

1. Introduction

1.1 General Introduction of Adsorption

The phenomenon of concentration of a substance on the surface of a solid liquid is called adsorption^[4]. The material on the surface of which adsorption takes place is known as adsorbent and the substance undergoing adsorption is called adsorbate. Adsorption occurs by the effect of residual force operating at the surface of adsorbent due to unsatisfied valence or bond deficiency.^[1]

Adsorption study can be carried out by two methods:

I) Column method II) Batch method

I) Column method

In this method, adsorbent is filled in a glass column of fixed length and diameter. The sample solution of adjusted pH and a particular concentration is percolated into the column at a controlled flow rate. The metal concentration before and after adsorption is detected by AAS.^[9,44]

II) Batch adsorption method

In batch method, a fixed mass of adsorbent is added to a stoppered bottle containing a fixed volume of sample solution at a fixed pH. The stoppered bottle is shaken in a mechanical shaker till equilibrium. The metal concentration before and after adsorption is measured by spectrophotometer or AAS.^[9,44]

1.2 Definition of Heavy Metal

A heavy metal is a member of an ill-defined subset of elements that exhibit a metallic properties which would mainly include the transition metals, some metalloids, lanthanides and actinides. Many different definitions have been proposed. Some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. ^[45]

The term heavy metal has been called “meaningless and misleading” in an IUPAC technical report due to the contradictory definitions and its lack of a “coherent scientific basis”. ^[45]

Heavy metals refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. e.g. mercury, cadmium, arsenic, chromium, lead etc. ^[45]

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Cadmium, iron, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries etc. ^[38]

Among different heavy metals, iron is one of the major constituent of the lithosphere and comprises approximately 5% of it. It is routinely detected in municipal waste effluent, particularly in cities where iron and steel are manufactured. Iron is commonly found in rocks and soil. Under proper conditions, iron will leach into the water resources from rock and soil formations. ^[13] Iron readily complexes with sulphates in the sediments of

many surface waters. The primary concern about the presence of iron in drinking water is its objectionable taste.^[13]

1.3 Guideline value and harmful effects of iron

The US Environmental Protection Agency (USEPA) has established a secondary drinking water regulation of 0.3 mg/L for iron. Exceeding iron concentration greater than 0.3 mg/L causes water staining that adversely affect plumbing fixtures, dishware and clothes and produce a yellow to reddish appearance in water. These levels may also impart taste and odor to the drinking water.^[31]

Higher values of the iron content are responsible for effects as the growth of the iron bacteria. The decay of such organisms has as consequence bad taste and odor. The most popular bacteria are *Crenothrix*, *Leptothrix*, *Sphaerotilus* and *Gallionella* that transform in their own metabolism the ferrous iron into the ferric one.^[6]

Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge.^[38]

For example, there are many problems that result from iron toxicity. These include anorexia, oliguria, diarrhea, hypothermia, diphasic shock and metabolic acidosis and even death. In addition to these, patients may experience vascular congestion of the gastrointestinal tract, liver, kidneys, heart, brain, spleen, adrenals and thymus. With acute iron poisoning, much damage to the gastrointestinal tract and liver, may result from the high localized iron concentration and free radical production leading to liver toxicity via lipid peroxidation and destruction of the hepatic¹³ mitochondria.^[13] There are several total iron storage diseases such as

cirrhosis, hepatoma (primary liver cancer), siderosis, myocardial disease and impotence.^[13]

1.4 Low cost adsorbents and importance of biosorption

Research interest into the production of cheaper adsorbents to replace costly water treatment methods such as chemical precipitation, ion exchange, electro-floatation, membrane separation, reverse osmosis, electro-dialysis, solvent extraction are attracting attention of scientists.^[38]

As classical methods apart from being expensive have demerits like incomplete metal removal high capital and operational cost, high reagent energy requirements and generation of toxic metal sludge and their disposal.^[44] On the other hand ion exchange, reverse osmosis and adsorption are more attractive processes because the metals can be recovered along with their removal from the effluents. Reverse osmosis and ion exchange do not seem to be economically feasible because of their relatively high investment and operational cost. Adsorption has advantages over the other methods because of simple design with a sludge free environment and involve low investment in terms of both initial cost and land requirement.^[36]

To date, the majority of heavy metals in wastewater are removed by means of precipitation by adding calcium hydroxide in which large amounts of non toxic metal compounds such as calcium sulphate are also precipitated together with heavy metals as a precipitated sludge, which are dumped in the landfill sites.^[17] It is not only difficult to meet stringent environmental regulation by means of precipitation technique but also there is unavailability of landfill sites due to the occupation by large amounts of polluted sludge within a few years. On the other hand, many heavy metals contained in these wastes are valuable and

indispensable resources. Therefore, for a sustainable society in future, it is necessary to recover metal resources from various wastes instead of discarding in the landfill sites.^[17]

Adsorption is one of the physico-chemical treatment process found to be effective in removing heavy metals from aqueous solutions. An adsorbent can be considered as cheap or low cost if it is abundant in nature, requires little processing and is a by product of waste material from industry. Plant wastes are inexpensive as they have no or very low economic value. Most of the adsorption studies have been focused on untreated plant wastes. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration.^[38] However, the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic compound (TOC) due to release of soluble organic compounds contained in the plant materials. The increase of COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals.^[38]

The adsorption efficiency of the agricultural wastes can be enhanced by various methods such as thermal activation, steam activation, chemical modification chemical activation and so on.^[44]

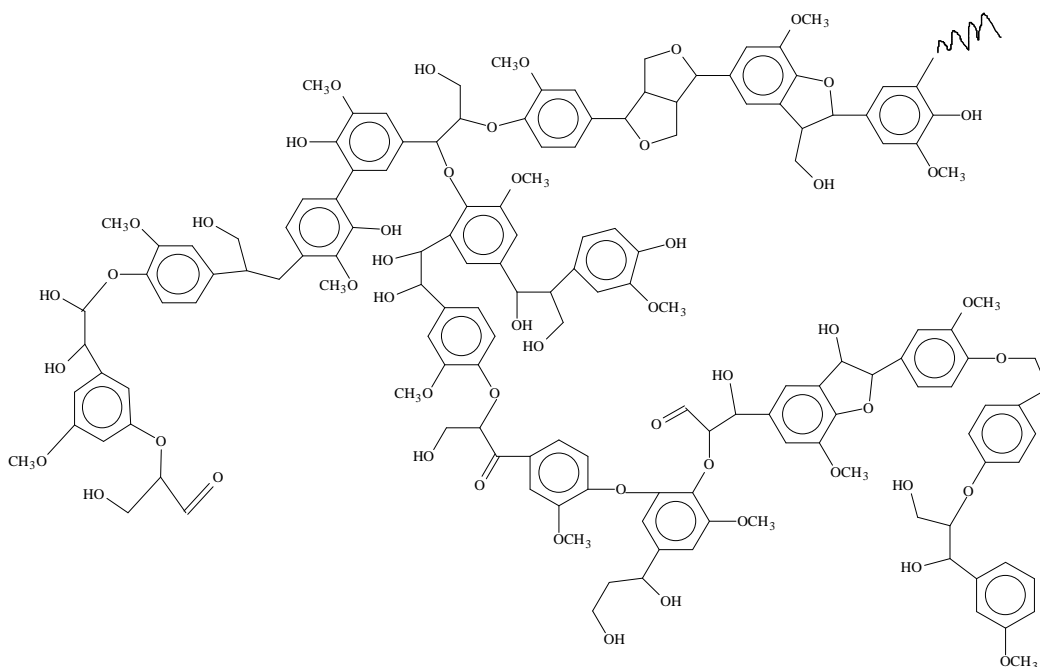
Recently, low cost adsorbent materials from forestry, fishery and agriculture have attracted much attention to several workers. Some of the reported sorbents include peanut hulls, maize bran, saw dust, sugar beet

pulp, crab shells, corn starch, exhausted coffee, rice husk, chitin, orange waste and biological methods include bacteria, fungi, yeast and micro algae just to mention a few in literature. Those biomaterials have been recognized as the potential alternative to conventional technologies for the removal of heavy metals from the wastewater. Thus, it is possible to effectively recover valuable metals and remove toxic metals from the wastewater by using low cost biomass wastes as such and, consequently, it would be a good solution for the difficult problems as mentioned above.^[17]

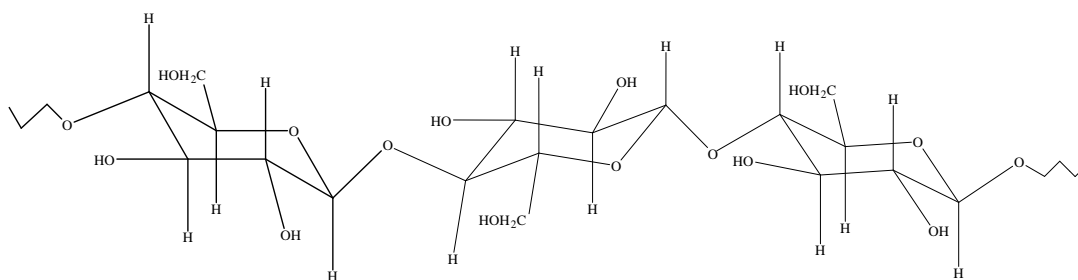
Sugarcane bagasse which is the waste product from sugar refining industry, juice ship etc. It consists of cellulose (50%), polyoses (27%) and lignin (23%). The presence of these three biological polymers makes sugarcane bagasse rich in hydroxyl and phenolic groups and these groups can be modified chemically to produce adsorbent materials with new properties.^[38]

1.5 Structure of Lignin and Cellulose

Lignin is an amorphous multifunctional phenolic network containing hydroxyl, ether and carbonyl groups. [12]



Structure of lignin



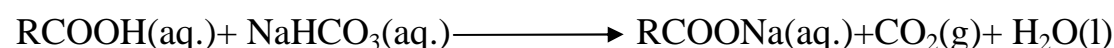
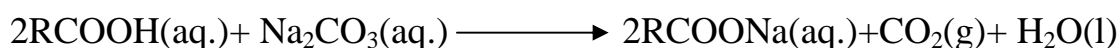
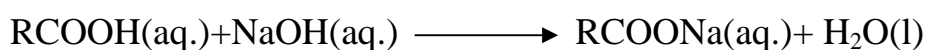
Structure of cellulose

Cellulose is made up of chains of D-glucose units, each unit joined by a glycoside linkage to C-4 of the next. X-ray analysis and electron microscopy indicate that these long chains lie side by side in bundles, undoubtedly held together by hydrogen bonds between the numerous

neighboring -OH groups. These bundle are twisted together to form rope like structure which themselves are grouped to form the fibers we can see. In wood, these cellulose ropes are embedded in lignin to give a structures that has been likened to reinforced concrete. ^[3]

1.6 Determination of surface functional groups: Boehm's titration

The Boehm's titration is a typical chemical analysis that can be used to quantify the amount of surface acidity as well as basicity of the activated charcoal. The method involves neutralization with bases such as sodium hydroxide(NaOH), sodium bicarbonate(NaHCO₃) and sodium carbonate(Na₂CO₃) for acidic groups and neutralization with acids such as hydrochloric acid(HCl) for the basic functional groups. The acidity constants of acidic groups like carboxylic, lactones, and phenols differ over several orders of magnitude and it is possible to distinguish the acidic groups on the basis of their neutralization behavior. The various free acidic groups are measured using the assumption made by Boehm that NaHCO₃(pKa =6.37) neutralizes carboxylic group only, Na₂CO₃(pKa =10.25) neutralizes carboxylic group including lactone group and NaOH(pKa =15.74) neutralizes carboxylic, lactones, as well as phenol group. The neutralization reaction in aqueous solution in the Boehm titration is given as :



where R is generalized representation for the surface bound carbon atom.

Therefore,

- i. NaHCO_3 neutralizes carboxylic group only
- ii. Na_2CO_3 neutralizes carboxylic group and lactone group
- iii. NaOH neutralizes carboxylic, lactones, as well as phenol group
- iv. If A, B, and C referred to the number of equivalents of NaHCO_3 , Na_2CO_3 , NaOH respectively neutralized by charcoal then,
number of equivalents of carboxyl group = A
number of equivalents of lactone group = B
number of equivalents of phenol group = C

These calculations may be illustrated by the help of the following figure:-

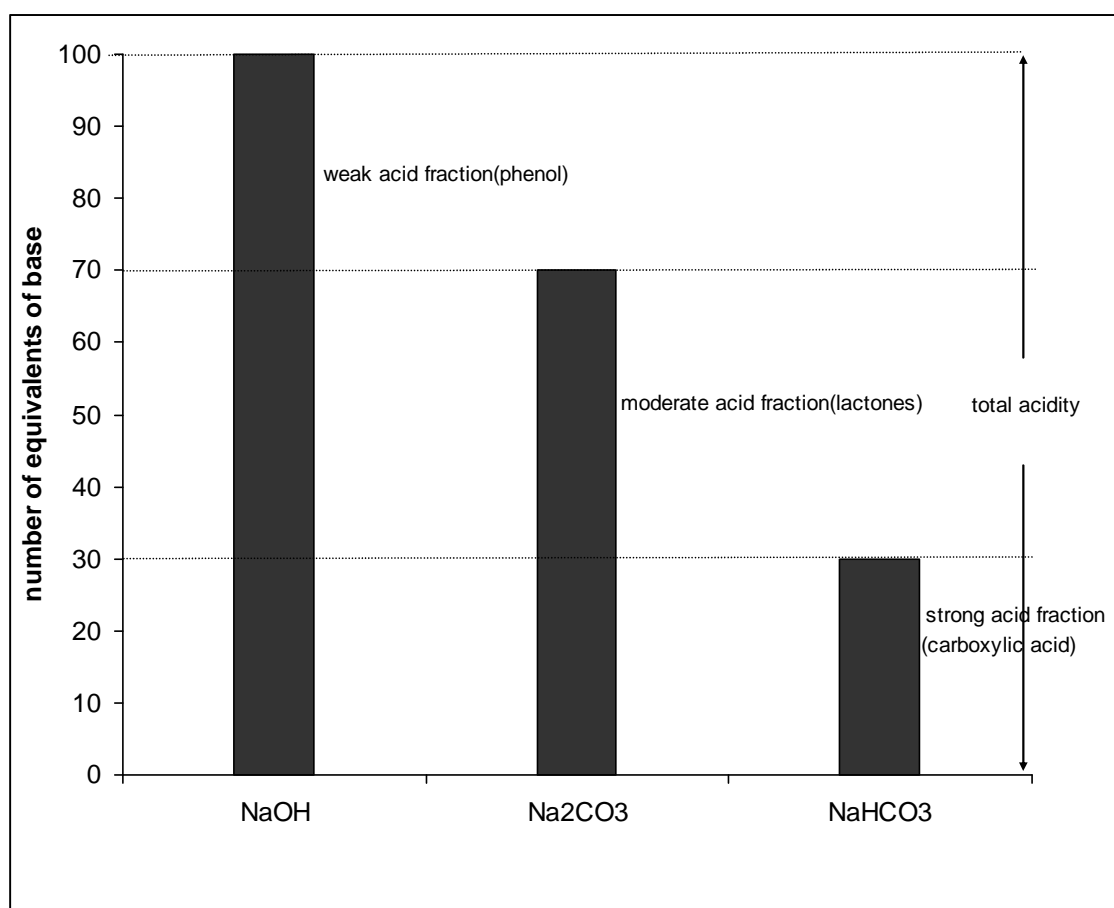


Illustration of the calculation based on Boehm titration

1.7 Adsorption Isotherm

The equilibrium between an adsorbate immobilized on the active sites of an adsorbent and the adsorbate remaining in aqueous phase is usually presented by adsorption isotherms. ^[10]

The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinities of the sorbent. ^[10]

In order to describe the adsorption characteristics of low-cost sorbents used in water and wastewater treatment, experimental equilibrium data are most frequently modeled by the relationships developed by Freundlich and Langmuir ^[10]

1.7.1 Freundlich Adsorption isotherm

The Freundlich isotherm is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for non ideal sorption that involves heterogeneous sorption and is expressed by the following equation. ^[39]

$$q_e = k_F C_e^{1/n}$$

the linearised form of which can be written as,

$$\log q_e = \log k_F + 1/n \log C_e$$

where C_e is the equilibrium concentration in mg/L, q_e is the amount adsorbed at the equilibrium time (mg g^{-1}), k_F and n are the Freundlich equilibrium constant and exponent respectively.

k_F is an indicator of adsorption capacity and n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity. [10]

The values of $1/n$ varies between 0.1 and 1.0 indicate the favorable adsorption of heavy metals. [37]

1.7.2 Langmuir Adsorption Isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. [35]

The Langmuir isotherm is given by the following equation

$$q_e = q_m k_L C_e / (1 + k_L C_e)$$

The linearization of which leads to the following form

$$C_e/q_e = 1/bq_m + 1/q_m C_e$$

where, q_m is maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface (mg g^{-1}) where b is a constant related to affinity of binding sites with the metal ions (1 mg^{-1}).

The plots of C_e/q_e Vs C_e should be straight line, slope of which will be equal to $1/q_m$ and intercept will be $1/bq_m$. From the linear plot q_m and b can be calculated.

The more favorable sorbent is indicated by the higher value of the slope of an adsorption isotherm. It means that potentially a "good" sorbent can be comparatively evaluated from values of q_m and b . [7]

1.8 Adsorption Kinetics

The adsorption kinetics is studied with an aim of obtaining a deeper insight into how the amount of adsorbed metal changes with time and about the process time required to achieve equilibrium between the aqueous and solid phase. ^[10]

Adsorption Kinetics deals with the study of the rate and mechanism of the adsorption phenomenon. It is well recognized that the characteristics of sorbent surface is a critical factor that affects the sorption rate parameter and that diffusion resistance plays an important role in the overall transport of the solute. ^[42]

Kinetics of heavy metals adsorption was modeled by the first order, Lagergren equation, the pseudo-second order equation and the second order rate equation. ^[24]

1.8.1 The Pseudo First-order model

The first order kinetic model is applicable for reversible reaction with an equilibrium being established between liquid and solid phases. ^[42]

A simple kinetic analysis of adsorption is the pseudo-first order equation in the form ^[42]

$$dq_t/dt = k_1 (q_e - q_t) \dots (i)$$

where, k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption, q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium and

q_t (mg g^{-1}) is the amount of metal ion on the surface of the adsorbent at any time t (min).

On integrating and applying boundary condition $q_t = 0$ at $t=0$ equation (i) becomes

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

or, $\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \dots (ii)$

from the plot of $\log (q_e - q_t)$ against time t of equation (ii) value of k_1 and q_e can be determined with the help of slope and intercept respectively. ^[42]

1.8.2 The Pseudo-second order model

Most of the sorption systems followed a pseudo-second order kinetic model as reported by Ho and Mc Kay. It is based on the sorption capacity on the solid phase. The pseudo second order reaction rate equation used to study the kinetics of adsorption of heavy metal is expressed as the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites; ^[42]

The pseudo-second order kinetic rate equation is

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \dots (iii)$$

where, k_2 is the rate constant for pseudo second-order adsorption ($g \text{ mg}^{-1} \cdot \text{min}^{-1}$), q_t and q_e are the amount of metals adsorbed ($mg \text{ g}^{-1}$) at any time t and at equilibrium time, respectively.

Integrating the equation (iii); under boundary condition, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives rearranged linear form as,

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (iv)$$

If the initial adsorption rate is q_0 ($g \text{ mg}^{-1} \cdot \text{min}^{-1}$), then $q_0 = k_2 q_e^2$.

The equation (iv); can be written as,

$$t/q_t = 1/q_e + 1/q_e k_2 t \quad (v)$$

From the linear plot of t/q_t against t , q_e and k_2 can be determined experimentally with the help of slope and intercepts of plot, respectively. [42]

1.8.3 The second-order model

The second-order reaction rate equation is generally expressed as, [42]

$$dq/dt = k'_2(q_e - q_t)^2 \quad (vii)$$

where, k'_2 is the second-order rate constant for adsorption ($\text{g mg}^{-1} \cdot \text{min}^{-1}$)

Integrating the equation (vii); under boundary condition, as $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the linear form of equation (vii); becomes,

$$1/q_e - q_t = 1/q_e - k'_2 t \quad (viii)$$

The plot of $1/q_e - q_t$ against t gives linear plot, from which k'_2 and q_e can be evaluated from the slope and intercepts, respectively. [42]

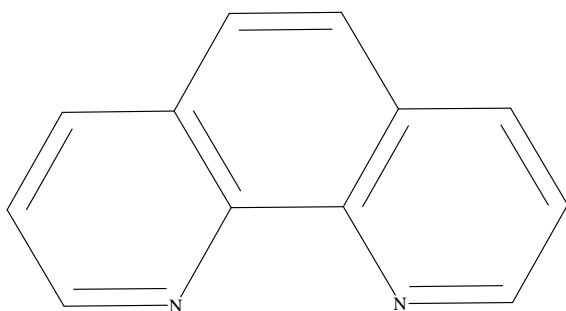
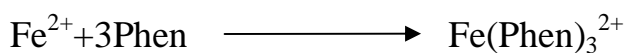
The validity of the kinetic models can be investigated by studying the kinetics at different time interval with different initial metal concentration. The equilibrium uptake of metal should nearly equal to the experimental equilibrium. If it couldn't do so, then the reaction is not likely to be following that model, even if that particular model gives high correlation coefficient with the experimental data. [42]

Opposing to other well established model, pseudo second-order model predicts the behavior over the whole range of studies and it is in agreement with a chemisorptions mechanism being the rate controlling step with the formation of monolayer coverage on the adsorbent surface. [42]

1.9 Spectrophotometric Determination of Fe(II)

Sensitivity and detection limit for the atomic absorption spectroscopy (AAS) methods, the inductively coupled plasma method, and the phenanthroline colorimetric procedure are similar and generally adequate for analysis of natural land treated waters. ^[5]

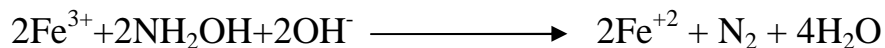
A commonly used method for the determination of trace amounts of iron involves the complexation of Fe^{2+} with 1,10-phenanthroline to produce an intensely red-orange colored complex. ^[5]



1,10-phenanthroline (Phen)

The molar extinction coefficient of the complex $[(\text{C}_{12}\text{H}_8\text{N}_2)_3 \text{Fe}]^{2+}$, is 11,100 at 508 nm. The intensity of the color is independent of pH in the range of 3 to 9. The complex is very stable and the color intensity does not change appreciably over long periods of time. Color standards are stable for at least 6 months. ^[5]

The iron must be in the ferrous state, and hence a reducing agent is added before the color is developed. Hydroxylamine, as its hydrochloride, can be used to reduce any ferric ion that is present.



The pH is adjusted at 4.5 by using the acetate buffer. ^[5]

1.10 Interference

Among the interfering substances are strong oxidizing agents, cyanide, nitrite, phosphate, chromium, zinc in concentration exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/L and nickel in excess of 2 mg/L. Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline. ^[5] The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanides and nitrite that otherwise would interfere. Adding excess hydroxylamine eliminates error caused by excessive concentrations of strong oxidizing reagents. In the presence of interfering metal ions, a larger excess of phenanthroline should be used to replace that complexed by the interfering metals. ^[5]

2. Literature Review

On searching the history of adsorption process, literatures reveals that using the adsorption process for the removal of heavy metals from wastewater has a short history compared to other water purification processes. Adsorption was first observed by Lowitz in 1885 and was soon applied as a process for removal of color from sugar during refining.^[7] In the later half of the nineteenth century, American water treatment plants used inactivated charcoal filters for water purification.^[7] In 1929 the first granular activated carbon (GAC) units for treatment of water supplies were constructed in Hamm, Germany and in 1930 at Bay city, Michigan.^[7] Currently, adsorption on activated carbon is a recognized method for the removal of heavy metals from wastewater while the high cost of activated carbon limits its use in adsorption.^[7]

Many researchers have used different chemicals for the pretreatment of the biological wastes; some of the relevant literatures are:

K.N. Ghimire et al. (2002) ^[20] prepared a novel adsorbent by simple chemical modification of orange juice residue (OJR) with the substitution of phosphate groups on the alcoholic analogue of cellulose. Phosphorylated gel was further loaded with iron(III). The loading capacity for iron(III) on the gel was as high as 3.7 mol/kg. maximum adsorption capacity for As(V) and As(III) was as 0.94 and 0.91 mol / kg at their optimum pH values 3.1 and 10.0 respectively.

K.N. Ghimire et al. (2003) ^[16] modified orange juice residue and prepared two types of adsorbent

- a) Phosphorylated orange juice residue (POJR)
- b) Saponificated orange juice residue (SOJR)

SOJR was found to be highly effective for lowering of arsenic concentration below the maximum acceptable level over a wide pH. ^[16]

Similarly, lanthanum(III) and cerium(IV) loaded POJR shown better fluoride removal behavior as compared to the commercially used adsorbent such as activated alumina. ^[16]

The loading capacities of fluoride on cerium(IV) and lanthanum(II) loaded, gel was determined to be 1.7 and 1.8 mol kg⁻¹, respectively. ^[16]

Wong et al., (2003) ^[38] used tartaric acid for the modification of rice husk. This modified rice husk removed Pb(II) from waste water very efficiently.

D. Parajuli et al. (2005) ^[12] prepared crosslinked lignocatechol gel by immobilizing catechol onto wood lignin followed by cross linking. In this method the extractives contained in the wood powder of Japanese Cedar trees was removed with a mixture of ethanol and benzene. From the extractive free wood powder lignocatechol was prepared according to the phase separation method of Funaoka et al. The adsorbent was efficient for the removal of Pb(II) and Zn(II).

Ganji et al (2005) ^[38] modified *Azolla filiculoides* with hydrogen peroxide- magnesium chloride mixture. It was used to remove Pb(II) with appreciable q_{\max} value of 228 mg g⁻¹.

Noeline et al. (2005) ^[38] modified Banana stem with formaldehyde solution. The adsorbent removed Pb(II) from wastewater and its q_{\max} value was 91.74.

Junior et al. (2006) ^[38] modified sugarcane bagasse with different modifying agents and removed three metals Cu(II), Pb(II) and Cd(II) very effectively.

<u>Modifying agent</u>	<u>Heavy metal</u>	<u>q_{max} (mg g⁻¹)</u>
NaHCO ₃	Ca(II)	114
	Pb(II)	196
	Cd(II)	189
Ethylenediamine	Cu(II)	139
	Pb(II)	164
	Cd(II)	189
Triethylene tetramine	Cu(II)	133
	Pb(II)	313
	Cd(II)	313

N. Sankaramakrishnan et al. (2006) ^[25] modified chitosan flakes with 4% w/w acetic acid, 2 M NaOH solution to make beads. Those chitosan beads and flakes were crosslinked with glutaraldehyde and the crosslinked product was xanthated with 14% NaOH and carbon disulphide such crosslinked xanthated chitosan flake had maximum adsorption capacities of 625 mg g⁻¹ for Cr(VI) white beads had q_{max} equal to 256.4 mg g⁻¹.

Ozer and Pirincci (2006) ^[38] used sulphuric acid as modifying agent for wheat bran that removed Cd(II) from waste water, its q_{max} value was 101 mg g⁻¹.

K.N. Ghimire et al. (2007) ^[9] prepared La(III), Ce(III) and Fe(III) - loaded orange waste and used it for the adsorption of phosphate from aquatic environment, Maximum phosphate uptake at equilibrium was 13.94 mg g⁻¹. It is noted that significant amounts of phosphate was

adsorbed by small amount of the modified adsorbent as compared to other adsorbents.

K.N. Ghimire et al. (2007)^[17] prepared an efficient and cost effective non conventional adsorbent from seaweed *Laminaria japonica* by crosslinking with epichlorohydrin. The maximum adsorption capacity for Pb(II), Cd(II), Fe(III) was found to be 1.35, 1.1, 1.53 mol kg⁻¹, respectively while 0.87 mol kg⁻¹ for both La(III) and Ce(III).

On searching literature, it was realized that adsorptive work on iron removal is quite few. It may be due to two reasons

- (1) Excessive precipitation of iron above pH value 2.5 and challenges put forward by this problem.
- 2) Ease of removal of iron by precipitation.

Though at very low concentration of iron one must apply adsorption method for iron removal and this method should not be over looked. Some of the available literatures on iron removal are:

Hideko Koshima (1985)^[14] in his short letter to editor has reported that “iron(III) has to be collected or adsorbed to some extent by activated charcoal, however, adsorption from hydrochloric acid medium has been overlooked. Present note will show that iron(III) is adsorbed by activated carbon from 6-10 mol dm⁻³ hydrochloric acid solution. Author has reported that removal upto 99% was observed from 10 M HCl solution after contact time of 19 hr”.

A Duta et al. (2002)^[6] studied the adsorptive removal of iron from natural sparkling water and salty water ($C_{\text{NaCl}} = 3.4\%$) by different adsorbents such as river sand, sea sand, asbestos, kieselgel and different synthetic

cation exchangers. The best results were obtained using cation exchangers both in mono-cationic solutions and in salty waters containing low concentration of iron. It can be concluded that a fair water treatment using cation exchanger with $-\text{COONa}$ or $-\text{SO}_3 \text{Na}$ groups can solve the problem even if the metal is in traces. Sand may also be used after pretreatment.

Orawan Sirichote et al. (2002) ^[28] studied adsorption of iron(III) on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell. The activated carbons were prepared by carbonization of these raw materials and followed by activation with ZnCl_2 . The maximum amounts of iron(III) adsorbed per gram of these activated carbons were 0.66 mmol/g, 0.41 mmol /g and 0.18 mmol/g respectively.

Z Umriye Aksu (2002) ^[40] studied the simultaneous biosorption of iron(III) and iron (III) cyanide complex anions to *Rhizopus arrhizus* from binary mixtures compared with single metal and metal cyanide ion situation in a batch stirred system. Authors conclude that there is a synergistic interaction between these ions; the mono-component adsorption equilibrium data fitted very well to the mono-component Langmuir and Redlich-Peterson models for both the components at moderate ranges of concentration. A modified synergistic Langmuir model was proposed for dual-component system and model parameters were also estimated by the non-linear regression. The pseudo second order kinetic model was applied to single and multi-component experimental data assuming that the external mass transfer limitations in the system can be neglected and biosorption is sorption controlled.

A. Selatnia (2004) ^[8] studied the iron biosorption capacity of a *Streptomyces rimosus* biomass treated with NaOH by batch method. After

pretreatment of biomass at the ambient temperature, optimum conditions of biosorption was found to be particle size 50-160 μm , contact time 4 h, a biomass concentration of 3 g/l and a stirring speed of 250 rpm. Under these optional condition, 122 mg Fe/g_{biomass} were fixed.

G. Karthikeyan (2005) ^[13] studied the adsorption of iron(III) on chitin. The influence of particle size, dosage of the adsorbent, contact time, initial concentration of adsorbate, temperature, effect of anions like chloride, nitrate and sulphate and also of cations like zinc, chromium and copper was studied. In addition, time dependence of fraction of adsorption at varying particle sizes and doses of chitin and the intrapartide diffusion rate constants, k_p of the adsorption process, thermodynamic and equilibrium parameters of the reaction were also determined.

Mustafa Tuzen et al. (2007) ^[23] studied the biosorption of copper(II), lead(II), Iron(III) and cobalt(II) on *Bacillus sphaericus* loaded Diaion SP-850 resin for preconcentration-separation. The sorbed analytes on biosorbent were eluted by using 1 mol L⁻¹ HCl and analytes were determined by flame atomic absorption spectrometry. They studied the influences of analytical parameters including pH, amount of *B. sphaericus*, sample volume etc. on the quantitative recovery of analytes. The effect of alkaline, alkaline earth ions and some metal ions on the retentions of the analyzes. The effect of alkaline, earth alkaline ions and some metal ions on the retentions of the analytes on the biosorbent were also examined. The presented method was applied to the determination of analyte ions in green tea, black tea, cultivated mushroom, boiled wheat, rice and soil sample with successful results.

R. Shokoohi et al. (2009) ^[31] removed iron by dried biomass of activated sludge. The equilibrium time for iron adsorption was determined to be 150 min. The iron removal efficiency was up to 95% at the adsorbent dose 0.9 g, initial concentration 10 ppm, pH 7 ± 0.2 and temperature $20 \pm 0.2^{\circ}\text{C}$.

D. Bozic et al. (2009) ^[10] studied the adsorption of iron and copper ion from synthetic solutions using saw dust of beech, linden and poplar trees. The kinetics of adsorption was reported to be relatively fast reaching equilibrium for less than 20min. The maximum adsorption capacity (7-8 mg g^{-1} of Sawdust) was achieved at a pH between 3.5 and 5 for all the studied kinds of sawdust. No influence of particle size was evidenced. A degree of adsorption higher than 80% was achieved for Cu^{2+} ions but it is very low for Fe^{2+} ions, not exceeding 10%.

Tariq S. Najim et al. (2009) ^[34] studied the adsorption of ferrous and copper ions on the raw pine fruit powder adsorbent. The optimum pH for the removal of Fe^{2+} was found to be 5 and that of Cu^{2+} was 7. Fe^{2+} ion was removed by 96.3-97.3 and copper ion by 94.1% - 96% along the whole range of initial concentrations. Isotherm studies showed that the data were best fitted to the Freundlich isotherm model. The kinetic data corresponded well with the pseudo-second order equation, suggesting that the adsorption process is presumably a chemisorption.

N.T. Abdel-Ghani (2009) ^[26] conducted a factorial experimental design for biosorption of iron and zinc using *Typha domingensis* phytomass. Authors have reported that this study is mainly dependent on using the statistical design of experiments over the conventional univariate procedure for optimization of the system. The information obtained by such design are much more than those obtained from conventional

procedures with significantly reduced number of experiments and henceforth, saving time, energy and cost. The observation shows that the pH is the most important factor affecting the biosorption of Fe^{3+} and Zn^{2+} by *T. domingensis* phytomass, while the second important factor is the temperature and then the interaction between the two factors.

3. Objectives of the Study

In context of Nepal, pollution caused by high concentration of iron in the ground water has been very nuisance for the safe use of water. Especially, in the city areas where water supply is limited, people depend on the groundwater. Due to color, odor and health hazard caused by iron, direct use of ground water is not safe. People are wasting a lot of money and labor in buying filtration plants which should be maintained and cleaned regularly. Iron from groundwater not only imparts color to the water storage tanks but also damages it in a short time causing more economic loss. Ironically, the research on iron removal is very few in our lab compared to other metals which are out of the context for our country.

As Nepal is an agricultural country biosorption method will be very suitable and economic for the iron removal. Therefore in this study the sugarcane-bagasse, which is easily available in the market, is selected as a biosorbent for the removal of iron from aqueous solution.

Although sugarcane bagasse is widely used for the adsorption of numerous metals with varieties of chemical modifications. Its use for the adsorptive removal of iron is sparsely found in literatures. Therefore, the present study is focused on the improvement of adsorption capacity of the sugarcane bagasse for the adsorptive removal of iron by different chemical modifications.

Specific objectives of the present study are:

1. to prepare a novel adsorbent introducing phosphate group onto the charred sugarcane-bagasse as phosphate group has high affinity for iron.
2. to investigate the amounts of functional groups present in the prepared adsorbents.
3. to study the adsorption behavior of Fe(II) on raw, charred, and phosphoric acid treated charred sugarcane bagasse.
4. to investigate the effect of pH, initial concentration of metal ions, and contact time on the removal of Fe(II) from aqueous solution.
5. to prepare adsorption isotherm of Fe(II) and check the validity of Langmuir and Freundlich adsorption isotherms.
6. to study the kinetics of the adsorption process .
7. to elucidate the values of maximum adsorption capacity (q_{\max}) of different adsorbents prepared.

4. Experimental Section

4.1 Instruments used

4.1.1 pH meter, Elico, EL 613, Hyderabad, India.

4.1.2 Spectrophotometer, WPA, Type S104, Linton, Cambridge, U.K.

4.2 Preparation of reagents

4.2.1 1000 ppm stock Mohr's salt solution

7.016 gm Mohr's salt was dissolved in 1L water and volume was made upto the mark.

4.2.2 10% Hydroxyl Amine Hydrochloride solution

10 gm Hydroxyl Amine Hydrochloride was taken in 100 ml volumetric flask and diluted to the mark.

4.2.3 0.2% 1,10-Phenanthroline Hydrochloride solution

0.2 gm 1, 10-Phenanthroline Hydrochloride was taken in 100 ml volumetric flask it was dissolved in some water by stirring and heating to about 80⁰C(do not boil) and diluted to the mark.

4.2.4 Ammonium Acetate buffer solution

250 gm Ammonium Acetate was dissolved in 150 ml water and then 700 ml glacial acetic acid was added to it.

4.2.5 0.1 M Nitric acid

12.7 ml concentrated HNO₃ (15.7M) was diluted to 2L using V.F.

4.2.6 0.02 N Na₂CO₃ solution

0.265 gm Na₂CO₃ was dissolved in water and the volume was made up to 250 ml

4.2.7 0.02 N NaHCO₃ solution

0.42 gm NaHCO₃ was dissolved in water and the volume was made up to 250 ml.

4.2.8 0.02 N NaOH solution

0.2 gm NaOH was dissolved in water and the volume was made up to 250 ml.

4.2.9 0.02 N HCl solution

0.42 ml conc. HCl was diluted to 250 ml.

4.2.10 0.04 N Oxalic acid solution

0.63 gm Oxalic acid was dissolved in water and the volume was made up to 250 ml.

4.2.11 5 M NaOH solution

50 gm NaOH pellets were dissolved in 250 ml V.F. and volume was made up to the mark and this 5 M solution was then diluted to 4 M, 3 M, 2 M, 1 M which are required for pH maintenance.

4.2.12 5 M HNO₃ solution

79.6 ml conc. HNO₃ was diluted to 250 ml with water and this 5 M solution was then diluted to 4 M, 3 M, 2 M, and 1 M which are required for pH maintenance.

4.3 Preparation of Adsorbents from Sugarcane Bagasse

4.3.1 Preparation of raw sugarcane bagasse

Sugarcane bagasse used in the study was collected from a juice-shop located in Kirtipur. The collected bagasse was washed and dried in sun for 8 days and it was cut into small pieces, crushed and pulverized.

4.3.2 Acid modification

100 gm of the powdered bagasse was charred with 200 ml conc. H_2SO_4 with occasional stirring, this acid modified bagasse was allowed to stand for 24 hours for completion of acid modification.

The modified adsorbent was then washed with water till neutrality and it was dried in sun and then in oven for 6 hours below 100°C . Finally, it was grinded and sieved to a particle size of $125\ \mu\text{m}$.

Similarly unmodified sugarcane bagasse was washed till neutrality, dried in sun and it was finally dried in oven below 100°C and sieved to $125\ \mu\text{m}$.

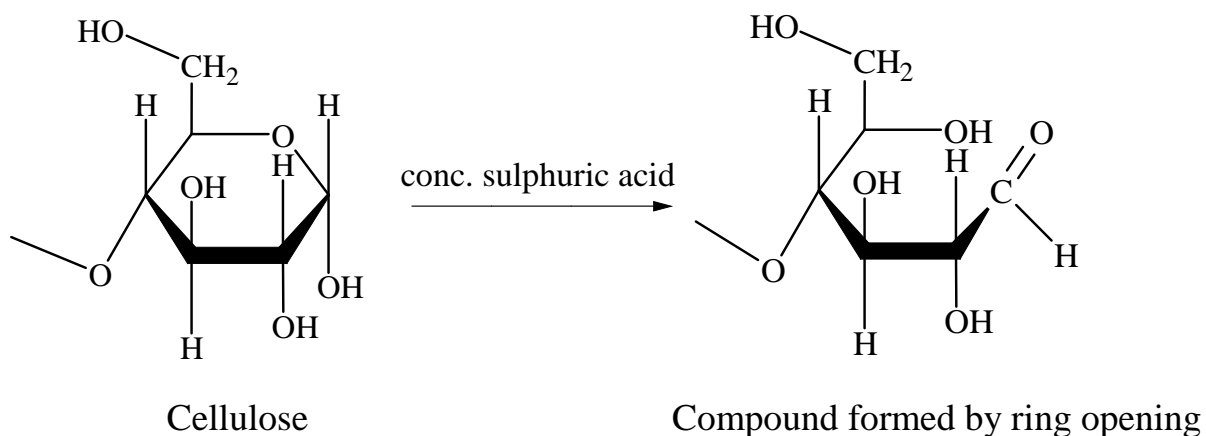
4.3.3 Phosphoric Acid modification

The 10 gm of acid modified adsorbent was treated with 40 ml conc. H_3PO_4 and was warmed at about 80°C for few hours then allowed to stand for 48 hours. That phosphoric acid modified was washed till neutrality and was at first sun-dried and then dried in oven at the temperature below 100°C .

4.4 Effects of chemical modification

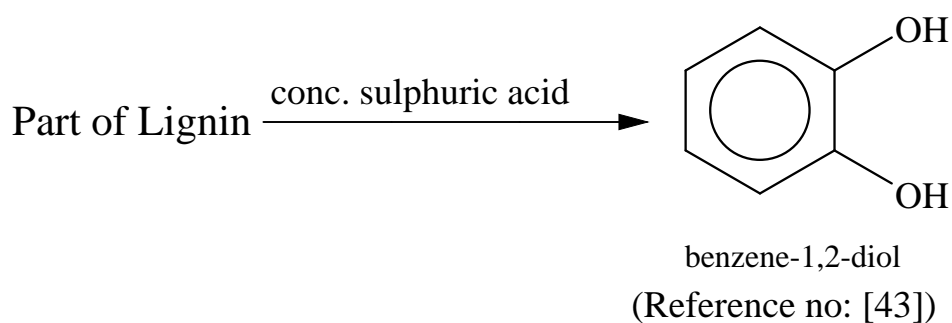
It is well known that acid treatment with such biopolymer creates a suitable environment for its ring opening²⁹. When raw sugarcane bagasse is treated with conc. H_2SO_4 the some of the glucose monomer of the

cellulose may be carbonized and ring of some of them may open up as follows :-

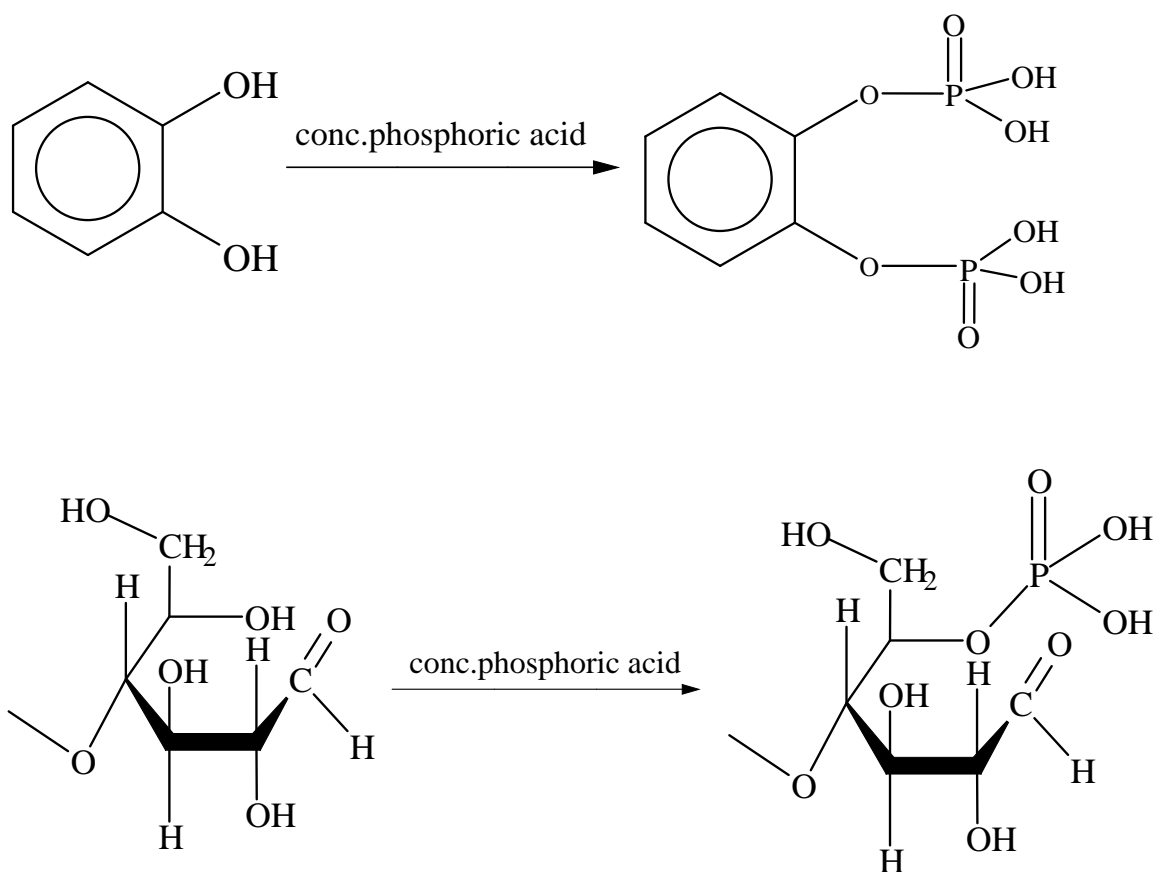


(Reference: [3])

Similarly on treating with conc. H_2SO_4 the large ring of the lignin is decomposed into smaller fragments to some extent but FTIR spectra shows that parent functional groups do not undergo too much change. One of the important fragment is benzene-1,2-diol as its phenolic -OH group can be chemically modified.



Those compounds obtained by treating with conc. H_2SO_4 contain large number of phenolic $-\text{OH}$ group. This fact is also justified by FTIR spectra of RSB and CSB. Therefore CSB can further be modified with phosphoric acid to introduce phosphate group into the adsorbent in order to increase the loading capacity of Fe(II) .

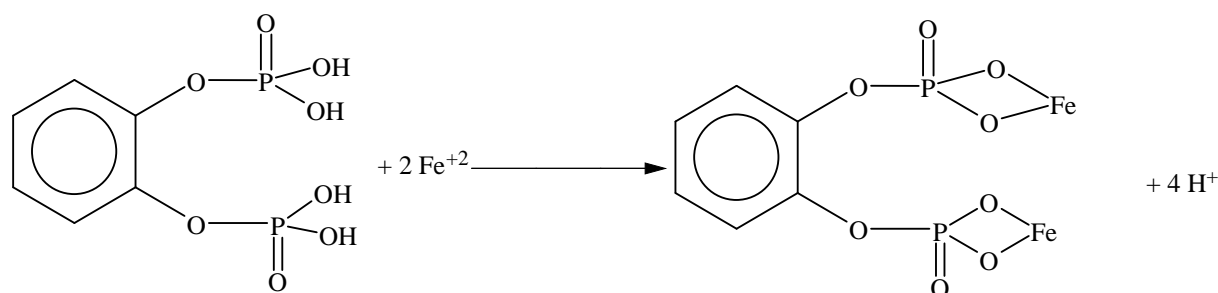
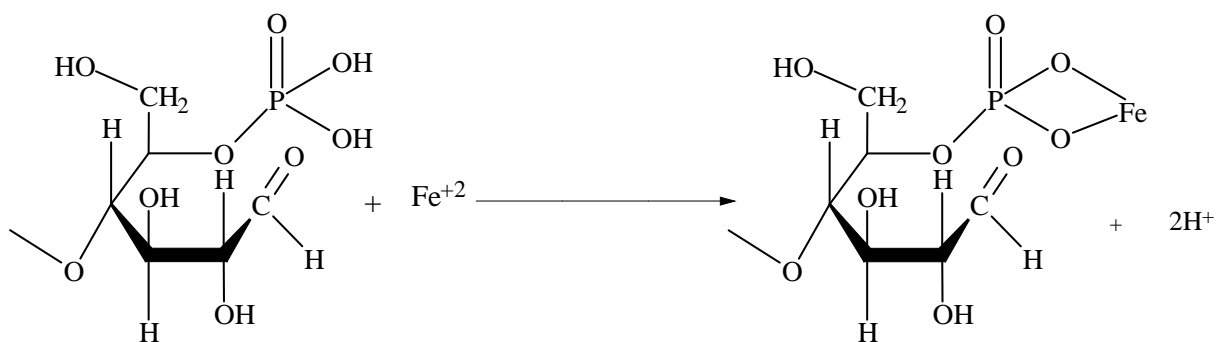


(Reference no: [20])*

* few modifications are made with the suggestion of the author.

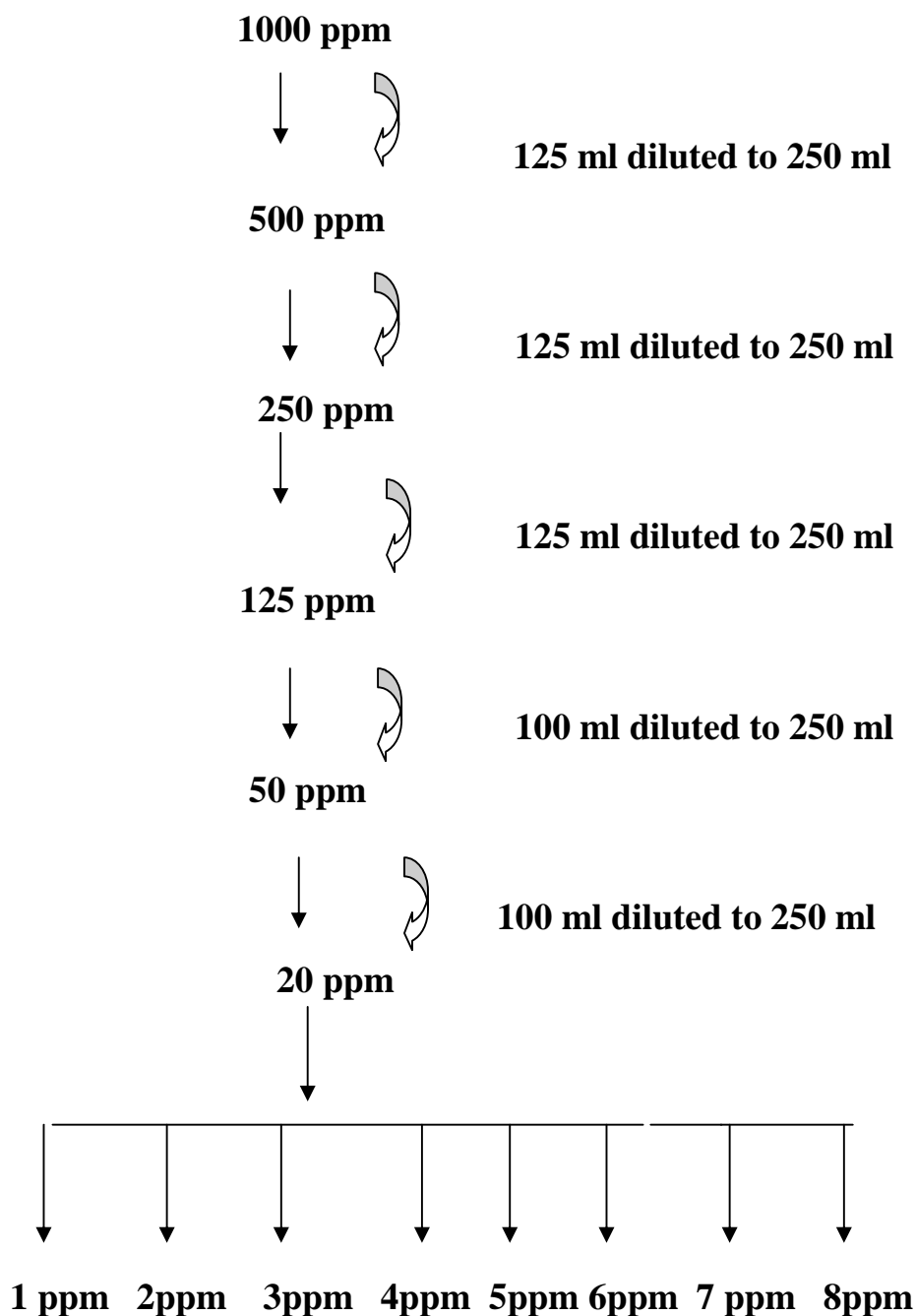
4.5 Mechanism of the Adsorption

The plausible mechanism for the adsorption of Fe(II) on the PSCB is:



4.6 Determination of }_{max} and Construction of Calibration Curve

First of all 1000 ppm stock solution was diluted to 500 ppm in a 250 ml V.F. by 0.1 M HNO₃ by series dilution method as direct dilution leads to large dilution error.



Series dilution

All the solutions of concentration 1 ppm to 8 ppm were prepared in 25 ml V.F., required volume of 20 ppm solution was taken with pipette, color developing reagents (Ammonium Acetate buffer, 10% Hydroxyl Amine Hydrochloride solution, Phenanthroline) were then added and remaining volume was made up to by water. Then the solutions were allowed to stand for 15 min. for color development. A blank solution was prepared by adding all the other reagents except iron solution.

The amount of color developing reagents and time was also optimized as follows:

- Amount of Hydroxyl Amine Hydrochloride:- 3ml
- Amount of Ammonium Acetate buffer:- 7ml
- Amount of Phenanthroline:- 3ml
- Time required for color development:- 15 minute

The solution having intermediate concentration (5 ppm) was taken for the determination of the λ_{\max} . The measurement was started from 400nm, after setting the wavelength blank solution was used to set zero absorbance value in the spectrophotometer; after that blank solution was taken out and the absorbance of the iron solution (color developed) was measured. Then wavelength was increased 10 nm and measurement was carried out as earlier. From the peak shaped plot of absorbance versus wavelength for maximum absorbance i.e. λ_{\max} can be evaluated.

Table: 1 Determination of λ_{\max} for Spectrophotometric determination of Fe(II)

S.N.	Wavelength(nm)	Absorbance
1	400	0.46
2	410	0.56
3	420	0.64
4	430	0.72
5	440	0.76
6	450	0.82
7	460	0.86
8	470	0.86
9	480	0.86
10	490	0.86
11	500	0.90
12	510	1.04
13	520	0.94
14	530	0.70
15	540	0.44
16	550	0.26
17	560	0.18

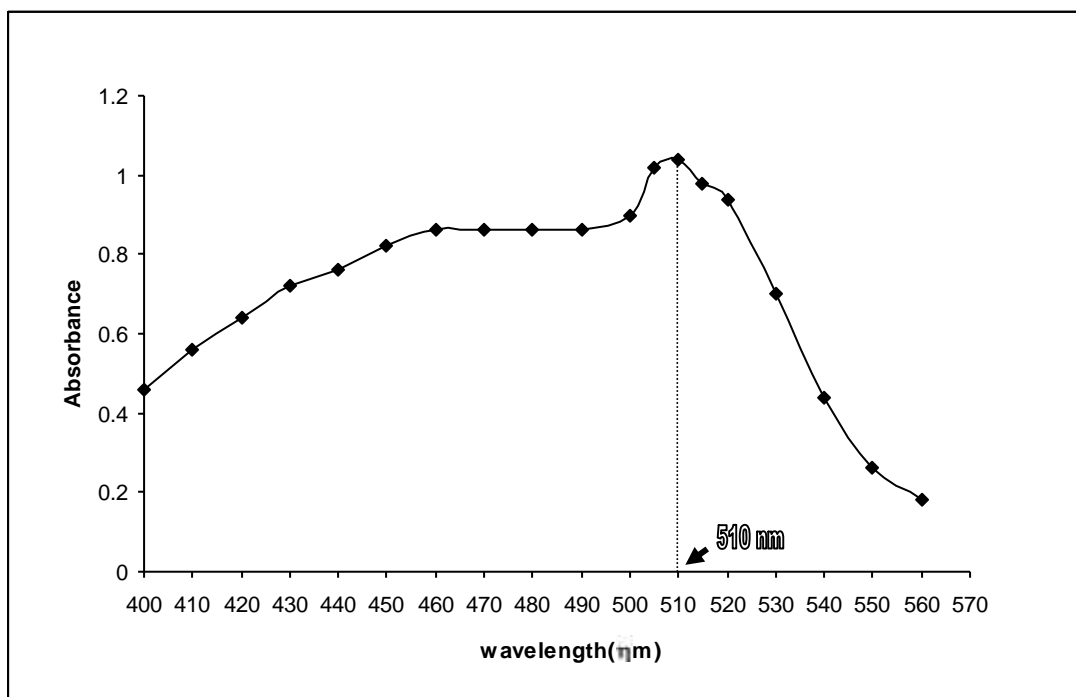


Fig.1 Plot of absorbance versus wavelength for the determination of λ_{\max}

After finding out the value of λ_{\max} the wavelength is set at 510 nm and the absorbance of the solutions of different concentration (1-8 ppm) was measured. Thus plot between absorbance and concentration was a linear curve passing through the origin having the calibration range from 0.00 to 1.60. The plot is known as Calibration Curve.

Table: 2 Construction of Calibration Curve for Fe(II)

S.N.	Concentration(mg/L)	Absorbance
1	1	0.20
2	2	0.40
3	3	0.61
4	4	0.80
5	5	1.00
6	6	1.22
7	7	1.40
8	8	1.60

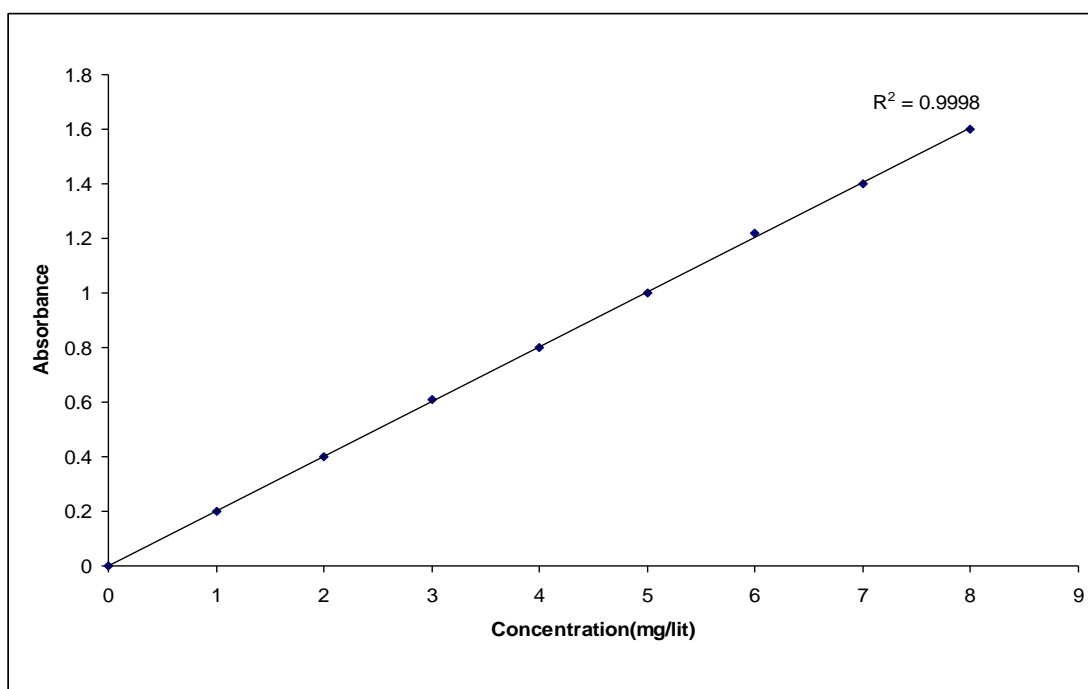


Fig.2 Calibration curve for the determination of concentration of Fe(II)

4.7 Characterization of Adsorbents

4.7.1 Boehm's titration

In order to determine the surface functional groups, 200 mg dry charcoal was agitated with 50 ml of 0.02 N bases NaHCO_3 , Na_2CO_3 , NaOH and acid 0.02 N HCl in mechanical shaker for 48 hours. The mixture was filtered and 5ml of filtrate was back titrated with 0.02 N HCl or 0.02 N NaOH using methyl orange as an indicator to determine the volume of bases and acid consumed. On the basis of volume of acid or bases consumed by the definite weight of charcoal the amount of functional groups per gram charcoal is calculated.

4.7.2 FTIR Spectroscopy

The Fourier Transform Infrared Spectra of the two adsorbents RSB and CSB were recorded on a FTIR/IR-410(JASCO, Japan) by sending the samples to Japan. These spectra are shown in figure 12. The main purpose of observing this spectra is to study the effect of charring on the functional groups of RSB.

4.8 Batch Adsorption Studies

Batch adsorption study was carried out with synthetic solution of Mohr's salt and the adsorption behavior of Fe(II) onto raw, charred and phosphoric acid modified charred sugarcane bagasse was studied. The effect of several parameters such as pH, initial concentration of metal and effect of contact time was studied.

pH of the metal solutions was adjusted by using 1, 2, 3, 4 and 5 M HNO₃ and 1, 2, 3, 4 and 5 M NaOH solution. For the adsorption study 25 ml of the metal solution was taken in a beaker its pH was adjusted to desired value, 5 ml of the pH adjusted solution was taken out for the determination of initial concentration and 25 mg of adsorbent was administered to 20 ml. of the remaining solution taking in the 125 ml. stoppered bottle. The bottles were shaken in mechanical shaker for 24 hour. Then the solutions were filtered by using filter paper and the filtrate was used to determined equilibrium concentration. The concentration of Fe(II) before and after the adsorption was determined spectrophotometrically by using 1,10-phenanthroline method. If the concentration of the analyte was out of the calibration range of spectrophotomer, its concentration was decreased by dilution and brought into the calibration range.

4.8.1 Batch pH Study

First of all, batch pH study was carried out to determine the optimum pH for the adsorption of Fe(II) onto different adsorbents. For the study, 25 ml. of the Mohr's salt solution of known concentration (50 ppm) was taken and its pH was adjusted to 1, 0, 1.5, 2, 2.5, and 3.0. 5 ml of the pH adjusted solution was used for the determination of initial concentration. To the remaining 20 ml of the solution taken in a stoppered bottle 25 mg of adsorbent was added. Those solutions were shaken for 24 hour in the mechanical shaker, filtered and equilibrium pH was noted. Finally, the equilibrium concentration of the filtrates was determined. From the obtained values of initial and equilibrium concentration, the percentage of the metal removed was calculated by using the following equations:

$$R\% = \frac{C_i - C_e}{C_i} \times 100\%$$

where,

R = Removal percentage

C_i = Initial concentration

C_e = Equilibrium concentration

From the plot of R% versus initial pH the optimum pH of adsorption was determined.

4.8.2 Batch Isotherm Study

For the batch adsorption study, Fe(II) solutions of concentrations 25 ppm to 650 ppm were prepared. The pH of the solution was adjusted to optimum pH=2.5 by using HNO₃ and NaOH. Due to the problem of precipitation pH maintenance was started from the solution with higher concentration than desired one. The greatest challenges in isotherm study was to obtain the solution with desired initial concentration at optimum pH.

After maintaining pH the solutions were filtered and the initial concentration was determined. To the 20 ml of the filtrate 25 mg of the adsorbent was added and shaken in the mechanical shaker as above. The initial and equilibrium concentration was determined spectrophotometrically.

The data obtained was tested with Langmuir and Freundlich isotherm models. From this study maximum adsorption capacity (q_{\max}) of the adsorbents were known.

4.8.3 Batch Equilibrium Time Study

For the determination of equilibrium time 25 ml of 50 ppm Fe(II) solutions was taken and their pH was maintained at optimum value. To the 20 ml. of the pH maintained solution 25 mg adsorbent was added. Those solutions were shaken for 5 min, 10 min, 20 min, 40 min, 1 hr, 2hr, 3hr, 4hr, 5hr, 6hr, 7hr, 8hr, 9hr, 10hr and 24 hr respectively. The metal ion concentration before and after adsorption was determined spectrophotometrically.

4.8.4 Batch Kinetic Study

For this study, 25 ml. of the 50 ppm solutions were taken and their pH was adjusted to optimum value. 5ml of the solution was used for determining initial concentration. In the remaining 20 ml of the solution 25 mg adsorbent was added. Separate sets of those solutions were shaken for the times ranging from 5 min to 90 min. Then the results was analyzed for pseudo-first order, pseudo-second order and second order kinetic models.

5. Result and Discussion

5.1 Determination of surface functional group

The amounts of different surface functional groups were determined by Boehm's titration and the results obtained for RSB and CSB are as follows:

Table: 3 Results for Boehm titration

Adsorbents	Volume consumed in mL			
	Vol. of NaOH	Vol. of Na ₂ CO ₃	Vol. of NaHCO ₃	Vol. of HCl
RSB	22.6	8.6	5.5	17.1
CSB	7.5	11.91	7.8	14

Table: 4 Amounts of functional groups

Adsorbents	Functional groups milliequivalents per gram(meq/g)				
	Carboxyl	Lactone	Phenol	Basic	Total
RSB	0.6	0.3	1.0	1.8	3.7
CSB	0.9	0.4	2.3	1.5	5.1

According to Boehm's titration RSB contains 3.7 meq/g total surface functional group among which 1 meq/g is phenolic group, similarly CSB contains 5.1 meq/g total surface functional group among which 2.3 meq/g is phenolic group.

This result is shown in the following figure as a bar diagram:

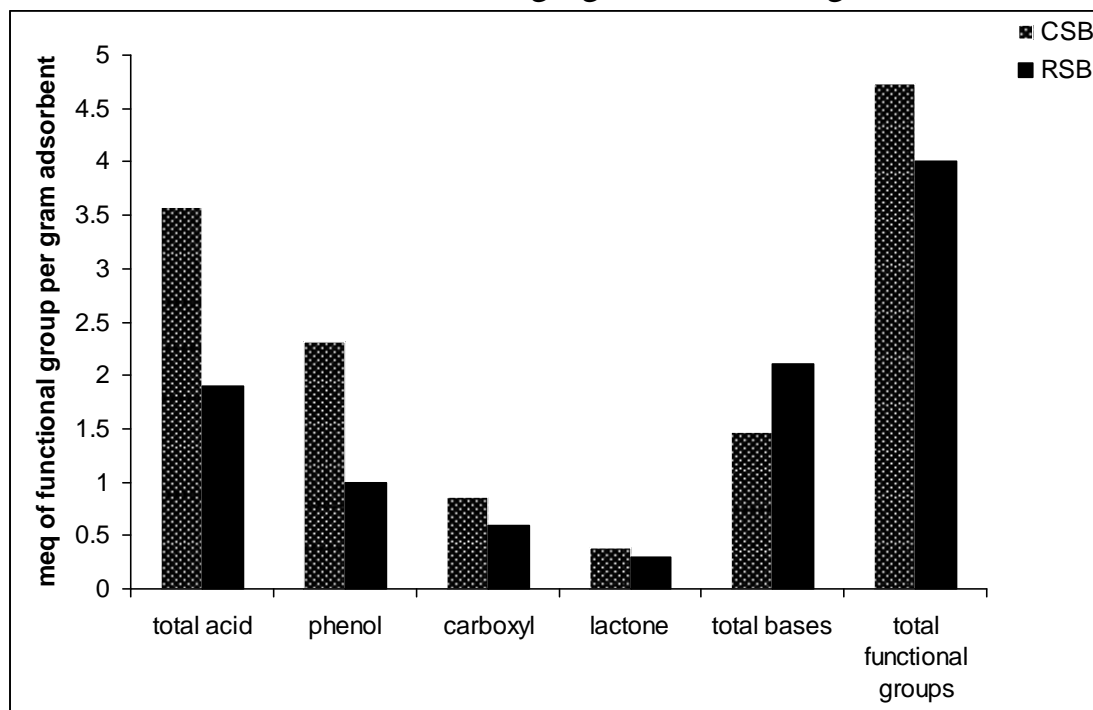


Fig.3 Plot showing the amounts of different surface functional groups on SB

The above result shows that on treating raw sugarcane bagasse with conc. H_2SO_4 there is increase in the amount of acidic functional groups and decrease in basic functional groups, the total functional group has increased by 37.84%. Therefore, it can be concluded that the oxygen containing acidic functional groups increases significantly on treating RSB with conc. H_2SO_4 . Another significance of charring with conc. H_2SO_4 is that the phenolic group in CSB has increased by 130%, and it is clear from the mechanisms illustrated earlier that phenolic group is increased by acid modification that plays a very important role in the adsorption of metal ions.

5.2 FTIR Spectroscopy

The spectra of adsorbents were measured within the range of 500-4000 cm^{-1} wave number. The FTIR Spectra of the adsorbents display a number of adsorption peaks, indicating the complex nature of the examined adsorbents.

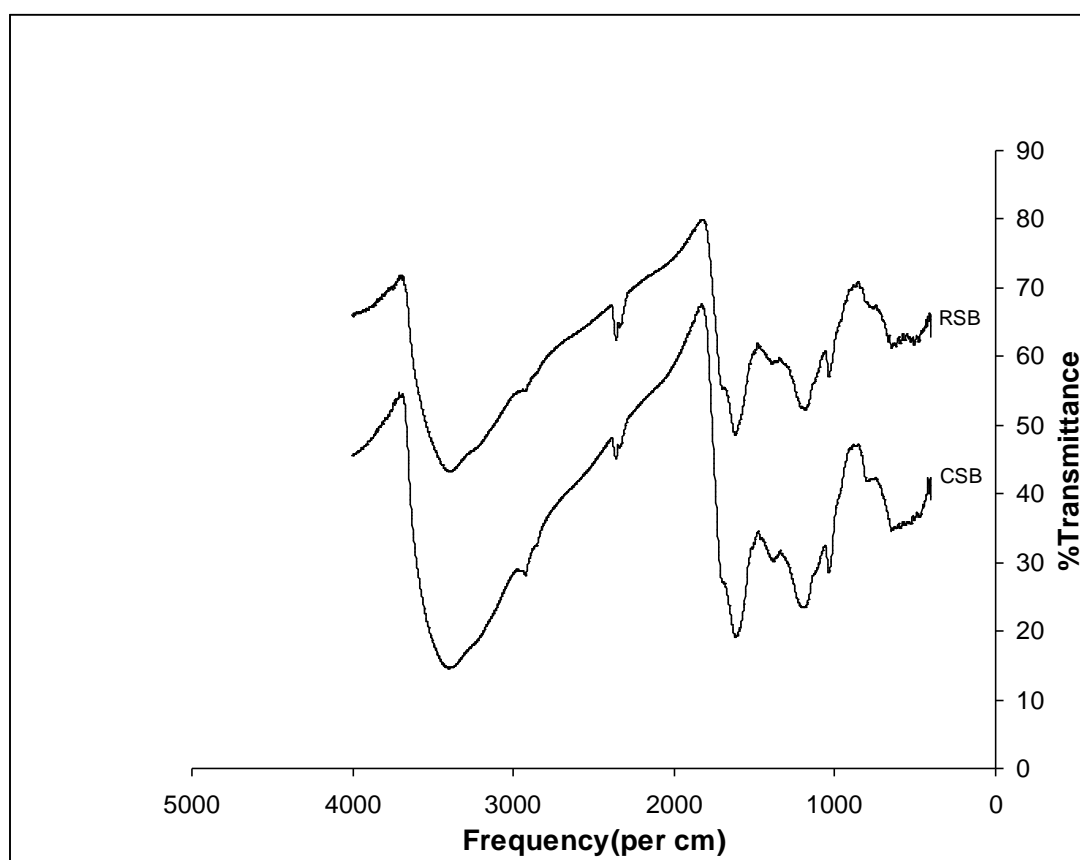


Fig 4: FTIR Spectra of the adsorbents

Table 5: Analysis of the FTIR-Spectra

Frequency (cm ⁻¹)	3403.74	2933.19	1380.78	1617.98	1039.44	646.03
Functional group	O-H bond stretch	C-H bond stretch	C-H bond bending	C=C bond stretch (aromatic)	C-O bond stretch	Bending mode of aromatic group

The adsorption peak around 3403.74 cm⁻¹ indicates the presence of hydroxyl group. The peak observed at 2933.19 cm⁻¹ can be assigned to stretching vibration of the C-H group and peak at 1380.78 can be assigned to bending mode of C-H group. The peak around 1617.98 correspond to the C=C stretching that may be attributed to the lignin aromatic group. The strong band at 1039.44 due to C-O group vibration indicates the presence of -OCH₃, it also indicates the presence of lignin structure in the sugarcane bagasse. Similarly, the broad absorption band around 646.03 can be assigned to bending mode of aromatic compound. This absorption pattern clearly indicates the presence of cellulose and lignin as major constituents in the sugarcane bagasse.

Comparison of the FTIR Spectra of RSB and CSB indicates that CSB is very rich in the functional groups as compared to the RSB. The amount of hydroxyl group in CSB has appreciably increased as compared to RSB as shown by intensity of the peak. It also justifies the conclusion derived from Boehm's titration. Similarly, the intensity of absorption of other functional group has also significantly increased in CSB. It is noteworthy that the basic absorption pattern, however, has remained unchanged in both of the adsorbents, it provides evidence to the mechanisms formulated earlier.

5.3 Batch pH study

Batch pH was carried out with the Fe(II) solution with initial concentration 50 ppm to study the influence of pH on the % adsorption.

Table: 6 Effect of pH on the adsorption of Fe(II) onto RSB

Volume of metal solution=20 mL

Concentration of the metal solution=50 mg/L

Amount of adsorbent=25 mg

S.N.	Initial pH	Equilibrium pH	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	% Adsorption
1	1.0	1.5	50.0	49.5	1.0
2	1.5	1.8	47.8	44.0	8.0
3	2.0	2.2	44.0	39.0	11.4
4	2.5	3.3	42.5	17.0	60.0
5	3.0	4.8	20.0	10.5	47.5

Table: 7 Effect of pH on the adsorption of Fe(II) onto CSB

Volume of metal solution=20 mL

Concentration of the metal solution=50 mg/L

Amount of adsorbent=25 mg

S.N.	Initial pH	Equilibrium pH	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	% Adsorption
1	1.0	1.7	50.0	49.0	2.0
2	1.5	1.9	47.0	42.0	10.6
3	2.0	2.2	43.0	36.0	16.3
4	2.5	4.0	40.0	5.8	85.5
5	3.0	5.6	23.0	8.1	64.8

Table: 8 Effect of pH on the adsorption of Fe(II) onto PCSB

Volume of metal solution=20 mL

Concentration of the metal solution=50 mg/L

Amount of adsorbent=25 mg

S.N.	Initial pH	Equilibrium pH	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	% Adsorption
1	1.0	1.2	50.0	45.0	10.0
2	1.5	1.8	47.0	38.0	19.2
3	2.0	2.3	44.0	32.0	27.3
4	2.5	3.5	40.0	36.5	87.5
5	3.0	5.3	21.5	5.9	72.5

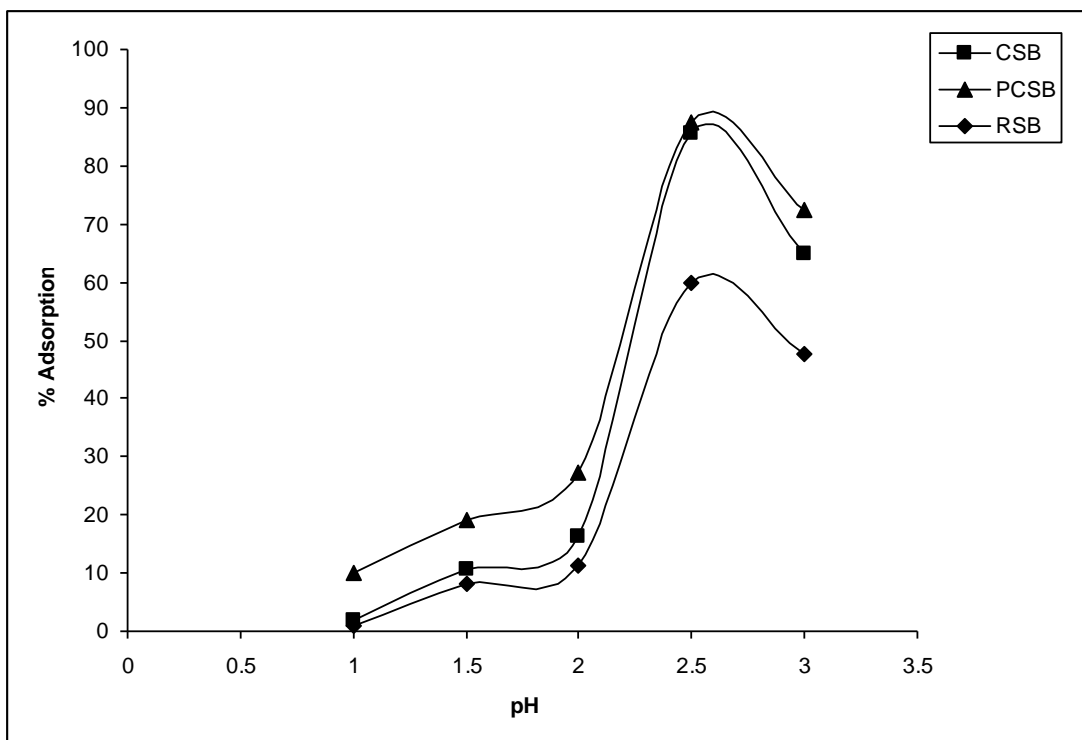


Fig.5 Effect of pH on the percentage adsorption of Fe(II) onto SB

Fig shows that the percentage adsorption of Fe(II) increased from 1% to 60%, 2% to 85.63% and 10% to 87.5% for RSB, CSB, and PCSB respectively, on increasing pH from 1.0 to 3.0. Precipitation poses a greatest problem in the adsorptive removal of iron, in this study it can be observed from table that the concentration of Fe(II) solution which is initially at 50 ppm decreases sharply to about 20 ppm at pH 3.

In an earlier study on the adsorption of iron on chitin Dr.K.N. Ghimire has plotted decrease in iron concentration in the aqueous solution after adsorption (mol dm^{-3}) against equilibrium pH. At $\text{pH} > 3$ the plot deviates downwards from the straight line with slope 3 which is attributed to the hydrolysis of ferric ion by the author.

Therefore it can be concluded that at the higher pH value hydrolysis of Fe(II) ion occurs in this case, which leads to sudden decrease in the Fe(II) ion concentration in the solution. Due to this reason pH study is limited to pH value of 3 beyond which there is extreme hydrolysis and Fe(II) ion concentration drops to extremely low value.

The optimum pH for the iron adsorption was found to be 2.5. As the percentage adsorption increases with the increase in pH the adsorption should occur by cation exchange mechanism. There is competition between the Fe(II) and H^+ ion for adsorption sites. At low pH there is high H^+ ion concentration it leads to low adsorption of Fe(II) ions, but at high pH there is low H^+ concentration and it leads to high adsorption of Fe(II) ions due to decreased competition.

5.4 Batch equilibrium time study

From the table.18 it was found that optimum time for the adsorption of Fe(II) ions on RSB, CSB, and PCSB is 9 hour, 7 hour, and 4 hour respectively. From the above data it can be concluded that PCSB is better adsorbent than CSB and RSB as it brings about equilibrium quickly.

Table: 9 Effect of Contact Time for the Adsorption of Fe(II) onto RSB

Volume of metal solution=20 mL

Mass of the adsorbent=25 mg

pH=2.5

S.N.	Time in min	Initial concentration, C_i (mg/L)	Concentration at time, C_t (mg/L)	q_t (mg/ g)
1.	5	49.50	37.50	12.00
2.	10	50.10	35.75	14.35
3.	15	48.50	33.50	15.00
4.	30	49.00	32.75	16.25
5.	45	50.20	31.00	19.20
6.	60	51.00	30.01	20.99
7.	120	49.50	27.75	21.75
8.	180	51.50	29.00	22.50
9.	240	49.00	25.60	23.40
10.	300	48.50	24.40	24.10
11.	360	50.00	25.50	24.50
12.	420	50.10	25.20	24.90
13.	480	47.90	22.60	25.30
14.	540	48.50	23.00	25.50
15.	600	49.50	24.00	25.50

Table: 10 Effect of contact time on the adsorption of Fe(II) onto CSB

Volume of metal solution=20 mL

Mass of the adsorbent=25 mg

pH=2.5

S.N.	Time in min	Initial concentration, C_i (mg/L)	Concentration at time, C_t (mg/L)	q_t (mg/ g)
1.	5	47.50	25.50	21.70
2.	10	47.30	23.20	24.10
3.	15	48.00	22.10	25.90
4.	30	46.90	20.40	26.50
5.	45	47.00	19.10	27.90
6.	60	47.30	18.80	28.50
7.	120	47.70	17.20	30.50
8.	180	47.00	14.60	32.40
9.	240	47.50	13.20	34.30
10.	300	47.00	11.30	35.70
11.	360	49.00	12.20	36.80
12.	420	48.00	10.10	37.90
13.	480	48.00	10.00	38.00
14.	540	47.30	9.30	38.00
15.	600	47.00	9.00	38.00

Table: 11 Effect of contact time on the adsorption of Fe(II) onto PCSB

Volume of metal solution=20 mL

Mass of the adsorbent=25 mg

pH=2.5

S.N.	Time in min	Initial concentration, C_i (mg/L)	Concentration at time, C_t (mg/L)	q_t (mg/ g)
1.	5	47.00	21.50	25.50
2.	10	47.50	20.00	27.50
3.	15	48.00	18.50	29.50
4.	30	47.10	15.35	31.75
5.	45	18.50	15.00	33.50
6.	60	46.80	12.30	34.50
7.	120	47.50	11.00	36.50
8.	180	47.10	8.60	38.50
9.	240	49.00	8.50	40.50
10.	300	48.50	8.00	40.50
11.	360	47.10	6.60	40.50
12.	420	47.00	6.50	40.50

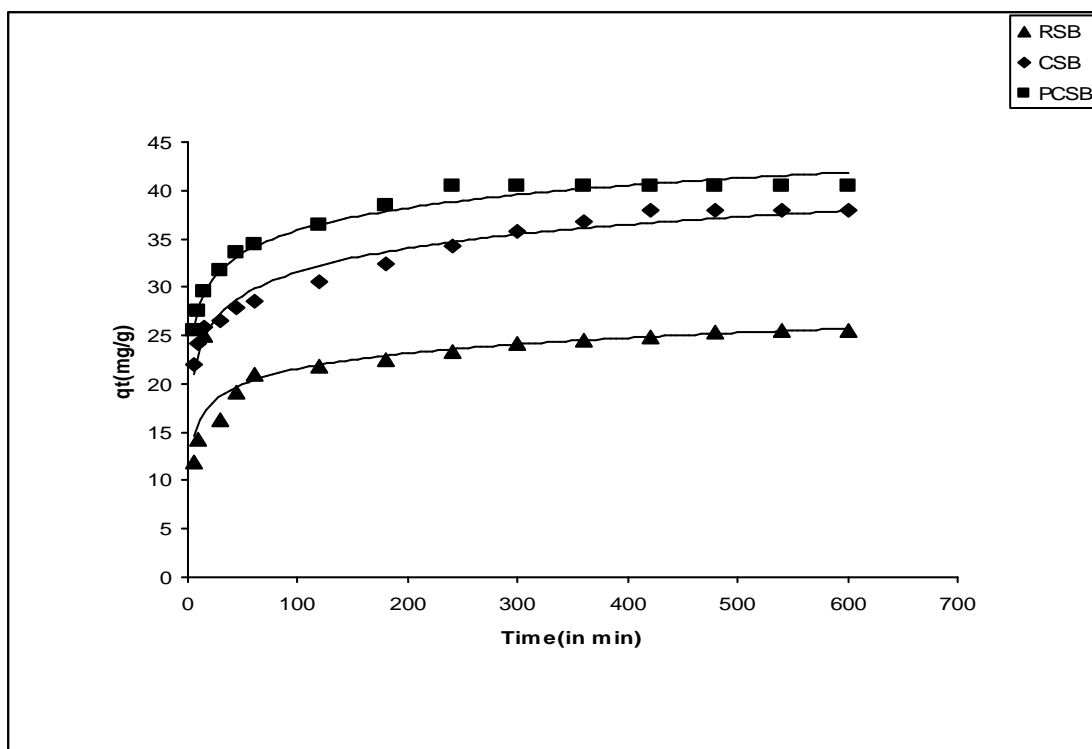


Fig.6 Effect of contact time on the adsorption of Fe(II) onto SB

The data also indicates that initially the rate of adsorption is high but it decreases with time. It is due to the fact that initially there are large number of surface cation exchange sites but with passage of time those sites are covered by metal ions. After certain time all the surface sites become fully occupied and the system acquires a dynamic equilibrium.

5.5 Batch kinetic study

The kinetic data was analyzed by using pseudo-first order, pseudo-second order, and second order kinetic models. On studying plots for pseudo-first order, pseudo-second order, and second order kinetic models it was found out that the adsorption of Fe(II) on all three adsorbents i.e, RSB, CSB and PCSB follow pseudo-second order kinetic model with high correlation coefficient (R^2) value.

Table: 12 Kinetics Study of adsorption of Fe(II) onto RSB

Volume of solution taken=20 mL

Amount of adsorbent=25 mg

pH = 2.5

S.N.	Time in min	C _i (mg/L)	C _t (mg/L)	q _t (mg/g)	q _e -q _t (mg/g)	1/(q _e -q _t) (g/mg)	log(q _e -q _t) (mg/g)	t/q (min.g/mg)
1.	5	49.50	37.50	12.00	13.50	0.07	1.13	0.42
2.	10	50.10	35.75	14.35	11.15	0.09	1.05	0.70
3.	15	48.5	33.50	15.00	10.50	0.10	1.02	1.00
4.	30	49.00	32.75	16.25	9.25	0.11	0.97	1.85
5.	45	50.20	31.00	19.20	6.30	0.16	0.80	2.34
6.	60	51.00	30.01	20.99	4.51	0.22	0.65	2.86
7.	120	49.50	27.75	21.75	3.75	0.27	0.57	5.52
8.	Infinite	51.50	26.00	25.50(q _e)	-	-	-	-

Table: 13 Kinetic study of adsorption of Fe(II) onto CSB

Total volume (V) =20 mL.

Amount of adsorbent (W) = 25 mg

pH = 2.5

S.N.	Time in min	C _i (mg/L)	C _t (mg/L)	q _t (mg/g)	q _e -q _t (mg/g)	1/(q _e -q _t) (g/mg)	log(q _e -q _t) (mg/g)	t/q _t (min.g/mg)
1.	5	47.50	25.50	22.00	16.00	0.06	1.20	0.23
2.	10	47.30	23.20	24.10	13.90	0.07	1.14	0.41
3.	15	48.00	22.10	25.90	12.10	0.08	1.08	0.58
4.	30	46.90	20.40	26.50	11.50	0.09	1.06	1.13
5.	45	47.00	19.10	27.90	10.10	0.10	1.00	1.61
6.	60	47.30	18.80	28.50	9.50	0.11	0.98	2.11
7.	120	47.70	17.20	30.50	7.50	0.13	0.88	3.93
8.	infinite	47.50	9.50	38.00(q _e)	-	-	-	-

Table: 14 Kinetic study of adsorption of Fe(II) onto PCSB

Total volume (V) =20 mL.

Amount of adsorbent (W) = 25 mg

pH = 2.5

S.N.	Time in min	C _i (mg/L)	C _t (mg/L)	q _t (mg/g)	q _e -q _t (mg/g)	1/(q _e -q _t) (g/mg)	log(q _e .q _t) (mg/g)	t/q _t (min.g/mg)
1.	5	47.00	21.50	25.50	15.00	0.07	1.18	0.20
2.	10	47.50	20.00	27.50	13.00	0.08	1.11	0.36
3.	15	48.00	18.50	29.50	11.00	0.09	1.04	0.51
4.	30	47.10	15.35	31.75	8.75	0.11	0.94	0.94
5.	45	48.50	15.00	33.50	7.00	0.14	0.85	1.34
6.	60	46.80	12.30	34.50	6.00	0.17	0.78	1.74
7.	120	47.50	11.00	36.50	4.00	0.25	0.63	3.29
8.	infinite	47.10	6.60	40.50(q _e)	-	-	-	-

Different parameters were calculated from the kinetic plots of the three adsorbents which are shown in the following table

Table: 15 Kinetic parameters for the metal biosorption with correlation coefficient

Adsorbent	q _{exp} mg/g	Pseudo first-order			Pseudo second-order				Second-order		
		k ₁ x 10 ⁻³ (1/min)	q _e mg/g	R ²	k ₂ x 10 ⁻³ g/mg.min	q _e mg/g	R ²	o mg/g.min	k ₂ ' x 10 ⁻³ g/mg.min	q _e mg/g	R ²
RSB	25.5	11.52	12.21	0.8709	5.78	23	0.9958	3.06	1.8	13.74	0.9296
CSB	38	14.51	13.64	0.9368	5.37	36.36	0.9976	7.1	2.6	20.96	0.9776
PCSB	40.5	11.05	13.35	0.9245	6.66	37.31	0.999	9.28	1.6	15.2	0.9937

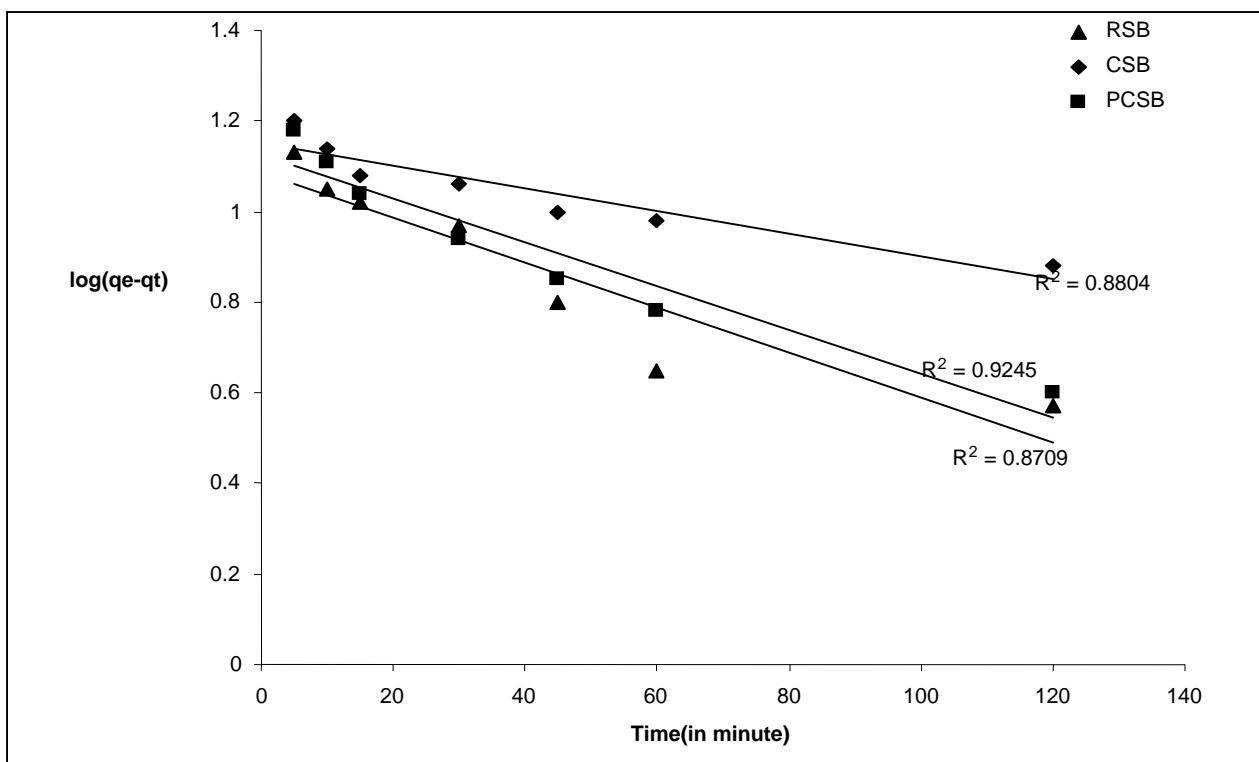


Fig.7 Pseudo-first order kinetic plot for the adsorption of Fe(II) onto SB

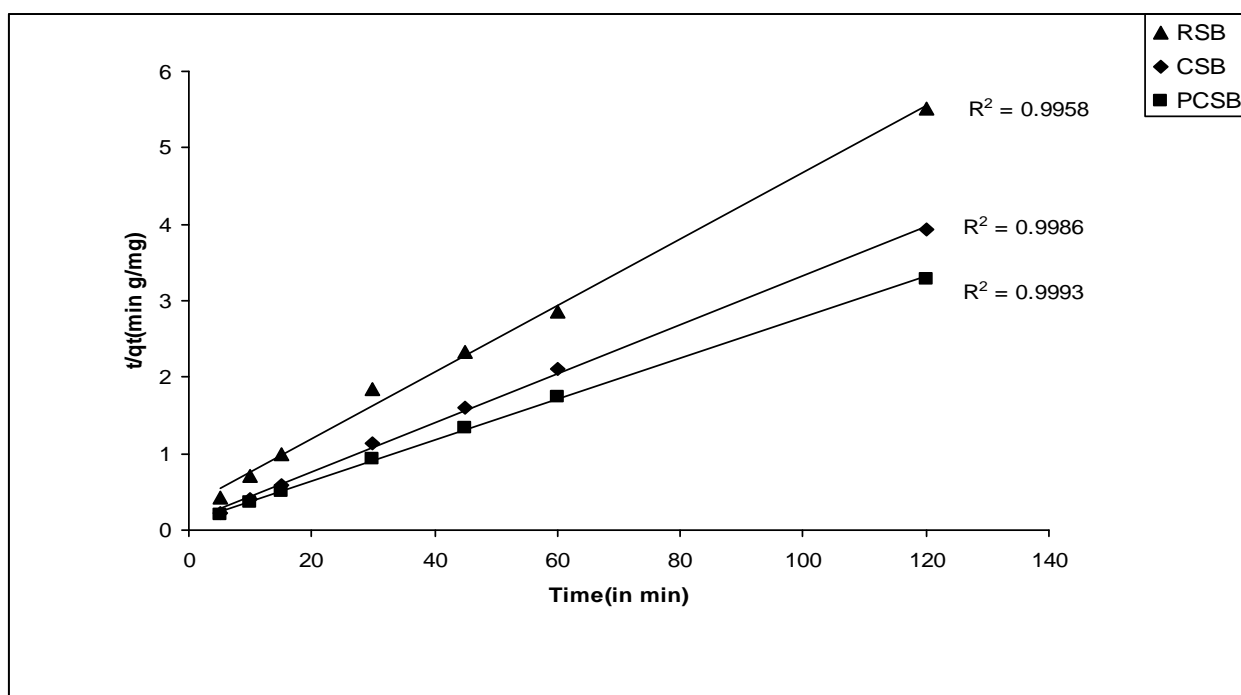


Fig.8 Pseudo-second order kinetic plot for the adsorption of Fe(II) onto SB

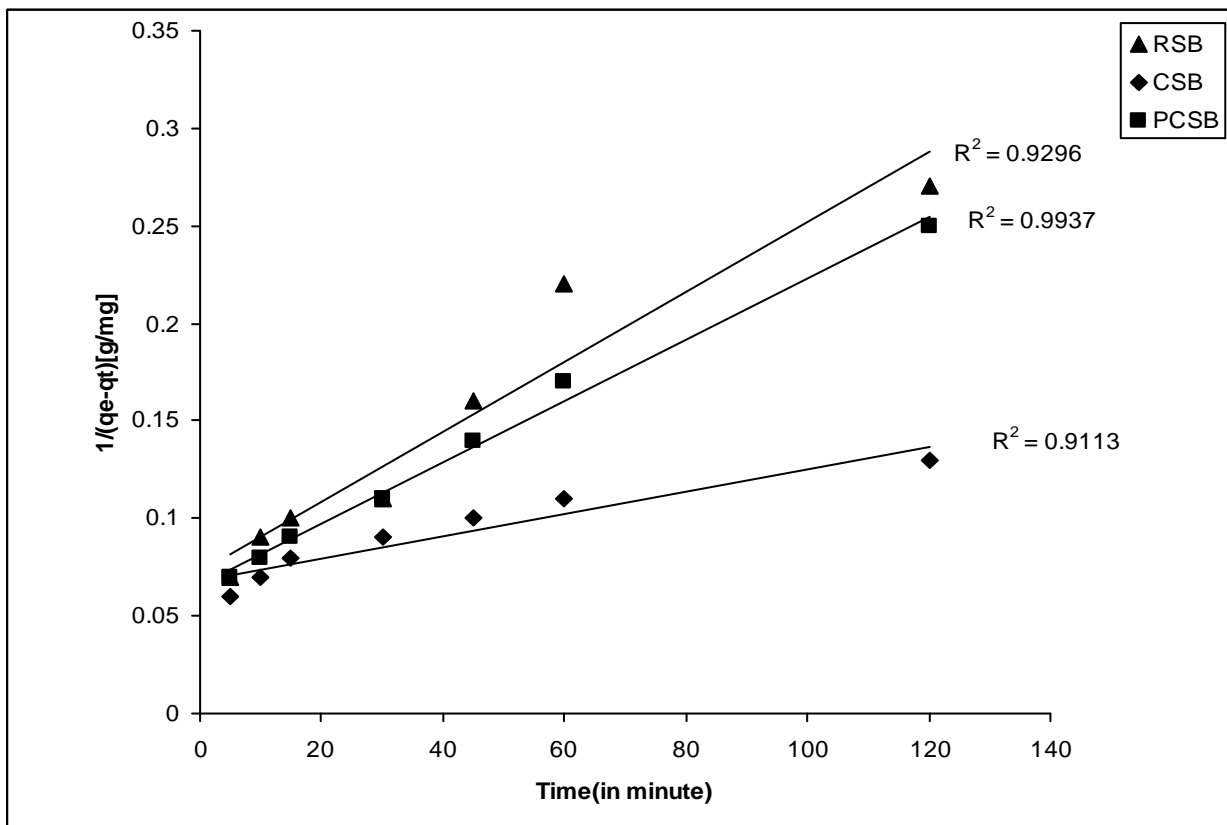


Fig.9 Second order kinetic plot for the adsorption of Fe(II) onto SB

5.6 Batch Isotherm study

The effect of concentration on the adsorption of Fe(II) onto different adsorbents prepared from SB is shown in the following tables. The data shows that percentage adsorption decreases with the increase in the concentration of Fe(II) ion.

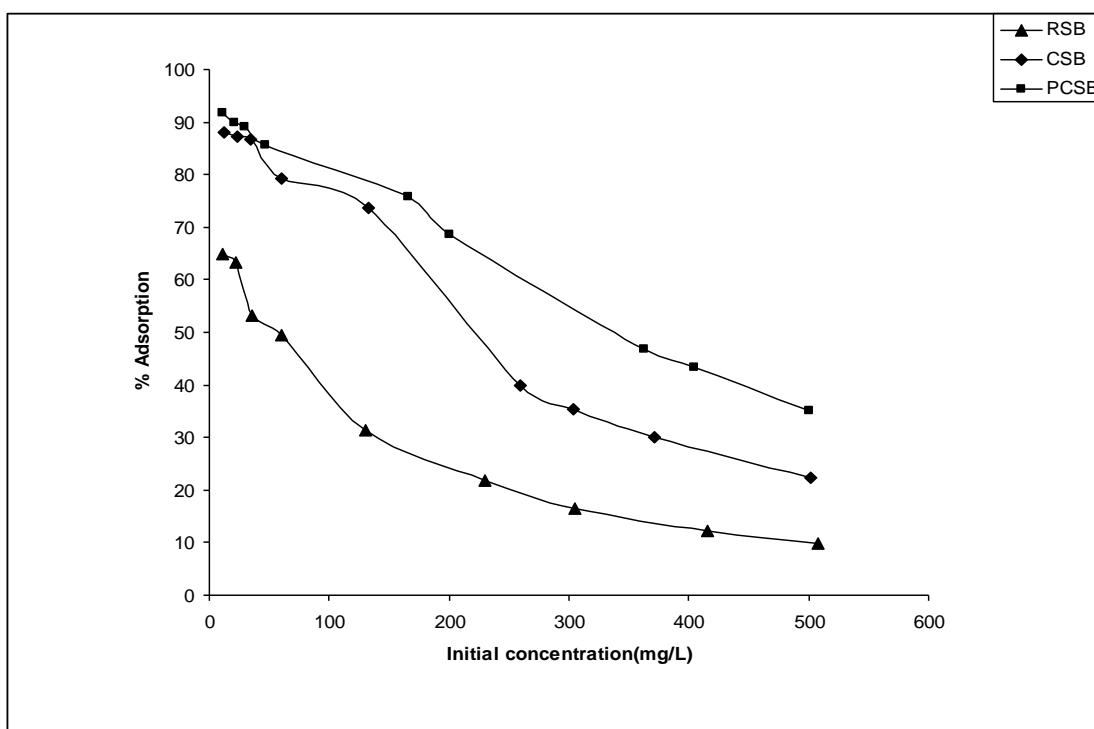


Fig.10 Effect of initial concentration on the percentage adsorption of Fe(II) onto SB

Table: 16 Effect of concentration on the adsorption of Fe(II) onto RSB

Volume of metal solution=20 mL

Amount of adsorbent=25 mg

pH= 2.5

S.N.	Initial concentration C_i (mg/L)	Equilibrium concentration C_e (mg/L)	Amount of Fe(II) adsorbed q_e (mg/g)	C_e/q_e (L/g)	$\log C_e$ (mg/L)	$\log q_e$ (mg/g)	% Adsorption
1	11.00	3.85	7.15	0.54	0.59	0.85	65.00
2	22.50	8.25	14.25	0.58	0.92	1.15	63.33
3	35.17	16.50	18.67	0.88	1.22	1.27	53.08
4	60.50	30.50	30.00	1.02	1.48	1.48	49.59
5	130.70	89.75	40.95	2.19	1.95	1.61	31.33
6	230.00	180.00	50.00	3.60	2.26	1.70	21.74
7	305.25	255.17	50.08	5.10	2.41	1.70	16.40
8	415.00	364.50	50.50	7.22	2.56	1.70	12.17
9	508.17	457.67	50.50	9.06	2.66	1.70	9.94

Table: 17 Effect of concentration on the adsorption of Fe(II) onto CSB

Volume of solution taken=20 mL

Amount of adsorbent=25 mg

pH = 2.5

S.N.	Initial concentration C_i (mg/L)	Equilibrium concentration C_e (mg/L)	Amount of Fe(II) adsorbed q_e (mg/g)	C_e/q_e (L/g)	$\log C_e$ (mg/L)	$\log q_e$ (mg/g)	% Adsorption
1	12.50	1.50	11.00	0.14	0.18	1.04	88.00
2	23.13	2.95	20.18	0.15	0.47	1.30	87.24
3	34.00	4.55	29.45	0.15	0.66	1.47	86.62
4	60.00	12.50	47.50	0.26	1.10	1.68	79.16
5	132.50	62.50	70.00	0.89	1.80	1.85	52.83
6	260.00	156.25	103.75	1.50	2.19	2.02	39.90
7	304.17	196.90	107.33	1.83	2.29	2.03	35.27
8	370.80	259.40	111.40	2.33	2.41	2.05	30.00
9	502.00	390.60	111.40	3.51	2.59	2.05	22.26

Table: 18 Effect of concentration on the adsorption of Fe(II) onto PCSB

Volume of solution taken=20 mL

Amount of adsorbent=25 mg

pH= 2.5

S.N.	Initial concentration C_i (mg/L)	Equilibrium concentration C_e (mg/L)	Amount of Fe(II) adsorbed q_e (mg/g)	C_e/q_e (L/g)	$\log C_e$ (mg/L)	$\log q_e$ (mg/g)	% Adsorption
1	11.50	0.95	10.55	0.09	-0.02	1.02	91.74
2	21.00	2.10	18.90	0.11	0.32	1.28	90.00
3	30.00	3.30	26.70	0.13	0.52	1.43	89.00
4	46.80	6.75	40.05	0.17	0.83	1.60	85.57
5	165.60	40.00	125.60	0.32	1.60	2.10	75.84
6	200.00	62.50	137.50	0.45	1.80	2.14	68.75
7	362.70	192.50	170.20	1.13	2.28	2.23	46.90
8	404.17	229.17	175.00	1.31	2.36	2.24	43.30
9	500.00	325.00	175.00	1.86	2.51	2.24	35.00

From the above data the Langmuir and Freundlich isotherms were prepared which are shown in the following figures.

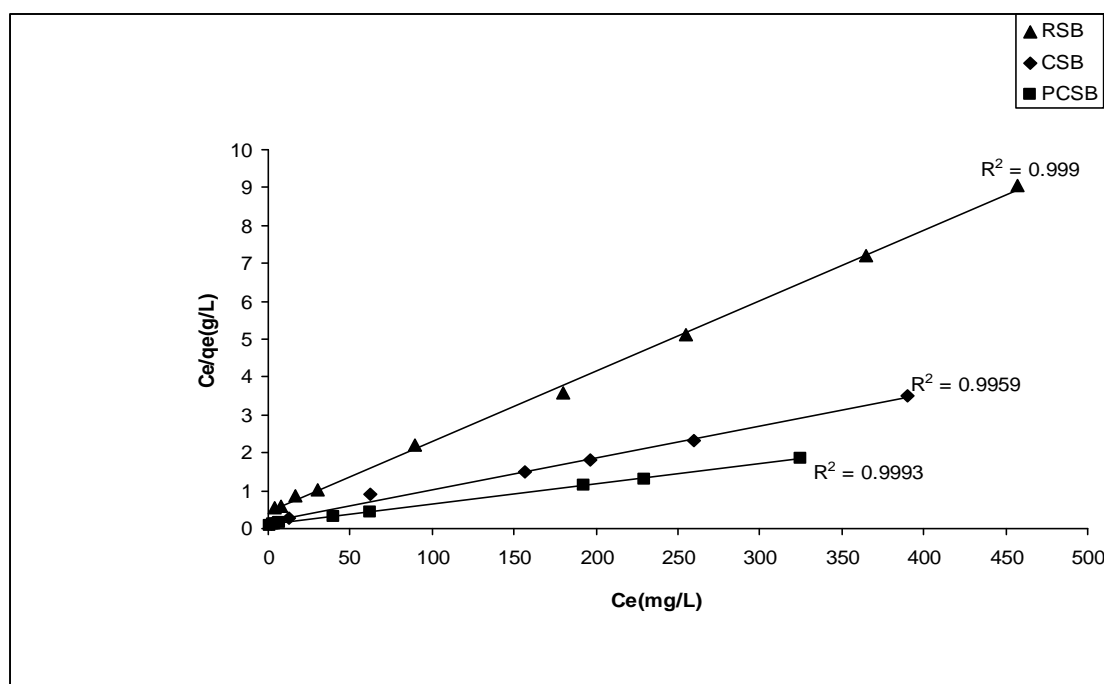


Fig.11 Langmuir adsorption isotherm for the adsorption of Fe(II) onto SB

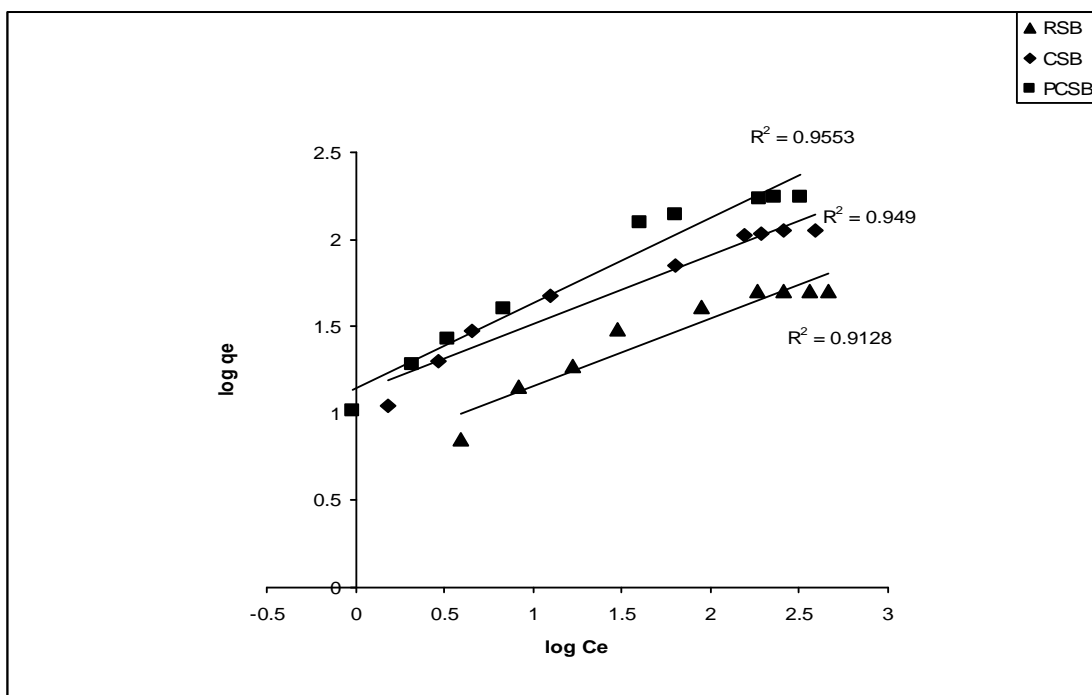


Fig.12 Freundlich adsorption isotherm for the adsorption of Fe(II) onto SB

The plots of C_e/q_e versus C_e are linear with higher value of correlation coefficient (R^2) value than that of Freundlich isotherm which shows the adsorption of Fe(II) on all the adsorbents follows Langmuir adsorption model more strictly than Freundlich isotherm. Value of slope was found to be lesser than unity implied that significant adsorption took place at low metal ion concentration.

The Langmuir and Freundlich parameters were calculated from their respective plots. Their values are presented in the following table.

Table: 19 Langmuir and Freundlich parameters and correlation coefficient with experimental q_{\max} for the adsorption of Fe(II)

S.N.	Adsorbents	Experimental q_{\max} (mg/g)	Langmuir isotherm			Freundlich isotherm		
			q_{\max} (mg/g)	b(L/mg)	R^2	k(mg/g)	1/n	R^2
1.	RSB	50.5	53.76	0.04	0.999	5.9	0.39	0.913
2.	CSB	111.4	117.65	0.05	0.996	12.76	0.41	0.955
3.	PCSB	175	188.68	0.05	0.999	14.10	0.49	0.955

k is an indicator of adsorption capacity therefore from the above data it is concluded that the adsorption capacity of those three adsorbents is in the order:

$$\text{RSB} < \text{CSB} < \text{PCSB}$$

In other words PCSB has the highest adsorption capacity among the three adsorbents prepared and RSB has the least adsorption capacity.

n is an indicator of adsorption intensity of the metal ions, above data shows that the intensity of adsorption of Fe(II) onto those three adsorbents is in the order

$RSB > CSB > PCSB$, which is just opposite to the order of adsorption capacity.

It may be due to the fact that adsorption capacity of the PCSB is the highest so it adsorbs large amount of metal ions as compared to other two adsorbents. As a result adsorptive force per metal ions should be least in this case and the adsorption intensity of metal ions towards this adsorbent is lowest and vice versa.

Another constant b , obtained from Langmuir isotherm, is related to the affinity of binding sites with the metal ions. Its value follows the order:

$$CSB = PCSB > RSB$$

It shows that CSB has better affinity towards metal ions as compared to RSB but due to high q_{max} value adsorption intensity of metal ions toward PCSB is less as described earlier therefore in PCSB equal affinity between adsorption site and metal ions as in CSB.

Another important parameter is q_{max} which is the maximum quantity of metal ions per unit mass of the adsorbent to form a complete monolayer on the surface. It is also called maximum adsorption capacity of the adsorbent, higher is the value of q_{max} , higher is the amount of metal ions adsorbed. Therefore, it is concluded that PCSB is the best adsorbent among RSB, CSB, and PCSB followed by CSB. PCSB has the q_{max} value of 175 mg/g which is better than that of other adsorbents reported in other literatures.

Table: 20 Comparison of q_{\max} values of the adsorbents

S.N.	Metal ion	q_{\max} (mg/g)	Adsorbents	Reference
1.	Fe(II)	50.5	Raw sugarcane bagasse, RSB (particle size-125 μm)	Present study
2.	Fe(II)	111.4	Charred sugarcane bagasse, CSB (particle size-125 μm)	Present study
3.	Fe(II)	175	Phosphoric acid treated charred sugarcane bagasse, PCSB (particle size-125 μm)	Present study
4.	Fe(III)	122	<i>Streptomyces rimosus</i> (NaOH treated)	A. Selatnia et al.
5.	Fe(III)	36.83	Sugarcane bagasse (carbonized by heating at 300 ⁰ C and treated with ZnCl ₂)	Orawan Sirichote et al.
6.	Fe(III)	22.9	Pericarp of rubber fruit (carbonized by heating at 400 ⁰ C and treated with ZnCl ₂)	Orawan Sirichote et al.
7.	Fe (III)	10.04	Coconut shell (carbonized by heating at 450 ⁰ C and treated with ZnCl ₂)	Orawan Sirichote et al.

6. Conclusion

The result of the present study shows that charred sugarcane bagasse and phosphoric acid modified sugarcane bagasse have excellent sorption capacity for the Fe(II) ion in aqueous solution. Such a simple and low-cost chemical modification on sugarcane bagasse viz. CSB, PCSB resulted in enhancing the sorption capacity of RSB for Fe(II) uptake from 50.5 to 111.4,175 mg/g respectively. The uptake of Fe(II) was pH dependent and was maximum at the pH value of 2.5, the adsorption data followed pseudo-second order kinetic model which agreed with chemisorption as the rate limiting mechanism. Sorption isotherms were better represented by Langmuir model than the Freundlich model. The highly efficient, low cost and the rapid uptake of PCSB indicated that it could be an excellent alternative for the removal of Fe(II) by sorption process. Sugarcane bagasse which is an abundant low cost biowaste can be used for the removal of Fe(II) from water and wastewater as the water pollution due to iron is a burning problem in the context of Nepal.

7. Limitations of the study

- Due to unavailability of the analytical grade chemicals all the study was conducted with laboratory grade chemicals.
- Due to unavailability of HEPES buffer pH of the solution could only be maintained up to pH value 2.5, above which precipitation of the iron started on adding alkali solution (NaOH).
- Adsorption study was carried out only on the synthetic solution. The adsorption study on the natural sample solution was not carried out.

8. Suggestion for further work

- As the adsorption of Fe(II) onto SB was found to be cation exchange phenomena, it is suggested to study the adsorption phenomena at the pH value greater than 2.5 by using HEPES buffer or any other suitable chemicals. For the cation exchange process as the pH increases the extent of adsorption also increases therefore pH value of 2.5 is not the optimum but maintainable pH value.
- It is suggested to search for anti-precipitating agent for iron before carrying out research on iron adsorption because at higher concentration, precipitation occurs even at low pH in case of iron.
- It would be better to study iron adsorption in natural iron-contaminated water sample rather than synthetic sample because in natural sample extent of adsorption is obviously lower due to competition of various ions in the sample.
- The determination of Fe(II) in sample solution should be done by modern technique like AAS rather than spectrophotometer. The spectrophotometric analysis is very tedious and time consuming moreover its detection limit is higher than that of AAS.
- Even if spectrophotometric method is used alternative colour developing agent should be looked for because the reagent 1,10-phenanthroline is quite expensive to afford. In place of this reagent thiocyanate can be used for Fe(II) determination.
- Proper care should be taken during optimization of color development. If some error is introduced during this process whole study will be ruined.

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