

## Application of Thermally and Chemically Modified Banana Peels Waste as Adsorbents for the Removal of Iron from Aqueous System

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### Abstract

In the present study the potential of modified banana peels for the removal of total iron from aqueous system was investigated. Batch mode study was carried out. Isotherm data was generated and fitted in Langmuir and Freundlich equation to explain the phenomenon of adsorption. The adsorption capacities based on Langmuir model ( $Q_m$ ) of the 3 adsorbents were found to be 1.47 for raw banana peel (RP), 0.93 for the grafted peel (GP) and 1.8 mg/g for the Charred peel (CP). The  $R^2$  values were 0.99 for raw banana peel (RP), 0.93 for grafted peel (GP) and 0.96 for charred peel (CP). Based on Freundlich model the adsorption capacities ( $K$ ) were 2.89, 2.78 and 3.95 mg/g for raw peel (RP), grafted peel (GP) and charred peel (CP). The  $R^2$  values were found to be 0.96, 0.94 and 0.95 for the raw banana peel (RP) grafted peel (GP) and charred peel (CP) respectively. Our results showed that modified banana peel products can be used as potential adsorbents for removal of iron from aqueous environment.

**Keywords:** Adsorption; Iron; Langmuir; Grafting; Isotherm

### Introduction

The removal of heavy and toxic metals such as Fe, Pb, Cd, Cr, Co, etc., from ground and industrial waste water is a matter of great concern in the underdeveloped countries. Of these, iron ions are the focus of attention for researchers because of its wide use in manufacturing industries like galvanized pipe and metal finishing [1]. The presence of iron ions in ground and industrial waste water becomes toxic at high level and then may cause environmental and human health problems [2]. The dissolved iron concentration in ground water can range from less than 1 mg/L up to 20 mg/L. [3]. The ferrous, bivalent and ferric or trivalent are the primary forms of concern in the aquatic environment, although other forms may be organic and inorganic waste water stream.

Different techniques for iron removal are used in water purification processes, i.e. limestone filters [1] ion exchange or cationic exchange resins and the oxidation-precipitation of iron(II) into iron hydroxides, especially the iron oxyhydroxide (FeOOH). The iron hydroxides colloids can be removed by membrane processes based on reverse osmosis, nanofiltration [4] and ultrafiltration. These operations are affected by different parameters such as temperature, pH, and oxygen flow. Moreover, most of these technologies are either extremely expensive or too inefficient in reducing metal ion levels in effluent to concentrations that are required by governmental legislation. Among all methods, the adsorption is a cost-effective technique and simple to operate [5]. Agricultural by-products have been used as adsorbents for the adsorption of hazardous substances from aqueous system.

Mohamed bin Saleh et al. [6] used Okra wastes as a food canning processes by products as potential adsorbent for cadmium(II), iron(II) and zinc(II) removal from various aqueous solutions. Batch studies were performed to evaluate the adsorption. process, and it was found that the okra wastes was found to adsorb 96.4% of cadmium(II) 93.8% of iron(II) and 79.8% zinc(II). This work proved that okra wastes can be used as an efficient adsorbent material for removal of heavy metals from water and wastewater.

Ghanshyam et al. prepared [7] two series of novel hydro gels consisting of different molar ratios of monomers were prepared for specialty applications as sorbents for some common metal ions. Hydrogels were further functionalized by partial saponification with 0.5M NaOH and were used as adsorbents for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cr}^{6+}$  ions. The metal ion sorption was observed in the order:  $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Cr}^{6+}$ .

Zaid et al. studied the adsorption of Fe(III) ions from the aqueous solution using olive cake as an adsorbent. The influences of the

initial pH, temperature, contact time and dosage of the adsorbent on adsorption performance have been experimentally verified by a batch method.

Rosliza et al. [8] used untreated sawdust (SD) and treated sawdust (SDC) for removal of the Fe(II) using batch test. The Langmuir and Freundlich isotherms were used to observe sorption phenomena of sawdust in the removal of iron. The results indicate that the sawdust was capable in removing Fe(II) in aqueous solution. The results also showed that Langmuir isotherm was found well fitted into the experimental data as compared to the Freundlich isotherm. It was found that, chemisorption's and physisorption were the prime mechanism for the process of adsorption to occur between the sawdust and Fe(II).

Benevolent et al. [9] the examined the biomass of, *Vitex doniana* leaf powder, in the adsorption of heavy metals from water. Batch pH profile experiment for Pb and Fe indicated that metal ion binding capacity of the biomass increased as pH increased. At room temperature and with good equilibrium the adsorption capacities of *V. doniana* leaf powder for Pb and Fe ions were 99.98 and 86%, respectively *V. doniana* leaf powder therefore showed good binding capacity for Pb and Fe.

Pakistan is a key player in the banana industry. Area under cultivation is 35,000 hectares. 90% is cultivated in Sind province. Sind is a major banana producing area with about 85 to 92 per cent in banana acreage and about 90 per cent of production.

The average area under the fruit in Sind was 32,200 hectares with a production of 126,000 tons. Pakistan is ranked 41 in banana production worldwide. The banana peels waste so produced is not only wasted but may also pose serious disposal problems. On the other hand this waste may be used effectively in water treatment technologies. In the present study we used various banana peel waste products to remove iron from aquatic system.

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## Materials and Methods

### Materials

**Banana peel:** Banana peels were used as adsorbent in 3 different form i.e raw, grafted and charred for the removal of iron from aqueous system.

**Chemicals:** Ferrous ammonium sulphate, hydroxylamine, ammonium acetate buffer, phenanthroline, sodium acetate, potassium permanganate, sulphuric acid, acrylonitrile were all of analytical grade chemicals provided by Merck Germany.

### Methods

**Air drying:** The fresh banana peels were subjected to air (in shadowing place) for 36-48 hours, and then weighed after drying.

**Oven drying:** The air dried peels are taken in Petri dish and kept it in oven for 4 hrs to find the moisture content in them. The % moisture content was determined and found to be 51.

### Preparation of adsorbents

**Raw peel (RP):** The oven dried peels were considered as raw peel adsorbent and they were directly treated for adsorption study.

**Grafted peel (GP):** Grafting was carried out by steeping 2 g of dried peel in acrylonitrile solution for 15 to 20 min, and after treatment of several chemical solutions the grafted peel was obtained.

**Charred peel (CP):** These were obtained by keeping the dried peels in muffle furnace for 3 to 4 hrs at 300°C. When the dried peel completely burns giving charred adsorbent.

### Iron adsorption

**Standard curve for iron adsorption:** Working standards of 100 µg, 200 µg, 300 µg, 400 µg and 500 µg were prepared from stock iron solution. 1 ml of hydroxylamine hydrochloride, 10 ml phenanthroline solution, and 10 ml of sodium acetate solution were added to each standard solution. The solutions were diluted to 100 ml with distilled water. The solutions were allowed to stand for about 10 minutes to develop color. The absorbance of each solution was recorded with a UV visible spectrometer at 506 nm. A sample blank with water was also proceeded in the same manner. The correct absorbance was determined for each standard by subtracting the absorbance of the blank. A calibration curve for adsorption of iron was drawn between absorbance and iron concentration [10].

**Determination of iron adsorption:** Various adsorbents selected include raw banana peel (BP), grafted peel (GP), and charred peel (CP) grafted peel (GP), charred peel (CP).

5 sample of each adsorbent (0.5 gm) was taken in a reagent bottle. Various doses of iron concentration in the range of 100-500 µgm were added to each solution and diluted to 100 ml with distilled water. The solutions were agitated on a shaker at 400 rpm for 4 hours. The samples were centrifuged at 4000 rpm to remove the residual adsorbents. The supernatants were transferred to volumetric flasks. 1 ml of hydroxylamine hydrochloride, 10 ml of phenanthroline solution, and 10 ml of sodium acetate solution were added. The volume was diluted to 100 ml and allowed to stand for 10 minutes. The absorbance was recorded for each solution on a UV visible spectrophotometer at 506 nm. The concentration of iron left in the supernatant was determined from calibration curve.

## Results and Discussions

### Characterization of bio sorbent banana peel (raw)

**SEM and EDX analysis of the bio sorbents:** Figures 1a and 1b represents the characterization of banana peel biosorbent scanning

electron microscopy (SEM). It show the porous nature and an irregular surface morphology. EDX analysis of banana peel is shown in the Figure 1b. It shows the percentage weight of various elements as: 49.60% of C, 28.34% of O, 12.02% of K, 1.46% of Si, 2.52% of Ca, 0.56% of Na, 0.67% of Al, and 0.73% of Mg [11,12].

**An FTIR spectrum of banana peel:** The Figure 2 shows the FTIR spectrum of raw banana peel. The bands in the region of 3486 and 3286 cm<sup>-1</sup> were assigned to O-H stretching, those at 2920 and 2951 cm<sup>-1</sup> to C-H stretching.

**Thermal treatment of banana peel at 300°C:** Indurin the carbonization process, the development of porosity of banana peel charcoal starts at 300°C and increases with increasing carbonized temperature. Scanning electron microscopy is used to visualise the surface morphology of the charcoal Figures 1a and 1b show a pore and a cellular structure of banana peel charcoals which is carbonized at 300°C to 400°C. A temperature of 300°C to 400°C led to incomplete carbonization of banana peel and the cell structure is maintained. There are seemed some small pores due to the release of some volatile compounds.

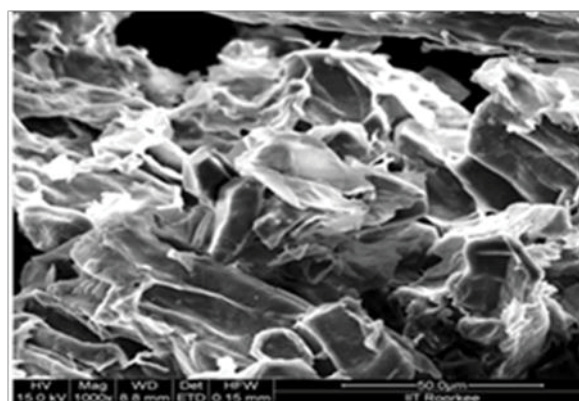
The study of Mendez et al. [13] showed that the main important weight changes are produced due to the light compounds volatilization and pyrolysis transformations at 450°C. This stage is primary pyrolysis (in the 300°C to 500°C range) with evolution of most gases and tars with formation of the basic structure of the char [14].

### FTIR Characterization of the grafted rice husk

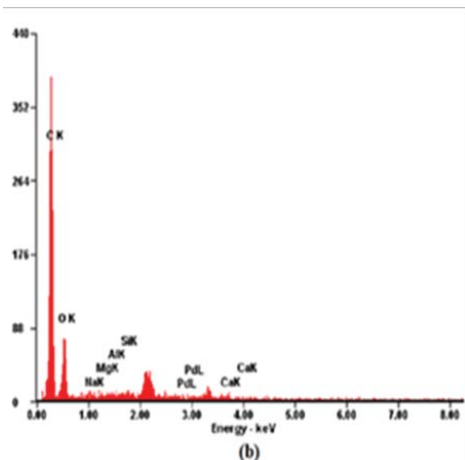
The banana peel was hydrolysed with 5% sulphuric acid followed by hydrolysis with 10% sodium hydroxide for 2.5 hours under reflux (liquor ratio: 1:15 w/v). The purpose of hydrolysis was to remove lignin as far as possible. Grafting was carried out by steeping 2 g hydrolysed rice husk in acrylonitrile solution for 15 minutes and then added the dissolved hydrogen peroxide (0.3 mL) and 0.5 g ferric sulphate in glacial acetic acid at 40°C for 2.5 hrs (total liquor ratio was 1:15 i.e. total quantity of grafting liquor was 100 mL). After grafting the sample was filtered washed with distilled water and then dried in air. This dried sample was extracted with distilled water in a Soxhlet device for 24 hrs to dissolve the formed homopolymer. After extraction, the sample was washed with distilled water and then air dried [15]. The functionalized banana peel was characterized by FTIR spectrophotometer Shimadzu Prestige-21 as shown in Figures 3a and 3b. The various band specification of the spectra are given in Table 1.

### Adsorption studies of iron

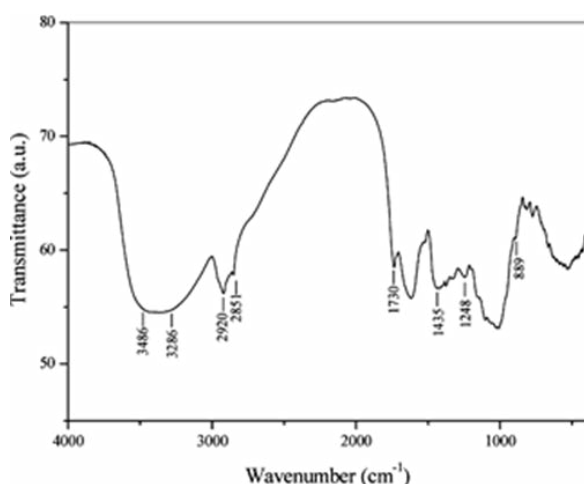
The adsorption of iron on modified banana peel was carried out by



**Figure 1a:** SEM micrograph of banana peel (RP).



**Figure 1b:** EDX analysis of banana peels (RP).



**Figure 2:** Infrared spectrum of banana peel obtained with 1 mg of adsorbent and 500 mg of KBr.

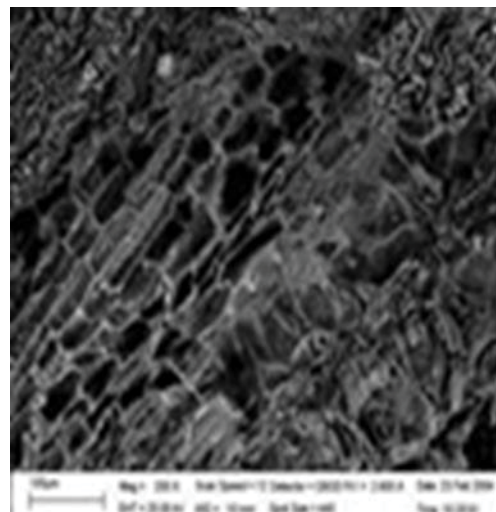
batch technique. Three adsorbents (RP), grafted (GP) with acrylonitril, charred peel (CP) were tested to assess their potential to remove iron from aqueous system by adsorption. The equilibria of the adsorption and the kinetics are two important physico-chemical aspects for the evaluation of the adsorption process as a unit operation. Equilibrium studies give the capacity of the adsorbent and are described by adsorption isotherms. Generally the ratio between the quantity adsorbed and that remaining in the solution at a constant temperature is at equilibrium. There are two types of adsorption isotherms i.e. Langmuir and Freundlich's Table 2.

**Langmuir isotherm:** The Langmuir model predicts that the uptake of the adsorbate occurs on a homogeneous surface by a monolayer adsorption without any interaction between the adsorbate molecules [16]. The linear form of Langmuir equation

$$C_e / Q_e = 1 / K + a / K C_e$$

Where

$C_e$  is the equilibrium concentration of adsorbate (mg/L).



**Figure 3a:** Surface images of banana peel charcoal with carbonized temperature of 300°C.

$Q_e$  is the amount of the adsorbate adsorbed at equilibrium (mg/g).

The linear plot of  $C_e/Q_e$  vs  $C_e$  gives a straight line. The various parameters of the Langmuir isotherm are as follows:

$$a / K = Q_m = \text{slope} = \text{adsorption capacity}$$

$$1 / K = \text{intercept of the line}$$

$$b = Q_m / K = \text{Energy of adsorption}$$

$$a = Q_m$$

**Freundlich isotherm:** The Freundlich isotherm assumes that the uptake of adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration [16]. The Freundlich isotherm is represented by the linear equation.

$$\ln Q_e = \ln K + 1/n \ln C_e$$

Where,

$K$  and  $1/n$  are Freundlich constants,

$Q_e$  is the amount of adsorbate adsorbed at equilibrium and  $C_e$  is the equilibrium concentration of the adsorbate in the solution.

A linear plot of  $\ln(Q_e)$  vs  $\ln(C_e)$  gives a straight line.

The intercept of the line is  $K$  (adsorption capacity),

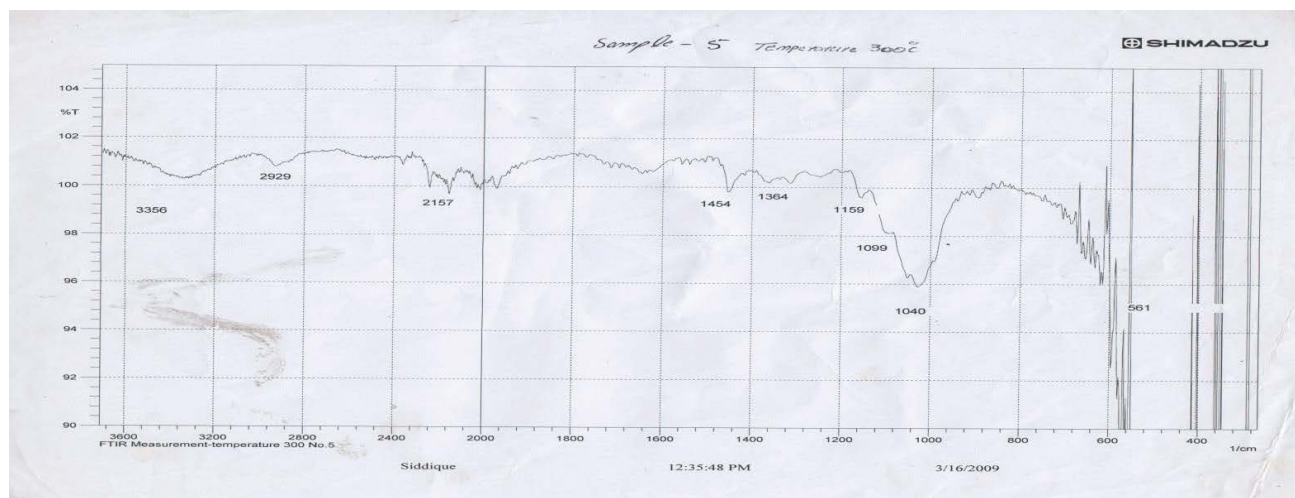
Slope is  $1/n$  (adsorption intensity) and

" $n$ " gives the favorability of adsorption ( $0 < n < 10$ )

These both are called isotherms because they give a straight line at constant temperature.

**Langmuir isotherm of iron:** The Langmuir adsorption isotherm data of iron on all the 3 adsorbents are given in Table 3 and 4; Figures 4-6. The Langmuir constants for various adsorbents are shown in Table 5. The adsorption capacities ( $Q_m$ ) of the 3 adsorbents shown in Table 6, shows that it is highest (1.8) for the charred peel (CP) and lowest (0.93) for the grafted peel (GP). The highest adsorption capacity of the charred peel (CP) shows that many sites on the surface of the adsorbent





**Figure 3b:** FTIR spectra of banana peel grafted with acrylonitrile.

S No.	Frequency in $\text{cm}^{-1}$	Functional group
1	3356	-OH stretching
2	2929	C-H stretching (aliphatic)
3	2157	-CN stretching
4	1450	C=C stretching aliphatic
5	1364	C-H bending aliphatic

**Table 1:** FTIR band of grafted banana peel with acrylonitrile.

S N.o	Conc	Raw peel (RP)		Grafted Peel (GP)		Charred Peel (CP)	
		Ce	Qe	Ce	Qe	Ce	Qe
1	100 $\mu\text{g}$	0.42	0.06	0.42	0.060	0.21	0.08
2	200 $\mu\text{g}$	0.92	0.11	0.91	0.12	0.64	0.14
3	300 $\mu\text{g}$	1.53	0.15	1.49	0.16	1.10	0.20
4	400 $\mu\text{g}$	2.20	0.20	2.04	0.21	1.72	0.23
5	500 $\mu\text{g}$	2.85	0.22	2.56	0.22	2.56	0.24

**Table 2:** Adsorption equilibrium data of iron on raw peel, grafted peel and charred peel: Equilibrium concentration in  $\text{mg/L} = \text{Ce}$  Adsorbed concentration in  $\text{mg/g} = \text{Qe}$ .

are unoccupied by the adsorbate molecules and most of the adsorbate molecules are still present in the solution and are not adsorbed by the adsorbent. The lowest adsorption capacity of grafted peel (GP) shows the reverse trend and mostly the adsorbate molecules are bonded to the adsorbent surface. The energy of adsorption (b) is found to be maximum (8.48) for raw peel (RP) and minimum (1.37) for charred peel (CP).

**Freundlich isotherm model of iron:** The Freundlich adsorption isotherm data is given in Table 5 and Figures 7-9. The Freundlich constants are given in Table 6. The adsorption capacities (K) of the various adsorbents show that it is highest (3.95) for charred peel (CP) and lowest (2.78) for grafted peel (GP). The adsorption intensities ( $1/n$ ) is highest (0.75) for charred peel (CP) and lowest (0.13) for grafted peel (GP). The n value (which is the measurement of the favorability ( $0 < n < 10$ ) of adsorption) ranges from 1.34 for charred peel (CP) to a

maximum of 7.62 for grafted peel (GP). The  $R^2$  which is measurement of the fitness of the adsorption model is in the range of 0.94 for grafted peel (GP) and a maximum value of 0.96 for raw peel (RP). The  $R^2$  value of all the adsorbents show that the adsorption isotherm data of iron on modified banana peels products can be well fitted on the Freundlich isotherm equation.

## Conclusion

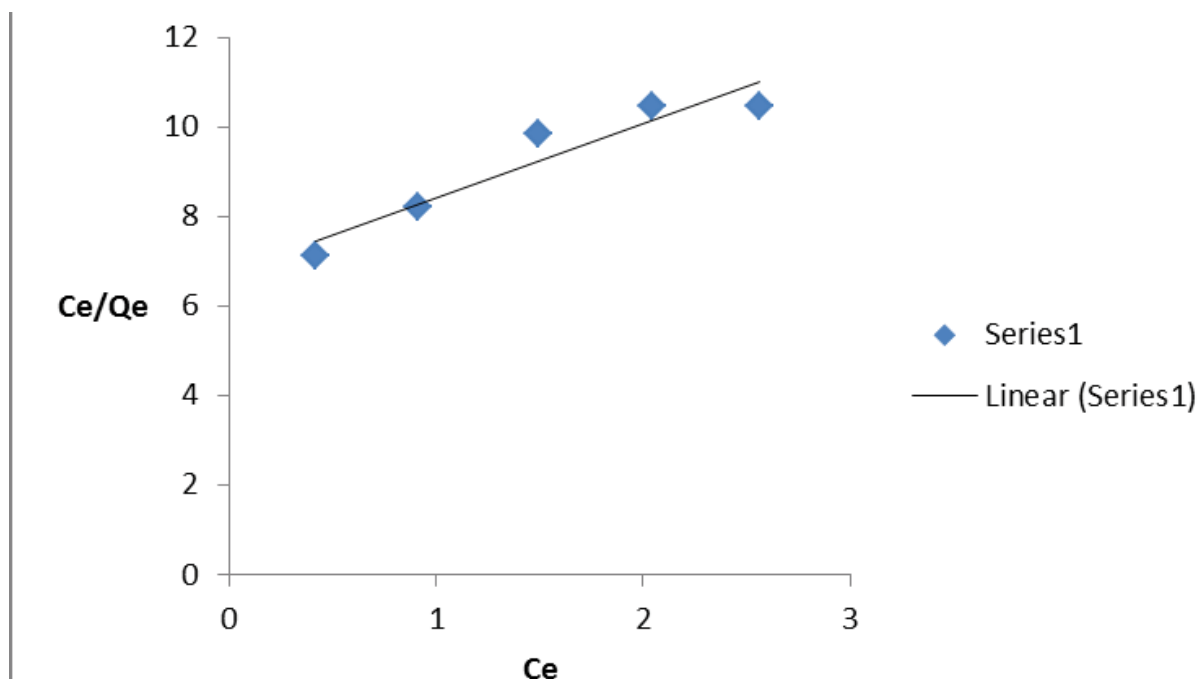
The above results show that agriculture residues including modified banana peels products can be efficiently and cost effectively used in water treatment technologies for the effective removal of various toxic metals and other hazardous substances. The use of these biowastes in water purification will not only help in the reduction of environmental pollution associated with them but will also convert them into valuable products which will be helpful in the economic growth of the community at large.

S No.	Conc	(RP)		(GP)		(CP)	
		Ce	Ce/Qe	Ce	Ce/Qe	Ce	Ce/Qe
1	100 µg	0.416	7.12	0.42	2.68	0.21	7.35
2	200 µg	0.91	8.21	0.92	4.73	0.64	8.50
3	300 µg	1.49	9.85	1.53	5.75	1.09	10.45
4	400 µg	2.04	10.45	2.20	6.20	1.72	11.45
5	500 µg	2.56	10.46	2.85	10.45	2.56	13.22

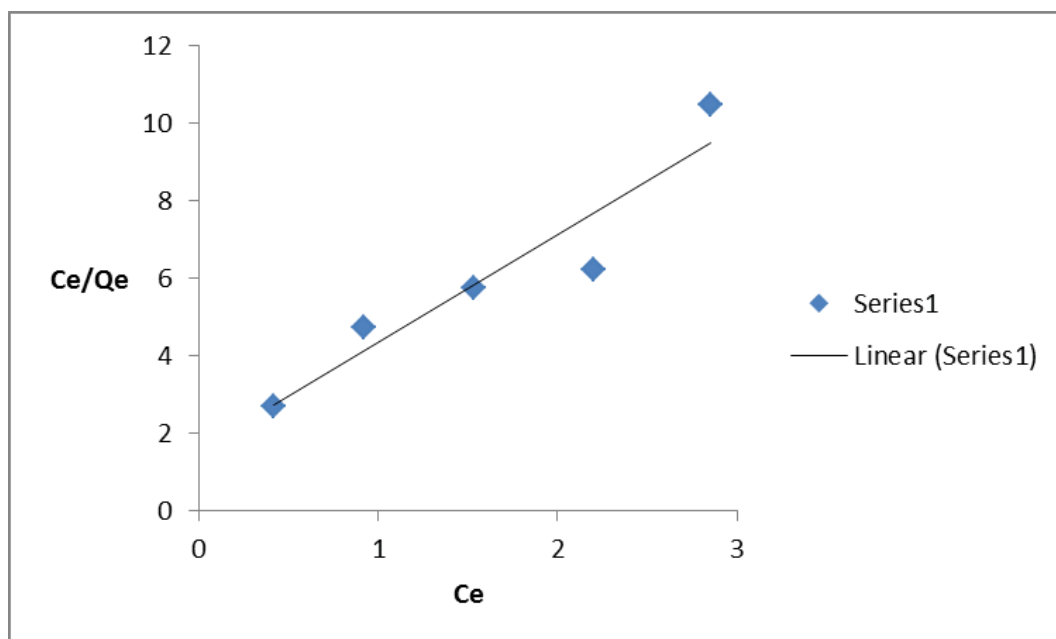
**Table 3:** Langmuir isotherm data of iron on banana peel (BP), grafted peel (GP) and charred peel (CP): Equilibrium concentration in mg/L=(Ce), Adsorbed concentration in mg/g=(Qe).

S No.	CONC	( RP)		(GP)		(CP)	
		Ce	Qe	Ce	Qe	Ce	Qe
1	100 µg	-0.86	-2.85	-0.87	-2.84	-1.55	-2.54
2	200 µg	-0.08	-2.22	0.1	-2.22	-0.44	-1.99
3	300 µg	0.43	-1.91	0.40	-1.88	0.09	-1.66
4	400 µg	0.71	-1.63	0.71	-1.63	0.54	-1.47
5	500 µg	1.05	-1.53	0.93	-1.41	0.93	-1.41

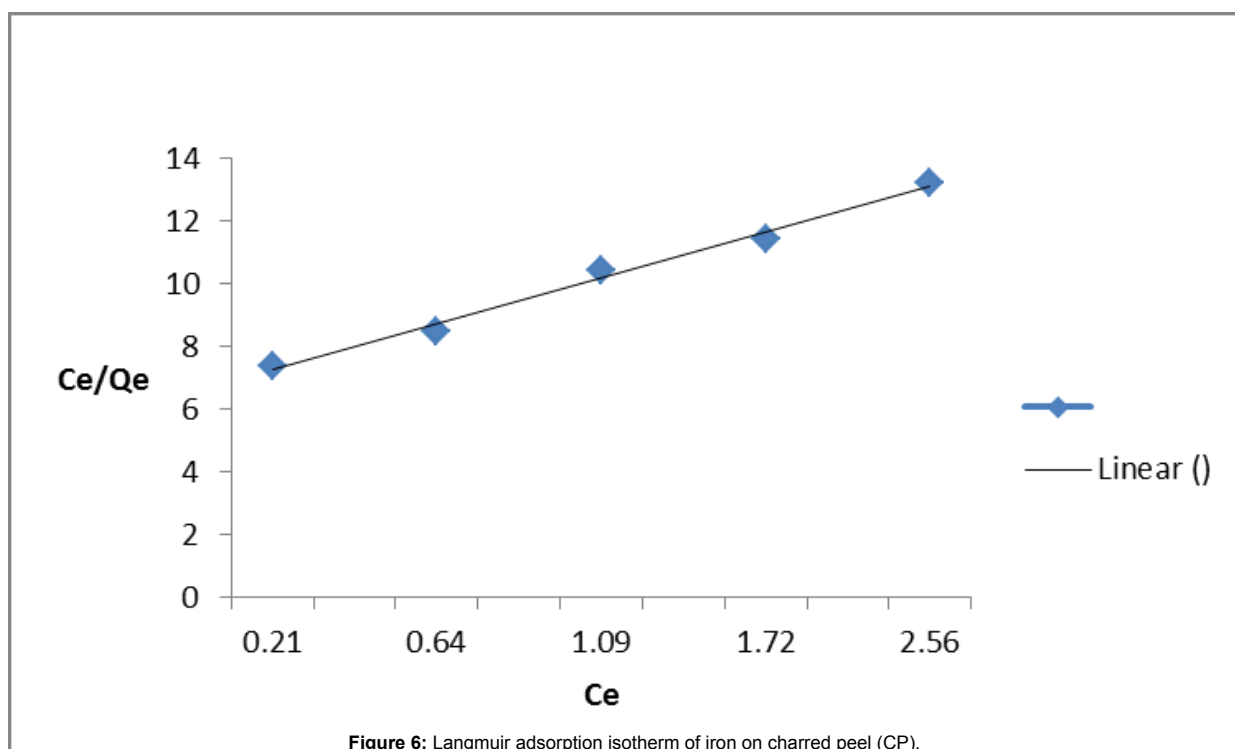
**Table 4:** Freundlich isotherm data of iron on banan peel, grafted peel and charred peel. Equilibrium concentration in mg/L=(Ce) Adsorbed concentration in mg/g=(Qe).



**Figure 4:** Langmuir adsorption isotherm of phenol on raw peel (RP).



**Figure 5:** Langmuir adsorption isotherm of iron on grafted peel (GP).



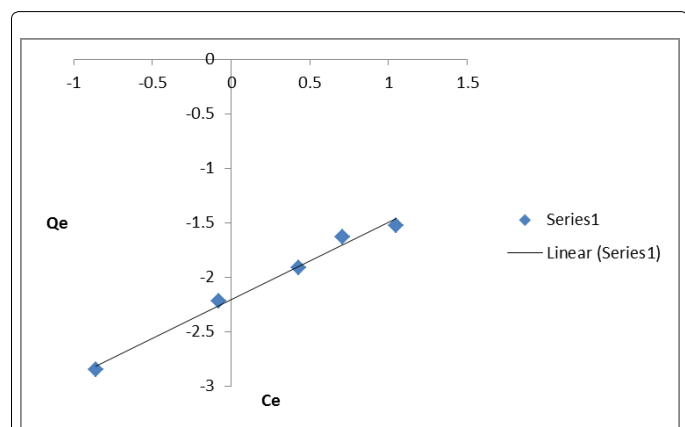
**Figure 6:** Langmuir adsorption isotherm of iron on charred peel (CP).

S No.	Adsorbent	1/K	K	Qm	R <sup>2</sup>	A	B
1	(RP)	5.79	0.17	1.47	0.99	0.25	8.48
2	(GP)	6.48	0.15	0.93	0.93	0.14	6.06
3	(CP)	0.76	1.32	1.80	0.96	2.37	1.37

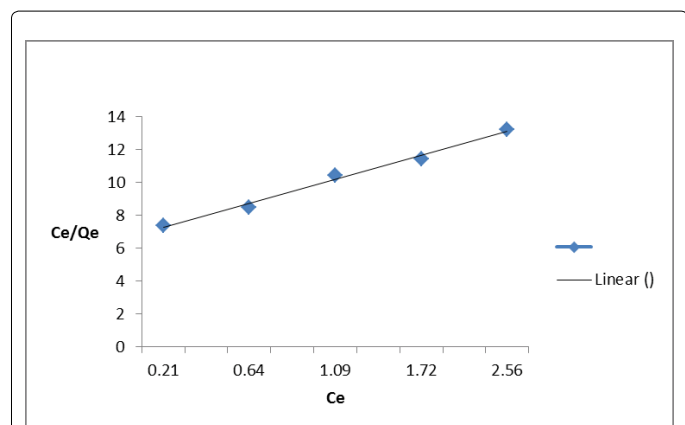
**Table 5:** Langmuir isotherm constants for banan peel, grafted peel and charred peel.

S No.	Adsorbent	K	1/n	N	R <sup>2</sup>
1	(RP)	2.89	0.14	7.34	0.96
2	(GP)	2.78	0.13	7.62	0.94
3	(CP)	3.95	0.75	1.34	0.95

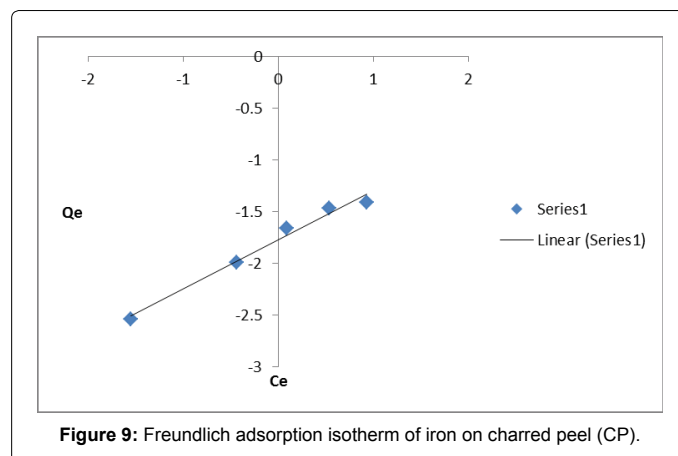
**Table 6:** Freundlich isotherm constants for banana peel, grafted peel and charred peel.



**Figure7:** Freundlich adsorption isotherm of iron on raw banana peel (RP).



**Figure 8:** Freundlich adsorption isotherm of iron on grafted peel (GP).



**Figure 9:** Freundlich adsorption isotherm of iron on charred peel (CP).

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