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Removal of Reactive Red 1 dye from aqueous solution using gypsum

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ABSTRACT

In order to establish the capacity of gypsum in the removal of dyes from aqueous solutions, the adsorption behaviour of Reactive Red 1 (RR1) from aqueous solution onto gypsum was investigated under several different operating parameters namely, contact time, adsorbent dosage, pH, particle size, and adsorbate dosage, at ambient temperature. The study employed the batch experiment method and utilized two different particle sizes (150 µm and 300 µm) of the adsorbent. Two portions of each particle size were subjected to two different treatments (acid and base) while a third portion remained untreated. Acidic medium favoured the dye removal at an optimal pH of 2 and an optimal contact time of 25-35 minutes. Optimal adsorption was also recorded at an adsorbent dosage of 0.8 g. Under optimal conditions, 89.8% adsorption was recorded with the 150 µm particle size of the adsorbent in the acid-treated medium. Both Langmuir and Freundlich isotherms could be used to describe adsorption of the dye, with the value of the separation factor of the Langmuir isotherm (RL) lying well in between 0 and 1. The Freundlich isotherm intensity parameter (1/n) also fell in between 0 and 1- indicating that both isotherm processes are favourable. The experimental data fitted well to the pseudo-second-order kinetics model with R2>0.99 indicating that chemisorption was the rate-controlling step in the adsorption of the dye. The smaller particle size (150 µm) adsorbed higher amount of the dye because of its larger surface area. Acid treated adsorbents yielded higher dye removal than the untreated and the base treated

Keywords: Reactive Red 1 dye; Adsorption; Isotherms; Kinetics; Gypsum.

INTRODUCTION

The use of dyes by textile, paper, plastic, food and pharmaceutical industries to colour their products is a common occurrence. These industries use substantial amounts of water in their processes- resulting in the discharge of highly coloured effluents (Suteu et al., 2010). The discharge of these untreated coloured effluents into water bodies is currently a major problem for environmental management especially in developing countries. Coloured substances in water bodies tend to reduce sunlight penetration which is essential for many photo-initiated chemical reactions necessary for aquatic life, thus affecting the growth of plants and impacting on invertebrates and other forms of wildlife (Crini, 2006). Furthermore, effluents containing dyes are difficult to treat because most of these chemicals are not prone to aerobic digestion (Alaton et al., 2008). Increased environmental awareness as well as environmental regulations on the organic content of industrial effluents makes it necessary to eliminate dyes from wastewater before they are discharged into water bodies.

Although, there are several methods for the removal of pollutants from effluents, there is no single process capable of treating these effluents (Ghoreishi and Haghighi, 2003). Practically, a combination of different processes is often used to achieve the desired water quality in the most economical way. Liquid-phase adsorption is one of the most studied methods in the removal of pollutants from wastewater (Al-Asheh et al., 2003; Khraisheh and Alg-Houti 2005; Cestari et al., 2008). The treatment of wastewaters by adsorption process is an excellent choice especially if the adsorbent is inexpensive and does not require any additional pre-treatment step before its application. The main adsorbents used to remove dyes in wastewater employs activated carbon because of its good adsorption ability (Tan et al., 2007; Iqbal and Ashiq, 2007). The use of activated carbon, however, is restricted due to its high cost. An attempt to develop cheaper, effective and non-conventional low-cost adsorbents such as clay, zeolites, agricultural and industrial waste products have also been suggested (Crini, 2006; Lehocky and Mracek, 2006; Bakaullah et al., 2007). This study is aimed at exploring the use of the commonly available commodity, gypsum in treating industrial effluents. It is a hydrated salt of Calcium Sulphate ($CaSO_4. 2H_2O$) abundantly found in sedimentary environments of high saline water. It is cheap to obtain and requires no pre-treatment compared with activated coal (Isa et al., 2007; Rauf et al., 2009). In this study, attention is focused on the use of gypsum as an adsorbent in the removal of Reactive Red 1 dye (RR 1) from aqueous solutions. Reactive Red 1 dye ((32) – 5 – [4.6 – diamino – 1, 3, 5 – triazin – 2yl) amino] – 4 – oxo – 3 – [(2 – sulfopheyl) hydrazinylidene] naphthalene 2, 7 – dissulfonic acid) has been reported to be employed in both textile and printing industries (Karstens and Kobs, 1980; Kubin and Fletcher, 1982). This dye, on discharge into water bodies, releases aromatic amines - a potential carcinogen (Boeningo,

1994). In Port Harcourt city, Nigeria, printing and plastic industries abound-arising from the commercial and industrial setting of the city. The city is criss-crossed with a number of streams which serve as a natural drainage system. Effluents and wastes from these industries are indiscriminately discharged into the streams. Rauf et al. (2009) in a study had demonstrated the potentiality of gypsum to remove methylene blue dye from aqueous solution. It is hoped that gypsum will also efficiently remove Reactive Red 1 dye from aqueous solution.

MATERIALS AND METHODS

The gypsum powder was sieved into 150 µm and 300 µm particle sizes. Each particle size was divided into three portions; two of which were subjected to acid and base treatments respectively for 48 hours. The third portion was kept unmodified. Each portion was filtered and dried in a desiccator. Serial dilutions of the stock solution of the RR-1 dye (100 mg/dm^3) were used to perform at ambient temperature the various batch adsorption processes involving the determination of optimal contact time and pH as well as maximum adsorbate and adsorbent dosages (Obunwo and Akassawei, 2011). Optimal contact time was determined by measuring into each sample bottle, 0.3 g of the powder (of a particle size) and 20 ml of a known concentration of the RR-1 dye stock solution. The mixture was shaken in a mechanical shaker at 600 rpm. Two sample flasks were withdrawn from the shaker at pre-determined time intervals of 30 minutes for a period of 180 minutes. The mixture in each of the flasks was filtered and the filtrate centrifuged at the speed of 2800 rpm for 5 minutes. The supernatant was decanted and the residual amount was determined using the ultraviolet-visible spectrophotometer. Optimal pH was also determined by measuring 20 ml of the stock solution and adjusted to a desired pH value with either 0,1 M NaOH or 0.1 M HCl solution. A mixture of the solution and

the powder was then shaken in the mechanical shaker followed by centrifuging. Different concentrations of the dye, ranging from 0.008 to 0.020 mg/l were each mixed to 0.3 g of the adsorbent. The mixture was shaken followed by centrifuging. Optimal contact time and pH were maintained. Into different sample flasks, adsorbent dosages ranging between 0.2 g and 1.2 g were each mixed with 20mls of the dye solution. The mixture was shaken followed by centrifuging. Optimal contact time and pH were maintained.

RESULTS AND DISCUSSION

The influence of particle size on the adsorption of reactive red 1 (RR1) dye onto gypsum was studied with two different particle sizes: 300 µm and 150 µm. The results (Figure 1) show that the smaller particle size, 150 µm, yielded higher adsorption. This trend may be attributed to the larger surface area of the 150 µm adsorbent. Studies by Nethaji et al. (2010) on the adsorption of malachite green dye onto activated carbon derived from *Borassus aethiopum* flower biomass reported that smaller particles created larger surface areas than bigger particles. The effect of chemical pre-treatment on the adsorption of Reactive Red 1 (RR1) dye onto Gypsum was in the order acid-treated > untreated base-treated. Irrespective of the particle size, this order was maintained. Martin et al. (2003) in their studies on the efficiency of chemically treated adsorbents to remove dyes from aqueous solution onto activated carbon confirmed that adsorbents treated or obtained in the presence of sulphuric acid possessed relatively high adsorption capacity for aqueous dyes of large molecular weight; those treated with base decreased adsorption due to negatively charged activated carbon. Other studies on chemical treatment of adsorbents (Inthorn et al., 2004; Gong et al., 2005 and Ncibi et al., 2007) have also shown that acid- treated biomass yielded higher adsorption. Optimal contact time was attained within the range of

25 – 35 mins (Figure 2) with both particle sizes of the adsorbent. This trend is in agreement with studies by Rauf et al. (2009) on the removal of methylene blue from aqueous solution by using gypsum. The optimal contact time was reported to be in the range of 20 – 40 mins. In terms of the effect of pH, the optimal pH was recorded at pH 2 (Figure 3) with both particle sizes of the adsorbent. The uptake of the dye decreased with increase in pH. An acidic medium may thus enhance the adsorption of the dye. Isa et al. (2006) had reported that positive charges which dominate the surface of the gypsum adsorbent tend to promote adsorption in the acidic medium. In varying the adsorbent dosage, optimal adsorption was recorded with 0.8 g of the adsorbent at the different particle sizes. However, the maximum percentage adsorption of 89.8% was recorded with the 150 µm particle size adsorbent in the acid-treated medium (Figure 4). For the known amount of the adsorbent (0.30 g), adsorption increased with increase in the adsorbate dosage (Figure 5). However, an optimal adsorbate dosage was not attained presumably as a result of the range of concentration of the adsorbate (0.008 - 0.02 mg/l). The kinetics of the adsorption processes with both particle sizes showed that the pseudo-second order fitted better than the pseudo-first order in the different treatments (R2 ≥0.9) – Figures 6 and 7. It is thus suggested that the rate-controlling step might be a process of chemisorption (Ozacar and Sengel, 2003; Chiou and Li, 2003). By the application of Langmuir and Freundlich isotherm model equations for the two particle sizes, the results of the adsorption isotherm indicated that both Langmuir and Freundlich models fitted well ($R^2 > 0.98$)-(Figures 8 and 9) . The Langmuir Isotherm separation factor R_L fell in the range of 0-1 in all cases, which clearly showed that the adsorption process was favourable. Freundlich Isotherm model also proved that the adsorption was favourable with 1/n < 1 in all cases.
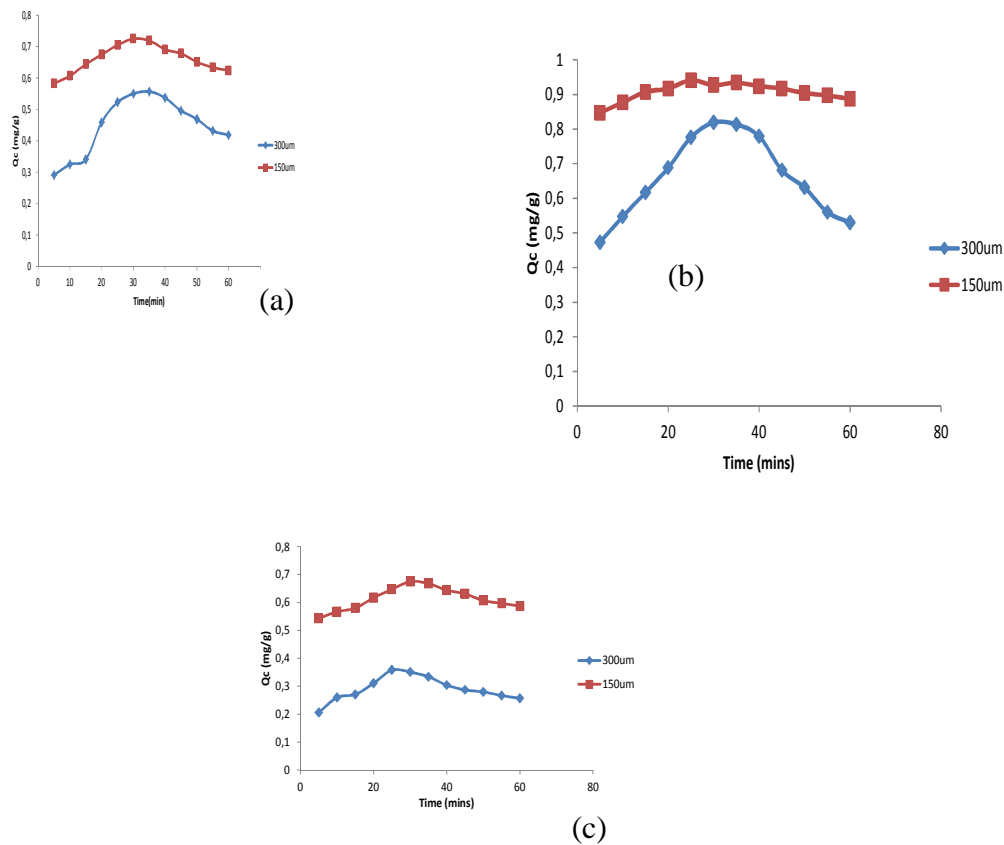
Figure 1: A comparison of adsorption with different particle sizes (a) untreated; (b) Acid-treated; (c) base-treated Gypsum.
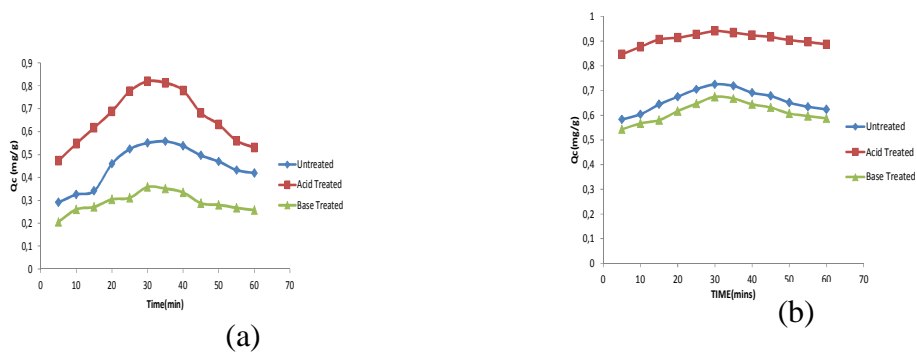

Figure 2: Plot of adsorption capacity against contact time (a) 300 µm; (b) 150 µm gypsum.
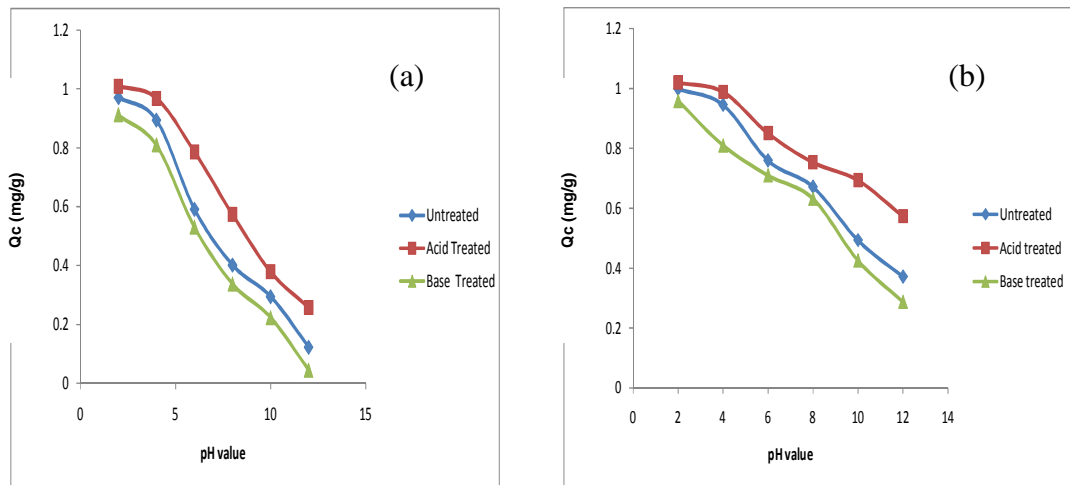
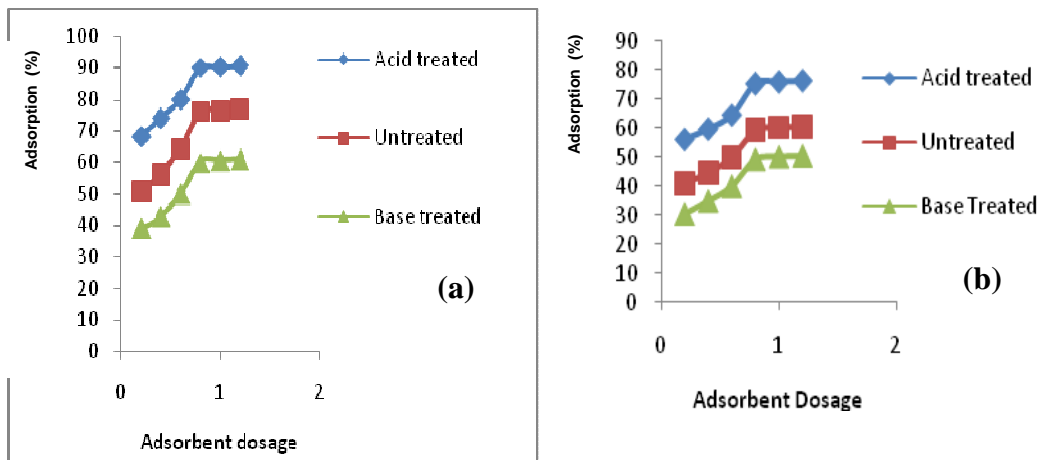**Figure 3:** Plot of adsorption capacity against pH (a) 300 µm; (b) 150 µm gypsum.

Figure 4: Plot of adsorption capacity against adsorbent dosage (a) 300 µm; (b) 150 µm gypsum.
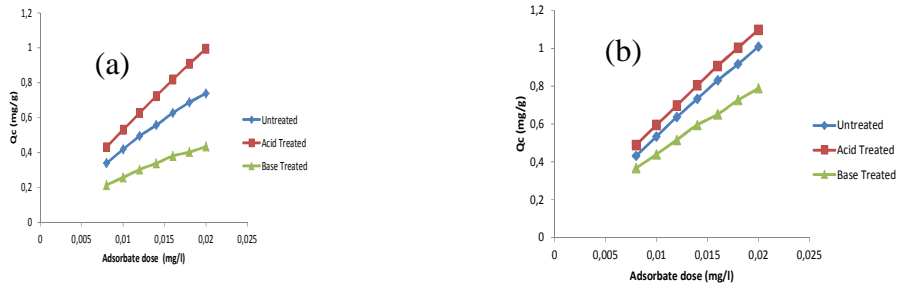
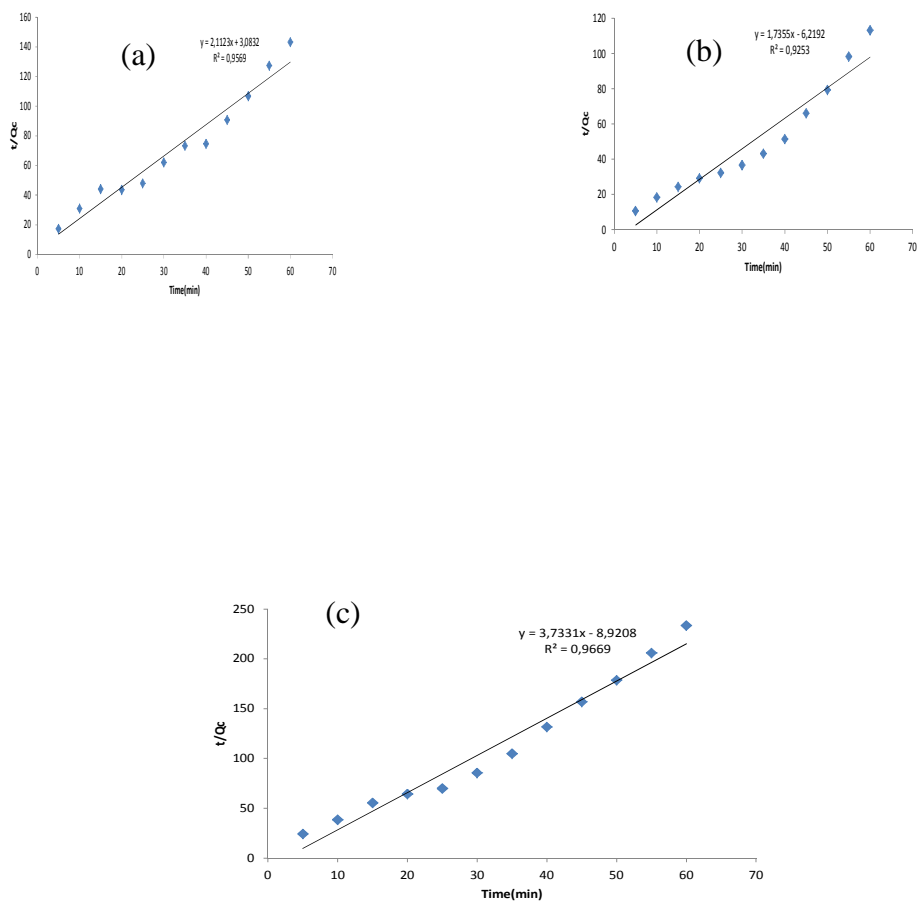**Figure 5:** Plot of adsorption capacity against adsorbate dosage (a) 300 µm; (b) 150 µm gypsum.

Figure 6: Pseudo-Second-order with (a) untreated; (b) acid-treated and (c) base- treated 300 µm Gypsum.
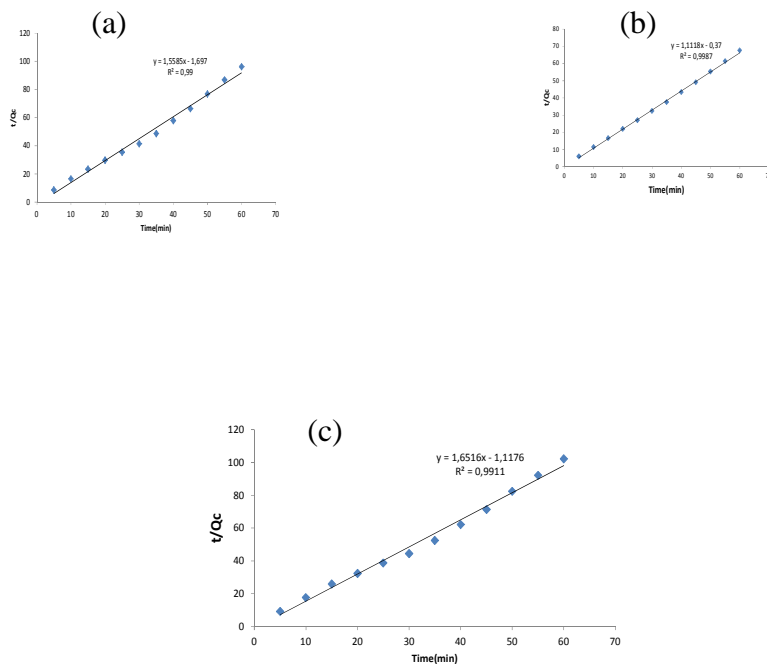
(a)

(b)

(c)

Figure 7: Pseudo-Second-order with (a) untreated; (b) acid-treated and (c) base- treated 150 µm Gypsum.
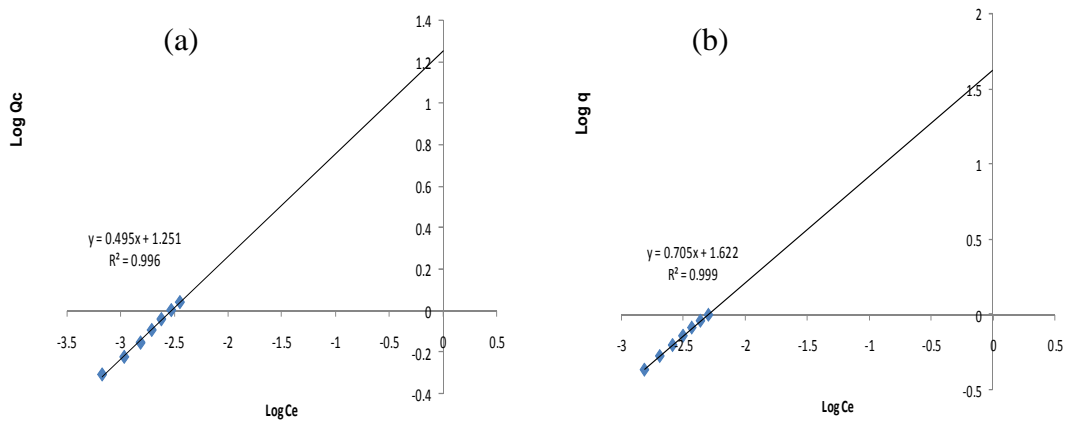

(a)

(b)

Figure 8: Freundlich Isotherm model with 150 µm (a), 300 µm (b) acid- treated gypsum.
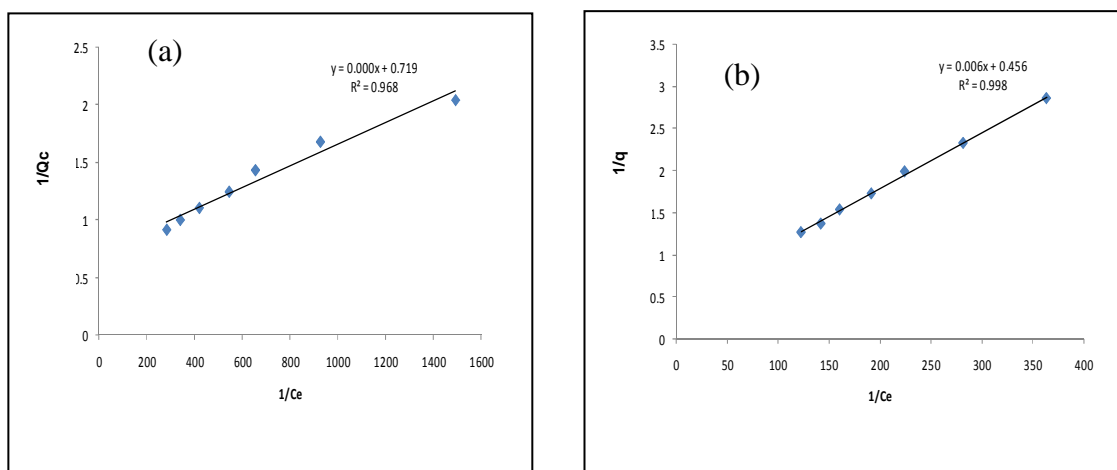
Figure 9: Langmuir Isotherm model with 150 µm (a), 300 µm (b) acid- treated gypsum.

Conclusion

From the various studies, gypsum served as an effective adsorbent in the removal of the Reactive Red 1 dye from aqueous solution. Optimal conditions were attained as contact time (25 – 35 mins), pH (2) and adsorbent dosage of 0.8 g. The smaller particle size (150 µm) was a more effective adsorbent attaining a maximum adsorption of 89.8% in the acid-treated medium. Both Langmuir and Freundlich models fitted well. It is suggested that the rate-controlling step might be a process of chemisorption as kinetically, the adsorption process fitted a pseudo second order.

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