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An investigation on the adsorption capacity of carbon particle for the removal of Fe^{3+} ion from water

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Abstract
Carbon particle was prepared from Sugarcane Bagasse by using carbonization method. The surface morphology of carbon particle was characterized by SEM and EDX. The results from EDX showed that this adsorbent is not a pure carbon. The iodine number suggests that this is a good activated charcoal. The capacity of SB charcoal to remove Fe^{3+} ion from water by adsorption technique was studied by Langmuir and Freundlich adsorption isotherm. Adsorption isotherm testing suggest the formation of multilayer and having heterogeneous surface energy. The Fe^{3+} ion adsorption capacity of SB charcoal was moderately satisfactory. The degree of elimination of Fe^{3+} ion was found to be dependent on pH, adsorbent dosage, initial metal ion concentration and milling time of adsorbent. Result shows that the optimum pH is 8 for about 74.75% Fe^{3+} ion adsorption onto the SB charcoal for 130 minutes contact time.

Keywords: Carbon particle, iron (III) ion, UV-visible spectroscopy, adsorption isotherm

Introduction
Contamination of water is a major environmental problem faced by modern society [1] that leads to ecological disequilibrium and health hazards. Water pollution possesses a great risk since water constitutes a vital necessity of all living beings [2]. Various factors such as sewage, pollution of oil, atmospheric deposition, global warming, marine dumping, industrial waste dumping, radioactive throw away eutrophication etc. are accountable for the water contamination. Groundwater is tainted by industrial waste water for various contaminants, such as- heavy metals into soil and water basins [3]. Extreme release of heavy metals into water is due to industrialization and urbanization [4]. As groundwater is a significant supply for livelihoods and food security of billions of people, contamination of iron in groundwater ia one of the major practical issues [5]. Groundwater is the main source of drinking water in Bangladesh because surface water is contaminated far and wide with human or animal pathogens [6]. In Bangladesh most of the sources of drinking water are infected by iron. A study showed that in the western part of Bangladesh the concentration of iron was very high (16.3mg/L) and regular iron utilization for a person was determined roughly 41.1mg [7]. Excessive existence of iron in ground water causes loss of body weight, scouring and the decrease of the production of milk for bovine animals [8]. Excess of iron also leads to weakening and critical problems such as poor growth, diabetes, heart failure, and siderosis and haemochromatosis illness [5]. The chance of developing of cancer is enhanced by the uptake of excess iron [9].That is why it is important to get rid of iron from its all probable sources.

Various processes are cast-off for the removal of heavy metals from waste water. For example- precipitation, co-precipitation, ion exchange, membrane filtration, etc. Adsorption techniques are found to be the most accepted techniques in elimination of heavy metals as compared to other techniques because of the simplicity, ease of handling and the removal of high efficiency [10]. The purpose of this lesson is to contribute in the investigation for cost effective adsorbents and their utilization possibilities for a variety of agricultural waste by-products. Cost is an important parameter for comparing the sorbent materials. However, cost information is hardly reported and the expenditure of individual sorbents varies depending on the degree of dealing required and local availability. If it requires slight processing, easily available, abundant in nature, a by-product or waste material from other industrial or agricultural sources, an adsorbent might termed as a cost effective or low cost adsorbent. Sometimes additional processing is required to improved sorption capacity may reduce the cost of total processing [11].

Here the adsorbent material is prepared from sugarcane bagasse (SB) as it is a waste product from sugar refining industry. It is the place where sugar has been extracted and sugarcane pulp remains as a waste product or may be sometimes used as fuel. Bagasse pitch is composed largely of cellulose, pentosane, and lignin [12]. Also it is low cost and an available in our country. Here the adsorption of Fe^{3+} ion onto the carbon particle prepared from SB, named SB charcoal, has been investigated. The adsorption capability was evaluated by batch experiments. The adsorption isotherms were also observed to ensure the nature of surface coverage.

Materials and Methods

Chemicals and equipment

$FeCl_3$ was purchased from Research Lab Fine Chem Industries, Mumbai, India. HCl was purchased from Sigma-Aldrich India. NaOH was purchased from Loba chemie Pvt. Ltd, India. Batch adsorption studies were performed with a UV-visible spectrometer (model no.: UVD-3200, Labomed, U.S.A.). pH was measured by pH meter (model no.: pH-5011, Hanna). The solutions were stirrer by mechanical shaker.

Preparation of carbon particle from sugarcane bagasse

Sugarcane bagasse (SB) was collected from the Mubarakganj sugar mill, Bangladesh. That was washed thoroughly with water to remove dust and solid particles. After that SB was dried in the sunlight for 48 hours. This treatment was done by using Pyrolysis process (Carbonization) which has been done in a closed stainless steel container which full with prepared SB to avoid presence of air. Carbonization process is carried out at High temperature for 3 hours. The heating material was the mixture of coal dust, boiled rice water and cow dung. These three materials were mixed together and dried in sunlight for 2 days. Then it was used as a fuel for carbonization process. After heating the container was allowed to cool at room temperature. Then the carbon particle formed by this process was named SB charcoal.

Experiments parameters for batch studies

Stock solution of 100ppm of Fe^{3+} ion was prepared by $FeCl_3$ salt in distilled water. Stock solution was diluted by serial dilution method with distilled water to have required concentrations. The pH of Fe^{3+} solution was adjusted by using 0.1 M HCL and 0.1 M NaOH solutions. The pH effect was determined by taking the adsorbent dose at 0.5g and the concentration of Fe^{3+} solution at 100ppm. At first the pH (2-11) solutions were prepared by using 0.1 M NaOH and 0.1 M HCl. The effect of dose of SB charcoal to iron solution was examined by keeping contact time and concentration by 45 min and 100ppm respectively. That process was done for 0.2g, 0.3g, 0.4g, 0.5g, 0.6g, 0.7g, 0.8g, 0.9g, 1.0g respectively using same parameters. To determine the effect of the concentration of the iron solution onto adsorbents, the adsorbent dose and different concentration of iron were taken at 0.5g and 50 to 120ppm with 10ppm intervals. To determine the effect of contact time of the iron solution onto adsorbents, the adsorbent dose and different concentration of iron were kept at 0.5g and 50, 100, 150, 200, 250 and 300ppm and following contact time was 10 to 160 minutes by keeping 10 minutes interval. To determine the effect of surface area of the iron solution onto SB charcoal, there the sample of different surface area of SB charcoal was prepared by hand milling for 1hour to 4hours using mortar and pastel. There the contact time and concentration were 45 min and 100ppm respectively. The solutions were shaken by mechanical shaker at 150rpm. After shaking, the solution was separated from adsorbent by using filter paper. Then for absorbance measurement by UV-visible spectrometer, the baseline was corrected by distilled water and the absorbance of fresh iron solution having specific pH was determined. Finally the separated part was put into UV-visible spectrometer and the final absorbance was determined.

In order to investigate the adsorption capacity of SB charcoal, tests were carried out in a series of 100mL conical flask containing 50mL Fe^{3+} solution. The specific amount of SB charcoal was added and shaken at room temperature using the mechanical shaker. After shaking, the solution was filtrated and the filtrate solution was collected for determining the adsorption capacity.

The removal percentage of Fe^{3+} ion was calculated by using the following equation [13].

$$\%\ Removal = \frac{(C_i - C_f) \times 100}{C_i}$$

Where, C_i and C_f are the initial and final concentrations of Fe^{3+} ion respectively in the solution?

The amount of Fe^{3+} ion adsorbed was calculated by using following equation-

$$We = \frac{(C_i - C_f) \times V}{M}$$

Where, We is the metal uptake capacity (mg/g), V is volume of iron chloride solution in flask (L) and M is the mass of dry SB charcoal (g).

In order to characterize the zero point charge of SB charcoal, solid addition method was applied. In this method 50mL of 0.1 M NaCI solutions were taken in ten bottles maintained with pH range of 2-11 and 0.5g of adsorbent was added to each bottle. These solutions were adjusted by 0.1 M HCI and 0.1 HCI/NaOH solutions. These solutions were shaken for 48 h at room temperature and the final pH of the solutions was measured [14].

For the determination of iodine no, 0.1g of dry SB charcoal and commercial activated carbon was separately taken in dried 100mL conical flasks. The samples were run in duplicates and 5mL of 5% HCl were added. The flasks were swirled until the charcoal was wetted. In each flask, 10mL of 0.1M iodine solution was and was shaken for 4 minutes. Then 10mL of filtrated was titrated against standard 0.1 M sodium thiosulphate solution using starch as indicator. The concentration of iodine adsorbed was calculated in milligrams [15]. It is equivalent to surface area of activated carbon inmg/g.

$$\text{Iodine number} = \text{C} \times \text{Conversion Factor (CF)}$$

The conversion factor can be calculated as follows:

$$CF = \frac{Mol.Wt.of\ iodine\ \times Morality\ of\ Iodine \times 10}{Wt.of\ activated\ carbon \times Blank\ reading}$$

C=Blank reading – volume of standard sodium thiosulphate consumed after the adsorption of activated carbon.

Results and Discussion

Morphological characterization of SB charcoal

In order to examine the surface morphology of SB charcoal, SEM micrographs of SB charcoal were taken and is presented in Fig 1. From the figure it is clear that the Surface of SB charcoal is characterized by irregular and porous surface. After analyzing the SEM images the average size of the adsorbent is found to be 21.37 µm. From SEM image we have seen that the surface is rough. It is not polished at all. It contains pits and grooves with uneven pores. Some agglomerations also detected which is responsible to decrease the crystallinity. As a consequence, the active adsorption edges of the particles decreased.

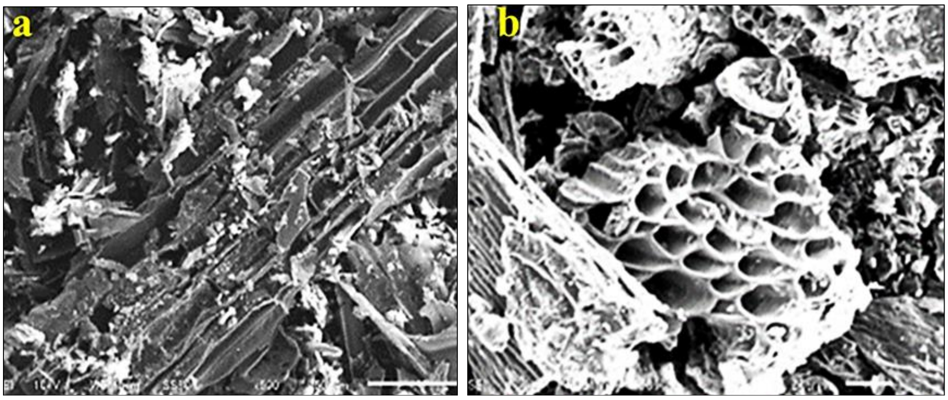

Fig 1: SEM images of SB charcoal; scalling a)10µm and b) 20µm

EDX microanalysis is a technique of elemental analysis that is based on the generation of characteristic X-rays in atoms of the specimen by the incident beam electrons. By analyzing the EDX image of SB charcoal from Fig 2, it was found that 83.62% carbon 9.64% oxygen and 6.72% sulfur is present in this adsorbent. So it contains mostly carbon in it. Due to present of oxygen and sulfur the absorption capacity is also decrease but there exist tiny percentages of oxygen and compared to the percentages of carbon which have literally no effect on the adsorption efficiency.

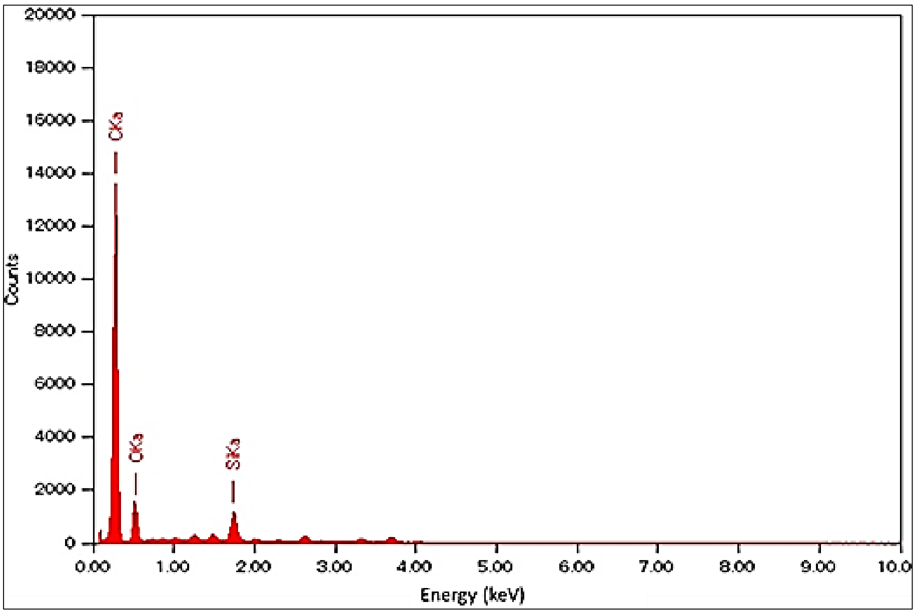

Fig 2: EDX image of SB charcoal.

Iodine number

Iodine number for the SB charcoal is 611.768mg/g. The typical range of the degree of activation ranges 500-1200mg/g [13]. So, it seems that SB charcoal has an appreciable degree of activation.

Point of zero charge

To determine the surface charge zero point charge of SB charcoal was done. The point of zero charge (pH_{zpc}) is the pH value of the solution, where the surface charge density is equal to zero, i.e. the number of positively charged centers is equal to the number of negatively charged centers. If pH <pH_{zpc} the adsorbent surface area is positively charged and if pH >pH_{ZPC}, the adsorbent surface area is negatively charged [16]. A graph (Fig 3) is plotted between ΔpH and pH_i, and the point at which they intersect each other and subsequently that point is recorded as pH_{zpc} of the surface of SB charcoal. The pH_{zpc} value of SB charcoal was found to be 7.3 which matched with the reported value of literature [16].

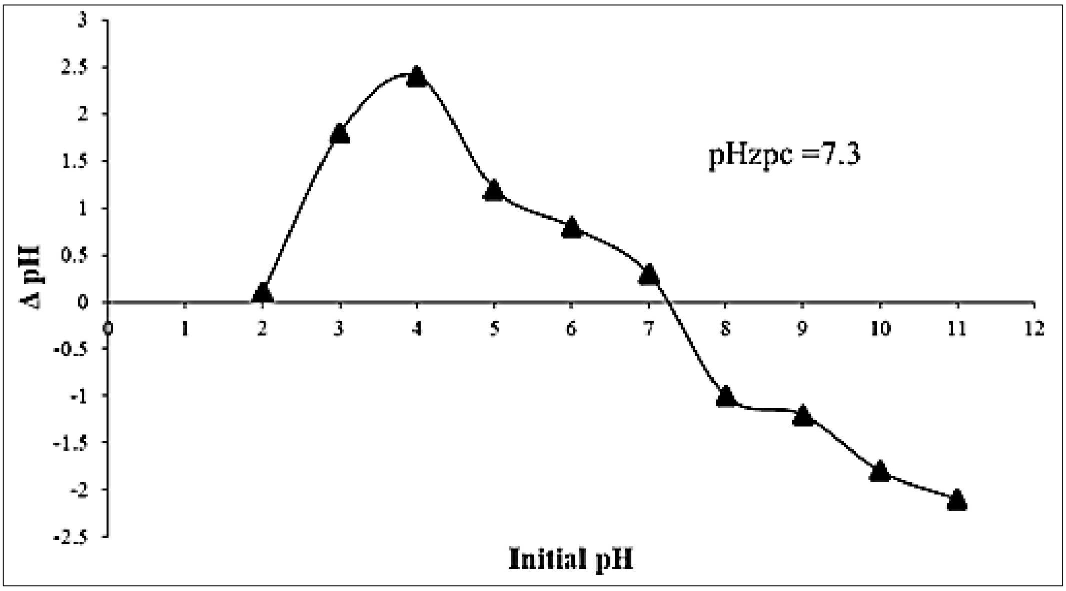

Fig 3: Determination of the zero point charge (pH_{ZPC}) of SB charcoal

Effect of pH

The percentage of removal of Fe^{3+} ion from solution depends on pH is shown in Fig 4. The percentage of removal was increased from 30.34 to 74.75% with the increase of pH from 2 to 11. The maximum removal was observed at pH 8. The removal efficiency was 74.75% at pH 8. This is due to the fact that at that point the Fe^{3+} ion started to precipitate [17].

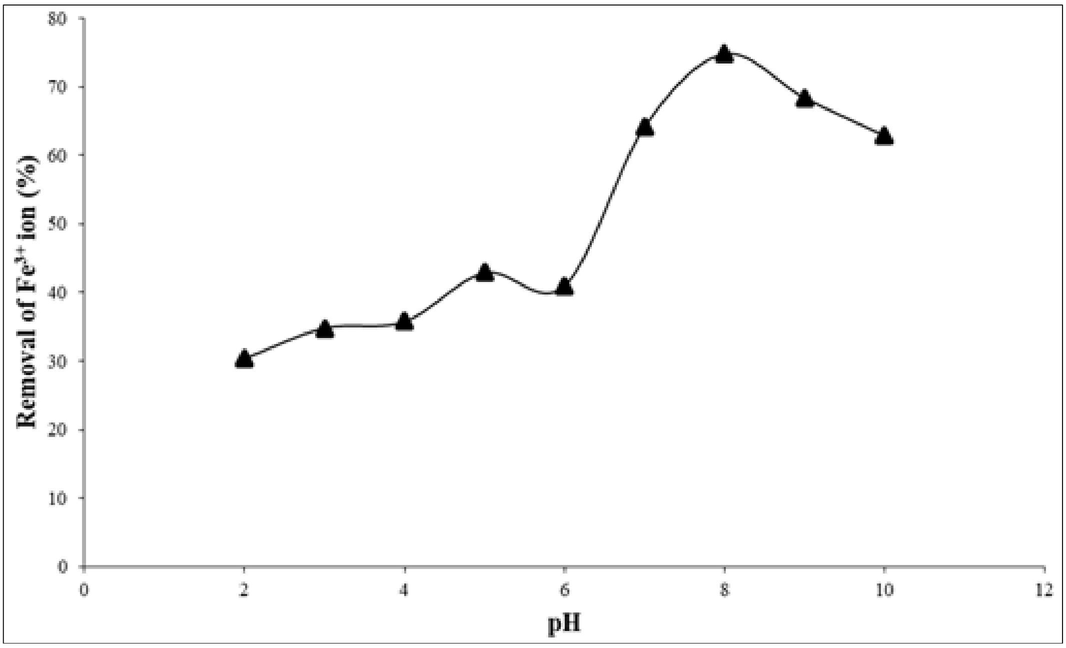

Fig 4: Effect of pH for removal of Fe^{3+} ion by using SB charcoal

The zero point charge for SB charcoal is found to be 7.3The optimum values for initial pH is found to be at 8. So the pH (8)>pH_{zpc} (7.3). Thus it is proven that surface of the SB charcoal is negatively charged.

Effect of dosage

With the increasing of adsorbent amount, the adsorbing surface area increases thereby the accessibility of additional binding sites of the adsorbent increases [18]. Fig 5 shows that the percentage of removal increases from 30.66% to 87.28% with the increase of dosage from 0.1g to 1.0g. The adsorption capacity of SB charcoal shows in Fig 5. Which indicates that the optimum adsorbent dosage of SB charcoal is 0.9g.

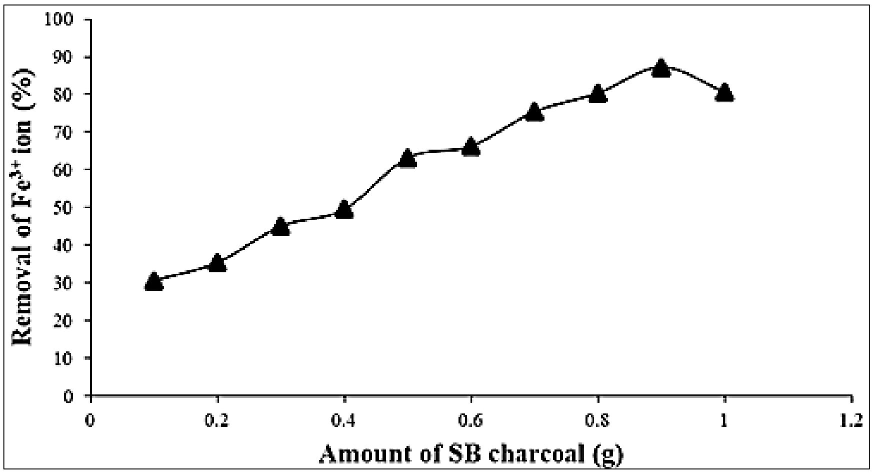

Fig 5: Effect of dosage for removal of Fe^{3+} ion by using SB charcoal.

Effect of Concentration

In adsorption process the increase in adsorption is due to the fact that the resistance to mass transfer between adsorbate and adsorbent is stunned by concentration gradient which perform like a driving force. The adsorption capacity of metal ion onto adsorbents as a function of initial concentration of metal ion is determined in order to achieve an effective adsorption. The removal percentage of Fe^{3+} ion at various concentration staring from 50 to 120ppm under specific condition (pH 8, 45 min, 0.5g of SB charcoal, room temperature) is shown in Fig 6. The highest percentage of removal 78% at 90ppm.

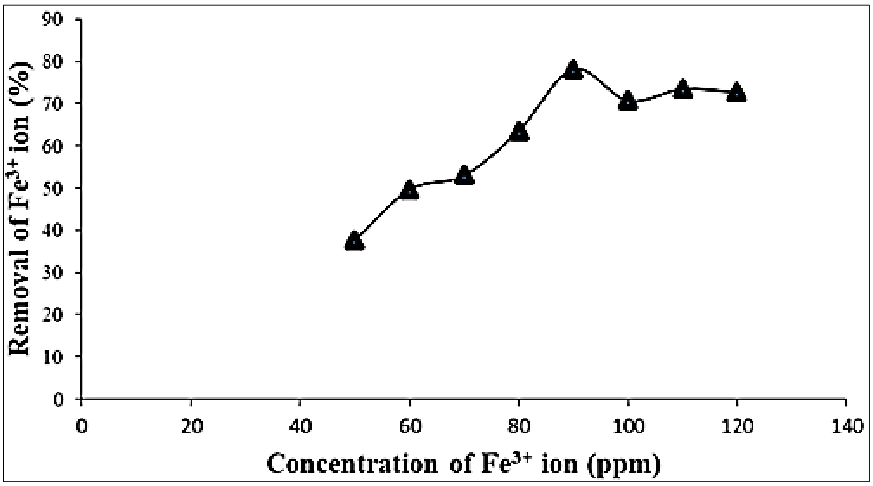

Fig 6: Effect of concentration for removal of Fe^{3+} ion by using SB charcoal

Effect of milling time

Due to the increase of surface area the percentage of removal of metal ion is increased because of accessibility of addition active binding site on the surface of the adsorbent is increased [18]. From the Fig 7 we can see that the removal percentage of Fe^{3+}ion by SB charcoal is increased from 61% to 85.33%with the increase of surface area.

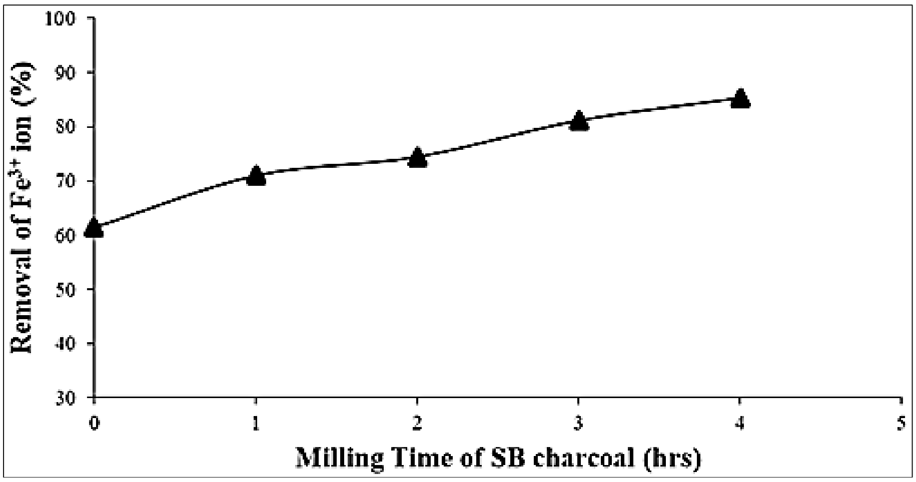

Fig 7: Effect of milling time for the removal of Fe^{3+} ion by using SB charcoal

Langmuir adsorption isotherm
Langmuir isotherm expresses the maximum adsorption occurs to a saturated monolayer surface with a finite no. of identical sites and the adsorption energy is constant. There is no transmigration of adsorbate in the plane of surface [19]. The linearized form of Langmuir equation is defined by following-

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m}$$

Where, Q_m and b is Langmuir constants interrelated to the adsorption capacity and adsorption energy; C_e is the equilibrium concentration of Fe^{3+} ion inmg/L and Q_e is the amount of Fe^{3+} ion adsorbed per unit weight of adsorbent (mg/g).
The plots of C_e/Q_e against C_e are represented in Fig 8. The evaluated parameters such as Langmuir isotherm constants and their correlation coefficients R^2 are given in Table 1. The values of R^2 confirms that the adsorption of Fe^{3+} ion onto SB charcoal is moderately favourable for Langmuir model.

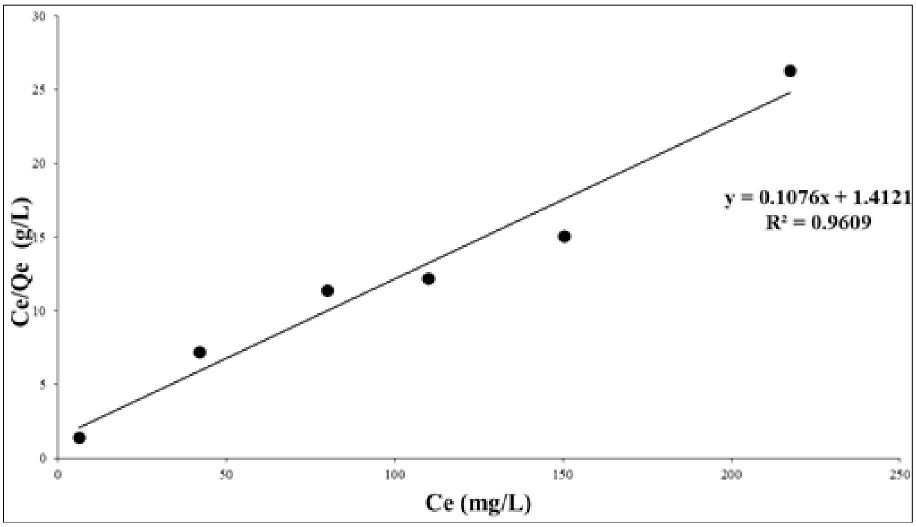

Fig 8: Langmuir plot for adsorption of Fe^{3+} ion onto SB charcoal

Table 1: Langmuir constants for the adsorption of Fe^{3+} ion onto adsorbent

Metal ion	Adsorbent	b	Q_m	R^2
Fe^{3+}	SB charcoal	0.076	9.2936	0.9609

Freundlich adsorption isotherm
This isotherm is used to explain adsorption on surface having heterogeneity and the exponential distribution of active sites and their energies. The linearized form of Freundlich isotherm is described by following equation-

$$\log Q_e = \log \mathrm{K} + \frac{1}{\mathrm{n}} \log C_e$$

Where, C_e represents the equilibrium concentration inmg/L and Q_e is the amount of metal adsorbed per unit weight of adsorbent (mg/g). 'K' is the parameter related to binding energy and 'n' is a measure of a deviation for the adsorption system under investigation. For good, difficult and poor adsorption, the value of 'n' is 2<n<10, 1<n<2 and n<1 respectively [20]. A plot of Log Q_e against Log C_e are shown in Fig 9. The points are not aligned on a straight line and the value of 'n' is 4.5, represents good adsorption [20]. The evaluated Freundlich constants and the value of correlation coefficient R^2 are represented in Table 2.

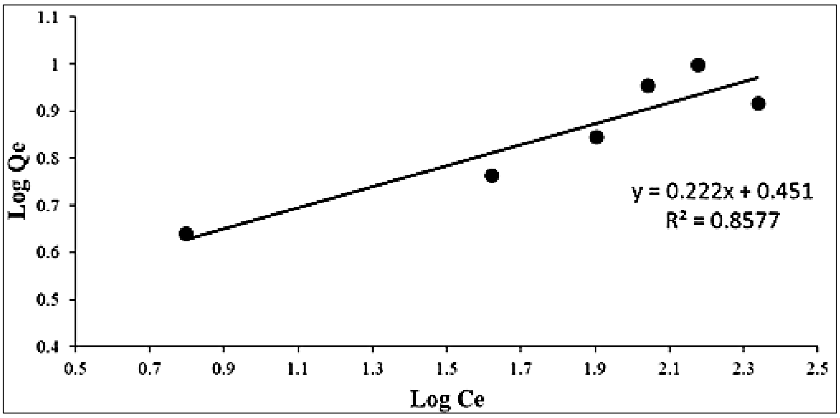

Fig 9: Freundlich plot for the adsorption of Fe^{3+} ion onto SB charcoal

Table 2: Freundlich constants for the adsorption of iron onto SB charcoal

Metal ion	Adsorbent	k	n	R^2
Fe^{3+}	SB charcoal	2.824	4.5	0.8577

Conclusion
This study showed that adsorbent prepared from sugarcane bagasse is effective adsorbent can be used to remove iron (III) from aqueous system. Different parameters governing the removal efficiency were investigated. From this experiment it

was seen that the surface of SB charcoal is negatively charged. Iodine value suggested that SB charcoal is a good activated carbon. For the SB charcoal, the optimum values of initial pH, adsorbent dose, Fe^{3+} concentration and contact time are pH 8, 0.9g, 90ppm and 130 min respectively. Batch adsorption experiment show that Fe (III) ion adsorption properties are great depends on pH, doges of adsorbents, surface area of adsorbent and initial metal ion concentration. The adsorption of Fe (III) on SB charcoal moderately satisfied Freundlich and Langmuir isotherm. Isotherms suggested that the energy on different location of the adsorbent surface is not homogeneous and there multilayer exist before the formation or uniform monolayer. SB charcoal is low cost, easily available and it can be used for commercial purposes.

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