LIBs anode.

3.1.4 FT-IR Analysis

The FT-IR technique is an important tool to identify characteristics functional groups. The infrared spectrum of the graphite anode after adsorption of rhodamine B is shown in the Figure 6.
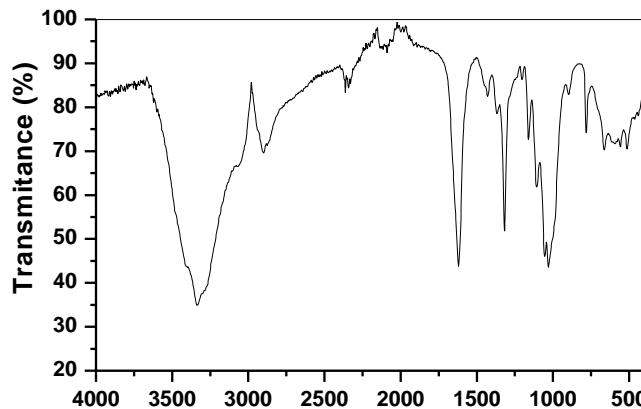

Figure 6: Infrared spectrum of the graphite after rhodamine B adsorption.

It is observed the presence of major bands of vibration of functional groups of rhodamine, indicating that the adsorption of rhodamine on the surface of graphite occurred. The broad band at 3405 cm⁻¹ is attributed to O-H vibration of the water adsorbed between the sheets of graphite. The band at 3340 cm⁻¹ is attributed to N-H bond stretching of rhodamine. The bands at 2901, 2873, and 1370 cm⁻¹ are assigned to the vibration of C-H bond (CH_2 and CH_3). The band at 1619 cm⁻¹ is attributed to vibration of the graphitic non oxidized backbone. The band at 1055 cm⁻¹ is attributed to stretching vibration of COO^-. The bands at 898 cm⁻¹ to 782 cm⁻¹ are assigned to the di-substituted aromatic ring. The bands at 664 cm⁻¹ to 560 cm⁻¹ are attributed to the presence of chlorine rhodamine b (cationic). The broad band at 1623 cm⁻¹ is attributed to vibration of C-C bond conjugated with benzene rings, characteristic of the rhodamine structure. In addition, this band appears intense in the spectrum, while the band in 1730 cm⁻¹ cannot be identified. This behavior is described previous, because of electrostatic interaction of nitrogen (ammonium ion) of rhodamine with the COO- group of the graphite oxidized surface [29].

3.1.5 Specific Surface Area (SSA)

The graphite from spent lithium-ion batteries anode has a black color and its specific surface area was 68.77 m²/g (Table 1). It is higher than others adsorbents used in removing Rhodamine B, such as, raphiahookerie fruit epicarp (0.00351 m²/g)[30], cadmium sulfite (17.0 m²/g)[31], bagasse pith (1.5 m²/g)[32], sodium montmorillonite (35.45 m²/g)[33], banana and orange peels (20.6–23.5 m²/g)[34], polyvinyl chloride (PVC) (0.28 m²/g)[35], fly ash (15.6 m²/g) [36], red mud (21.0 m²/g) [36].
20.6–23.5 m²/g

The decrease on the specific surface area, pore volume and average pore diameter for graphite from spent LIBs anode-RB) indicates that the used material removes satisfactorily lead from solution.

Table 1: Specific surface area, pore volume and average pore diameter of graphite from spent LIBs anode before and after RB adsorption.

Sample	Specific Surface Area (m²/g)	Pore Volume (cm³/g)	Pore diameter (A)
Spent LIBs anode	68.7692	0.069413	57.800
Spent LIBs anode-RB	20.029	0.035311	56.112

3.2Adsorption Studies
3.2.1 Effect of Contact Time on the Rhodamine B (RB)

The effect of the stirring time on the adsorption of rhodamine B graphite is shown in Figure 7. It was observed that for the initial concentration of 1 mg/L to adsorption was maximum (100%), reaching equilibrium within 20 minutes of contact. When used at an initial concentration of 10 mg/L, the removal was around 45% and the time to reach equilibrium was 60 minutes. Because of this analysis, the time of 60 minutes was adopted for the other trials.
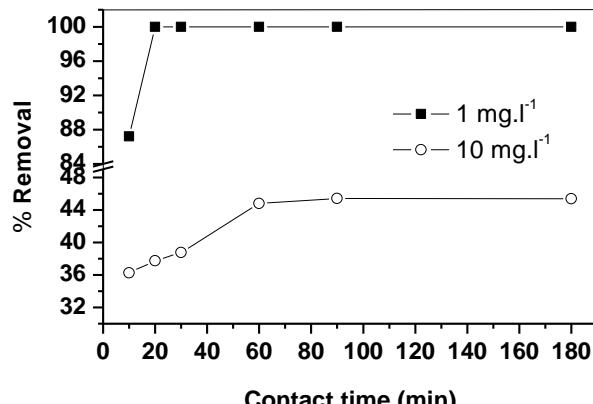

Figure 7: Effect of contact time on the removal of rhodamine B, 0.1 g of graphite from spent LIBs anode, 25 mL of RB solution, temperature 25ºC.

3.2.2 Effect of pH

The importance of the pH in RB adsorption process is of public domain. It is well known that the metal ions speciation and the adsorbent surface charges are affected by pH variation. In this study it was observed a variation in the Pb (II) adsorption with the pH variation, wherein the best results were obtained at pH 5 (Figure 8).It was observed that the absorption is favored by acidic pH. In laboratory tests was used to pH 7.0 due to the practice of neutralizing the actual effluents in wastewater treatment plants before being released in the environment.
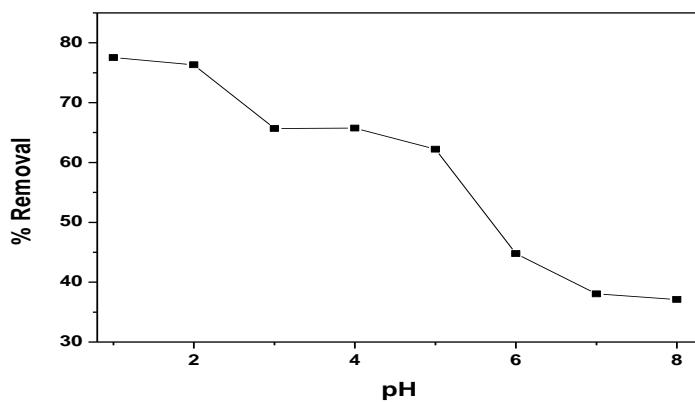

Figure 8: Effect of pH on the removal of RB by graphite from spent LIBs anode: 0.1 g of spent LIBs anode, 25 ml of solution, temperature 25ºC.

One explanation for the effect of the acid pH is more efficient in removing rhodamine B can be obtained from the analysis of the molecule structure in acid, basic or neutral media. The dye in an acid medium has positively charged surface, which facilitates the interaction with the adsorbent negative surface. This promotes the adsorption process, resulting in higher rhodamine removal. As the pH increase, the rhodamine turns less positive to neutral, which decrease the interaction with the adsorbent, resulting in the observed pH behavior (Figure 08).

3.2.3 Effect of RB concentration

The RB removal by the graphite from spent LIBs anode was evaluated as a function of the initial concentrations of added RB. The results pointed out that the adsorption process is favorable in low concentration solution (Figure 9). The concentration solution is a "driving force" that conducts the RB to the adsorption site, and facilitates the adsorption process.
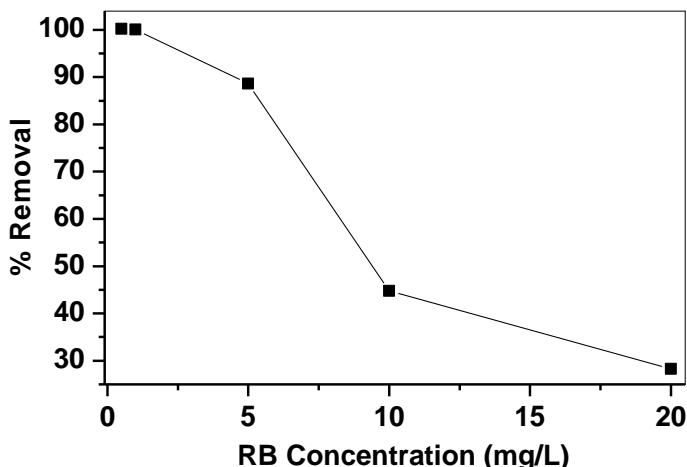

Figure 9: Effect of initial concentration of RB.

3.2.4 Effect of Adsorbent Dose

Using a dosage study is possible determines the capacity of adsorbent for a given initial concentration of rhodamine B solution. The effect of adsorbent dose on the percent removal of RB at an initial concentration of 10 mg/L is shown in Figure 10.
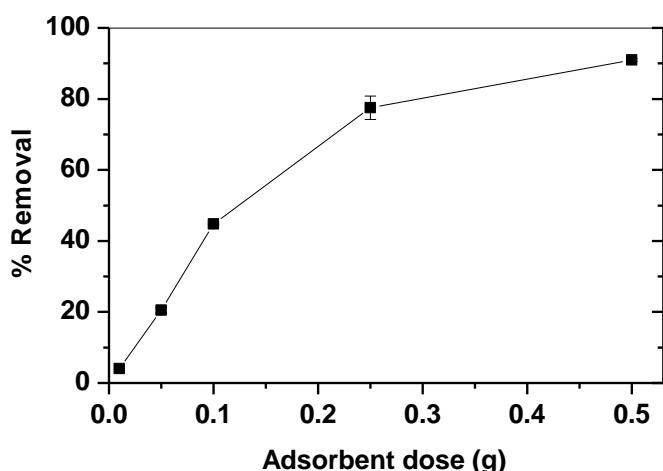

Figure 10: Effect of graphite from spent LIBs anode dosage on the removal of RB, 25 mL of solutions, contact time 60 min, temperature 25ºC.

3.2.5 Isotherm Study

The amount of heavy metals sorbed (q) was calculated using the following equation:

$$q = \left[\frac{(C_0 - C_e)}{m} \right].V$$

(2)

where Co is the initial concentration, Ce the equilibrium concentration, m the mass of adsorbent and V the volume of liquid containing lead.

The isotherm models were used the Langmuir (3) and linearized Langmuir (3.1):

$$Cs = \frac{K_L.q_m.C_e}{1 + (K_L.C_e)}$$

(3)

$$\frac{Ce}{Cs} = \frac{1}{K_L.q_m} + \frac{1.C_e}{q_m}$$

(3.1)

where $Cs = (Co - Ce)$, q_m and K_L are the Langmuir constants representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

It can be seen from Figure 11 that the isotherm data fits the Langmuir equation well ($R^2 = 0.9998$). The values of qm and K_L were determined from the figure and weres found to be 2.905 mg/g and 1.002 L/mg, respectively. It indicates the adsorption process took place at specific homogeneous sites within anode regarded as monolayer adsorption.
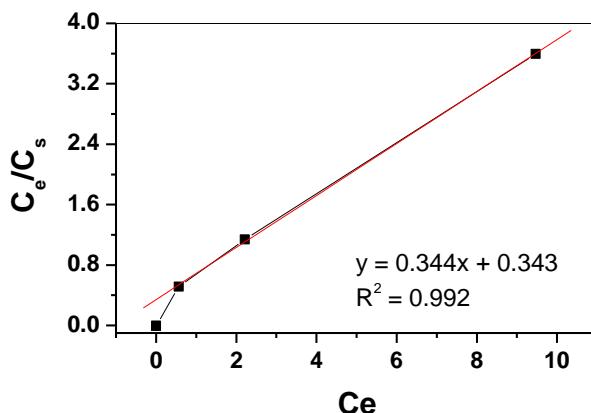

Figure 11: Langmuir adsorption isotherm.

The correlation coefficient value of pseudo-second-order kinetic model for the adsorption of RB suggests that the adsorption process of RB on graphite from spent LIBs anode may be controlled by chemical adsorption involving valence forces through sharing or exchange electrons between sorbent and sorbate.

The experimental data of the present investigations are comparable with the reported values in some cases. We note that our material (Graphite from spent LIBs anode, 2.905 mg/g) is more effective compared to Titania–silica (0.11mg/g)[37], Zeolite MCM-22 (1.11mg/g)[38], Australian natural zeolite (2.12mg/g)[39], Tannic acid in Leacril(2.7mg/g)[40] and Coal ash (2.86mg/g)[41].

However, the present experiments are conducted to find the technical applicability of the low-cost adsorbents to remove RB ions from industrial wastewater.

III.   CONCLUSIONS

The present study shows from spent lithium-ion batteries anode is an effective adsorbent for the rhodamine B removal from aqueous and wastewater solutions. The adsorption of RB by graphite from battery anode is a function of the adsorbent dosage, initial concentration of metal ions, pH and time of contact. The kinetic study shows that equilibrium is reached for RB ions at 60 minutes. The adsorption isotherm studies showed that the Langmuir adsorption isotherm model fits well with the experimental data. The maximum adsorption capacity was obtained for spent lithium-ion batteries anode 2.905 mg/g RB (at 25ºC). The adsorbent has a high capacity for removal of RB from contaminated water and wastewaters and it can be used for removal of RB from moderately acidic aqueous solutions. The cost of removal is expected to be quite low, as the adsorbents are cheap and easily available in large quantities. The spent lithium-ion batteries anode would be useful in treatment of wastewater containing rhodamine B.

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