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Removal of Congo Red Dye from Aqueous Solution using Sugarcane Bagasse and Bambara Groundnut Shell

Muhammad B. Ibrahim, Atika M. Ibrahim, Maje A. Haruna and Maimuna S. Yaro
Department of Pure and Industrial Chemistry, Bayero University Kano
P. M. B. 3011 Kano Nigeria
Email:mbibrahim.chm@buk.edu.ng

ABSTRACT
A methodology involving sugarcane bagasse (SB) and Bambara groundnut shell (BGS) as adsorbents was developed in order to remove the carcinogenic Congo red dye from aqueous medium. The effect of contact time, sorbent dosage, initial concentration and pH were investigated. The results showed high efficiency of ≈ 93% and 75% using 4.5g of SB and BGS respectively. The results also indicated that the % removal increases with increase in dye loading concentration, while it decreased with an increase in pH of the solution from 4 to 10. From the results, it is possible to conclude that sugarcane bagasse and Bambara groundnut shell are good adsorbents for dye effluent treatment.

Keywords: Bambara groundnut shell, Congo red, Sugarcane Bagasse, % Dye Removal.

INTRODUCTION
The introduction of waste products in the environment is a worldwide problem that has been highlighted by various environmentalist groups. High production and use of dyes generates coloured wastewater and pollute the environment. Textile, paper and food industries, tanneries, electroplating factories discharge coloured wastewater (McKay *et al*., 1997). Colour or dye being one of the recalcitrant, persist for long distances in flowing water, retards photosynthesis, inhibit growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen. Some dyes may cause allergic dermatitis, skin irritation, cancer and mutation in man. Dye concentrations lower than 1 mg/L may induce visible colouration and hence public complaints (Metivier-Pignon *et al.,* 2007). Synthetic dyes such as Congo red (CR) are difficult to biodegrade due to their complex aromatic structure, which provide them with physico-chemical, thermal and optical stability (Han *et al*., 2008; Mohan *et al.,* 2008). Congo red has been described as a type of dye that has carcinogenic properties (Chatterjee *et al*., 2007).

The methods of colour removal from industrial effluents include coagulation, flotation (Lin and Lin, 1993), electro flotation (Ogfitveren and Koparal, 1994), electrochemical destruction (Ulker and Savas, 1994) and adsorption using activated carbon (Pala and Tokat, 2002). Among these options, adsorption is the most preferred method and activated carbon is the most effective adsorbent widely employed to treat wastewater containing different classes of dyes (Namasivayam and Kavitha, 2002; Lin *et al*., 2008; Ong *et al*., 2008); however, recognizing the economical drawback of commercial activated carbon and considering the huge quantities of wastewater to be treated, efforts have been made to use the bioadsorbent of considerable low cost, such as cellulose (Annadurai *et al*., 2002), chitosan (Chatterjee *et al*., 2007), sawdust (Garg *et al*., 2003), sugarcane (Khattri and Singh, 1999; Pandey *et al*., 2000), montmorillonite (Yermiyahu *et al*., 2003), bentonite (Lian *et al*., 2009), fungi (Yuzhu and Viraraghavan, 2002; Binupriya *et al*., 2008), coir pith, olive stone, pine bark, coconut shell, tropical grass, almond shells etc (Arivoli, 2007; Selvarani, 2000), as carbonaceous precursors for the removal of dyes from wastewater.

Raw bagasse is a waste from sugar mills and has been used as a low-cost adsorbent for the removal of chromium and nickel from aqueous solution by Rao *et al*. (2002) who studied the effect of hydrogen ion concentration, contact time, sorbent dose, initial concentration of adsorbent and particle size in batch experiments. The efficiency of the material for the removal of Cr (VI) at pH 6 and Ni (II) at pH 8, with a sorbate concentration 100 mg/L, contact time 90 min, adsorbent particle size 75μm, and adsorbent dose 3.5g/L, was found to be 91 and 85.6%, respectively. The efficiency of bagasse was suggested to be comparable to costlier conventional powdered activated carbon.

Srivastava *et al*. (1995) converted bagasse fly ash into a low-cost adsorbent for the removal of substituted phenols. The authors compared the uptake of trinitrophenol on the bagasse fly ash with other commercially available adsorbents. It was suggested that the developed bagasse fly ash adsorbent is considerably effective and cheap. The removal of dinitrophenol has also been observed. The results showed that 86% of dinitrophenol can be removed using 10 g L^{-1} of activated bagasse fly ash.

The adsorption process has demonstrated to be relevant when compared to other techniques of water reuse, since it has very low initial cost, easy operation, flexibility and simplicity. For this process to be efficient, in addition to its low cost, it is necessary to choose an adsorbent with high adsorptive capacity, high selectivity, stability and availability (Crini, 2006). The bioadsorbent made using sugarcane bagasse is basically built by macromolecules with humic and fulvic substances, lignin, cellulose, hemicelluloses and proteins that have adsorptive sites such as carbonyl, carboxylic, amine and hydroxyl groups able to absorb the dyes by ion exchange phenomena or by complexation (Davila-Jimenez *et al*., 2005). It is important to highlight that the use of agricultural wastes for the treatment of aqueous effluents, primarily as alternative adsorbent material may be an advantage, since they remove inert pollutants from the wastewater and may contribute to minimize the environmental impacts caused by inadequate disposal of these wastes.

The aim of this study is to assess the capacity of sugarcane bagasse and bambara groundnut shell to remove the carcinogenic Congo red dye (Fig. 1) by using adsorption process.

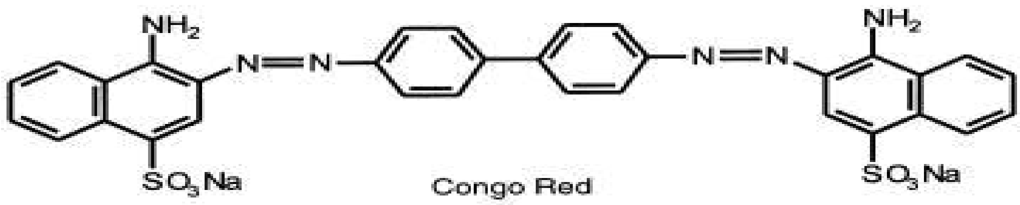

Fig. 1: Congo red dye structure.

MATERIALS AND METHODS

Materials

All glassware and plastic containers were washed thoroughly, rinsed with distilled water and allowed to dry in an oven. Both Sugarcane Bagasse and Bambara Groundnut Shell were collected from Dawanau market, the adsorbents were air dried in sunlight until almost all the moisture evaporated, and then in oven at 80^0C. The adsorbents were ground with laboratory motor and pestle and sieved with analytical sieve to the working size of 850µm and kept in a plastic container for subsequent use. Distilled water was used for the preparation of the Stock solution and kept in a refrigerator. Fresh working standards were prepared daily by appropriate dilutions (Ibrahim, 2011). pH adjustments and absorbance measurements were carried out using Jenway 3320 pH meter and Jenway 6051 colorimeter.

Methods

All batch adsorption experiments were carried out at room temperature as outlined below; and % removal of the dye by each adsorbent was calculated from the relation:

$$\frac{Co - Ce}{Co} \times 100\%$$

Where Co and Ce are the concentrations (mg/L) of the dye initially and at equilibrium time (Bhattacharya *et al*., 2008; El-Nemr *et al*., 2008; Ibrahim *et al*., 2006; Wang and Lin, 2008).

Effects of agitation time on % removal was studied by separately placing 1.0g of the adsorbents in a screw capped conical flask and $100cm^3$ of 10mg/L dye solution was added to each and agitated on a temperature controlled mechanical shaker for 5, 10, 15, 30, 45, 60, 75 and 90minutes. While for investigating the effects of the adsorbent weight on the dye removal 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5g were separately contacted with $100cm^3$ of 10mg/L dye solution and agitated for their respective equilibrium time. In order to test the effect of variation in the dye loading concentration on the other hand, optimal weight (4.5g) of the adsorbents was agitated separately in a $100cm^3$ of 10, 15, 20, 25 and 30mg/L dye solution for 30 and 90min respectively. Lastly, pH effect was investigated by agitating 4.5g of the adsorbents with $100cm^3$ of a solution of the optimal dye concentration after it has been adjusted to pH of 4, 6, 8 and 10 respectively using 0.5M solutions of HCl and NaOH as the case may be. The different mixtures were separately filtered using Whatman No. 1 filter paper; and the filtrates absorbance was measured at a predetermined λ_{max} of 490nm.

RESULTS AND DISCUSSION

Fig. 2 (a & b) shows the influence of residence time on the adsorption of Congo red by SB and BGS respectively. In the process of dye adsorption, the dye molecules have to first encounter the boundary layer effect, then adsorption from the surface and finally, they have to diffuse into the porous structure of the adsorbent. This phenomenon will take a relatively longer contact time (Malik, 2003). From Fig. 2a, uptake of Congo red was rapid in the first five minutes and after 30 minutes % removal was almost constant. Therefore, for batch experiments 30min equilibrium time was used for SB. From Fig. 2b, the % removal of the dye by BGS increases with time up to a maximum at 60min. This is followed by a region where there is gradual decrease in percentage adsorption with increase in agitation period, signifying possibility of desorption after saturation of the adsorbent which occurs at 75 and 90 min. (Namasivayam and Arasi, 1997). The result suggested that SB has higher affinity for the dye compared to BGS.

Adsorbent dosage is an important parameter in adsorption process. The effect of sorbent dosage on the % removal of the dye is shown in Fig. 3 which increased to approximately 93% and 75% for SB and BGS respectively. This is due to increase in availability of surface active sites resulting from increased dosage and conglomeration of the adsorbents (Al-Ghouti *et al.*, 2003). The result showed that a mass of 4.0g of SB is enough to remove a good amount of the dye. A similar trend was observed by Wong *et al.* (2009) for the adsorption of basic and reactive dyes by quartenised sugarcane bagasse.

Fig. 4 shows the influence of increase in dye loading concentration on % removal which increased from 93.9 to 95.9% on SB, while on BGS it increased from 74.7 to 86.7%. Similar observation was made by Rao *et al.* (2006) for the adsorption of Congo red with fly ash.

Fig. 5 shows the effect of pH of the dye solution. The pH value of the solution is an important process controlling parameter in the adsorption of the dye. The initial pH values of the dye solutions affect the surface charge of the adsorbent and thus the adsorption of the charged dye groups on it (Ozacar and Sengil, 2003). Congo red is a dipolar molecule. It exists as anionic form at basic pH and as cationic form at acidic pH. It has also been found that as the pH decreases, the colour of Congo red solution changes from red to dark blue. These variations of colour with pH suggest that the extent and nature of ionic character of Congo red molecule depends on the pH of the medium. The percentage removal of the dye decreased from 95 to 91.6% with increase in pH from 4 to 10 for SB and 67.5 to 62.6% for BGS.

At an acidic pH condition, the hydroxyl and carboxyl groups on the surface of the adsorbents are protonated and they favour the sorption of the anionic Congo red dye due to electrostatic attraction. With an increasing pH of the dye solution, the surface groups are deprotonated resulting in an increase of negatively charged sites that inhibit the sorption of the anionic dye due to electrostatic repulsion. A lower percentage of the removal of Congo red in alkaline pH may be due to the presence of excess OH^- ions competing with the dye anions for the adsorption sites. The electrostatic repulsion between the anionic dye and the negatively charged sites contributes to the decreased uptake of Congo red. Similar observations were reported by Malik, (2003), Tor and Cengeloglu, (2006). It is possible to suggest that an acidic pH is optimum for the removal of Congo red dye.

CONCLUSION

The removal of Congo red from aqueous solution using sugarcane bagasse and Bambara groundnut shell has been investigated. Optimum conditions for the adsorption process were found to be; contact time: 30 and 60min for SB and BGS respectively, sorbent dosage: $4.5g/100cm^3$; and a pH of 4. Percentage removal was found to increase with increase in initial dye concentration. This study shows the possibility of using Sugarcane Bagasse and Bambara Groundnut Shell for the uptake of Congo red dye.

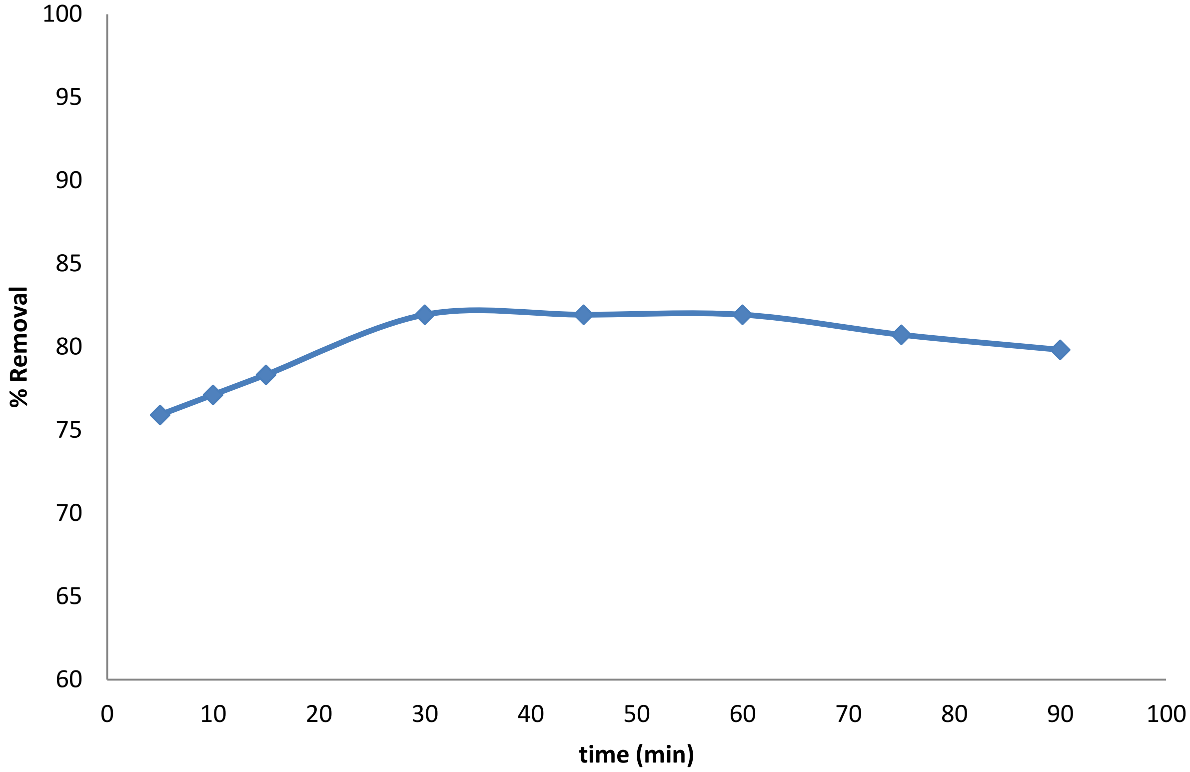

Fig. 2a: Estimation of Adsorption Equilibrium Time using Sugarcane Bagasse

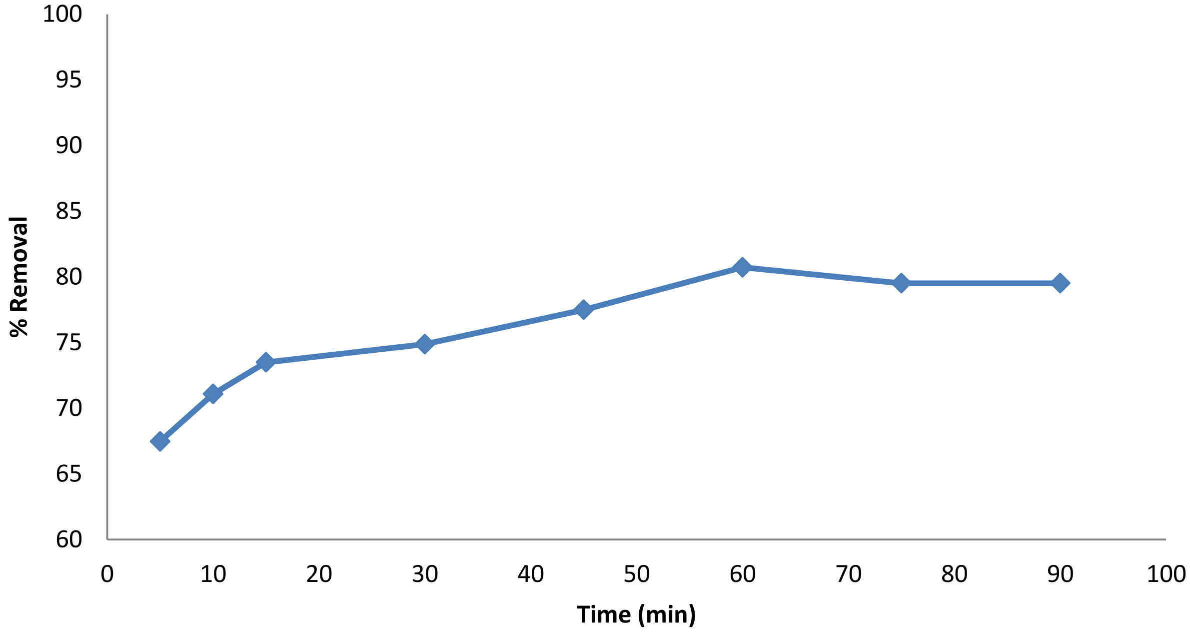

Fig. 2b: Estimation of Adsorption Equilibrium Time using Bambara Groundnut Shell

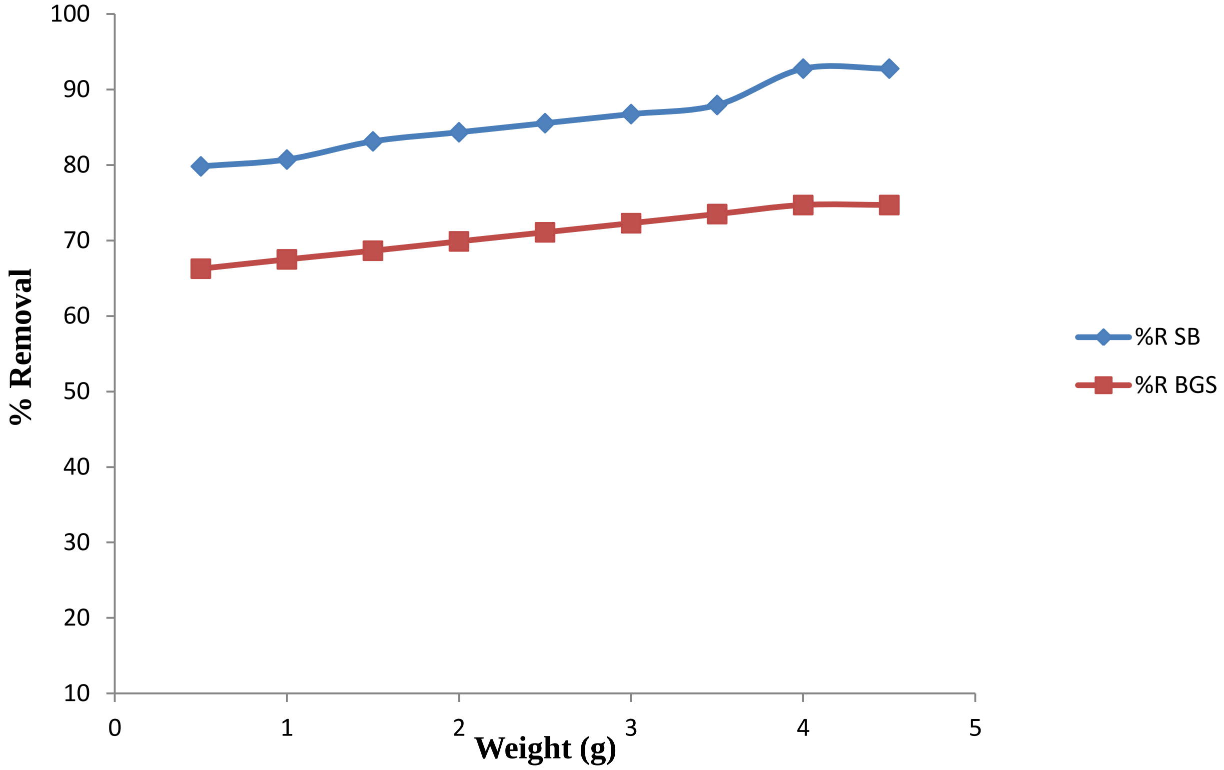

Fig. 3: Congo red % adsorption as a function of the adsorbent mass.

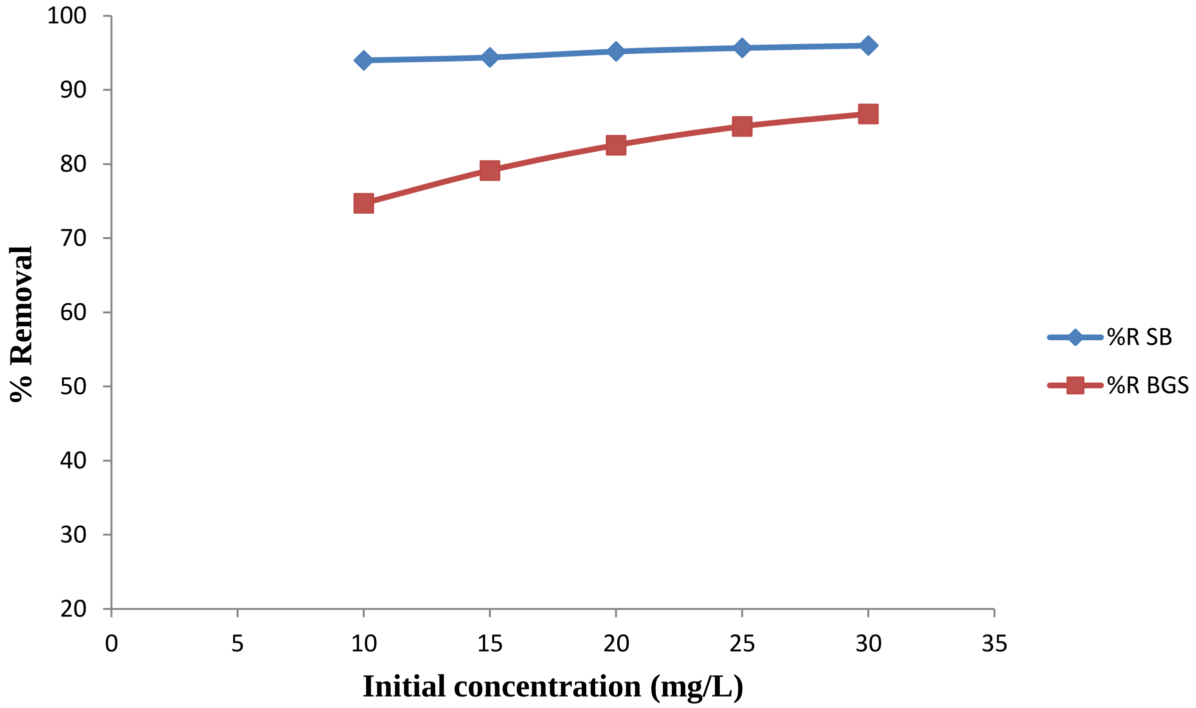

Fig. 4: Variation in % Removal with Initial Dye Loading Concentration

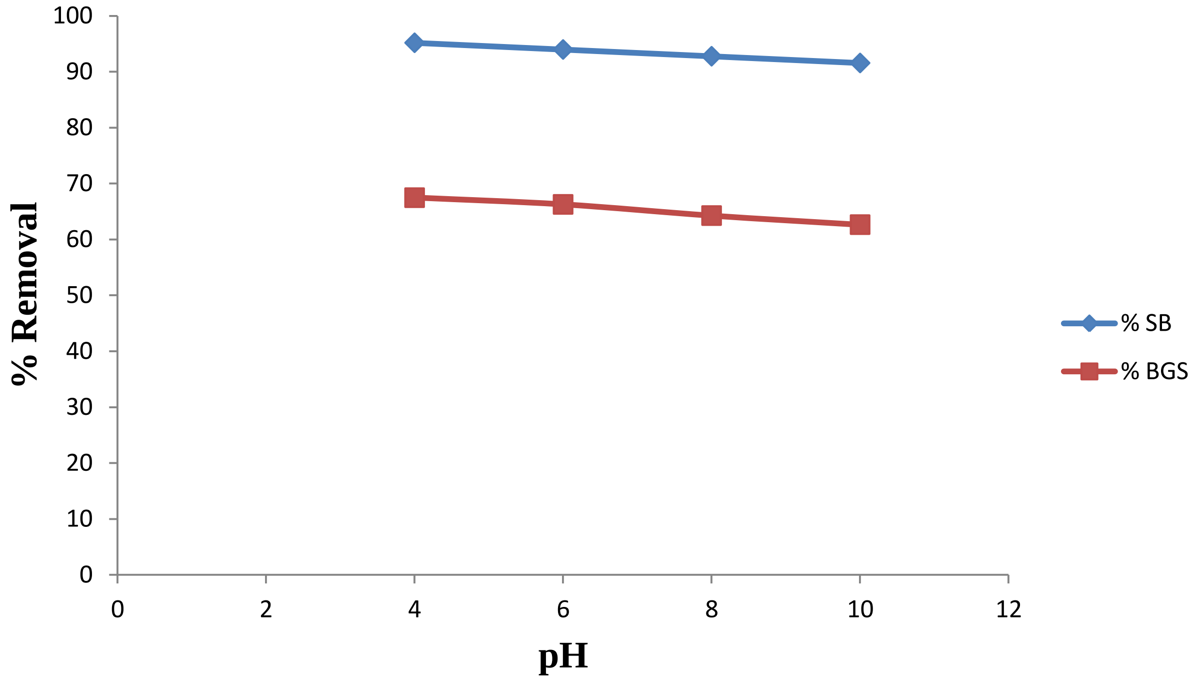

Fig. 5: Congo red % Removal as a function of pH.

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