

# Adsorptive removal of ferrous ions from aqueous solutions using plant materials as adsorbents

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**ABSTRACT:** Batch mode adsorption studies of Fe(II) ions on adsorbents originated from plant materials were carried out. Effects of initial Fe(II) ions concentration, adsorbent dose, pH, agitation time, agitation speed, particle size of adsorbent and temperature on adsorption were studied. All Freundlich, Langmuir as well as Temkin adsorption isotherm models showed linearity and were found to be the best fitting isotherm models. The monolayer adsorption capacities ( $q_m$ ) were found between 5.236 to 15.385 mg/g for adsorbents under study. Lagergen pseudo -second order and Elovich Second order kinetic models fits with the adsorption studies indicating adsorption depends on nature of adsorbent as well as adsorbate. Adsorption of Fe(II) ions increases with increase in pH, temperature and agitation speed but decreases with increase in particle size. Thermodynamic analysis also showed that adsorption of Fe(II) ions on the adsorbents under study was favourable. Adsorption capacity of Tamarind (*Tamarindus indica*) Fruit Shell Powder towards Fe(II) ions was found to be more than the other adsorbents under study.

**KEY WORDS:** Fe (II) ions, Plant materials, Adsorption isotherms

## I. INTRODUCTION

Industries like car, aeronautic, coating and steel generate large amount of wastewater containing different concentrations of iron [1]. Water Percolating through soil and rock can dissolve minerals containing iron and hold it in solution. Iron pipes also be a source of iron in water. Ferrous iron is a highly soluble in water that and is easily absorbed into biological species. Therefore, Fe(II) is considered to be the most acutely toxic form of iron. Fe(II) creates oxidative stress by inducing the formation of oxygen based radicals that can cause membrane and DNA damage.

Increased concern by environmentalists and governments on the effects of Fe(II) and an attempt to protect the public health has resulted in increased research in the development of advance methods and technologies to remove Fe(II) from water and wastewater [2]. It involved application of unit operations or unit processes such as chemical precipitation, adsorption, coagulation, ion exchange and membrane filtration [3]. A number of adsorbent materials have been studied for their ability to remove heavy Fe(II) ions and sourced from natural materials and biological wastes of industrial processes [4]. These materials include: chitosan and carrageenan [2], lignite [5], limestone [6], thioglycolic acid modified oil-palm [7],

Adsorption by activated carbon had reported as a technically and economically viable technology for Fe(II) removal [8] [2].

Different types of agriculture wastes such as maize tassel [9], banana peel [10], sawdust and neem bark [11], wheat straw, soybean straw, corn cobs and corn stalks [12] and Pinus sylvestris sawdust [13] have been studied,

In the present study, some plant residues used as biosorbents for the removal of Fe(II) ions from wastewater.

## II. MATERIALS AND METHODS

### 2.1 ADSORBENTS:

Adsorbents used in the present study are:

- 1) Pineapple (*Ananas comosus*) Peel Powder (PPP)
- 2) Mangrove (*Sonneratia apetala*) Plant Fruit Powder (MPFP)
- 3) Coconut (*Cocos nucifera*) Coir Pith (CCP)
- 4) Mango (*Mangifera indica*) Leaf powder (MLP)
- 5) Toor (*Pisum sativum*) Plant Leaf Powder (TPLP)
- 6) Tamarind (*Tamarindus indica*) Fruit Shell Powder (TFSP)

### 2.2 ADSORBATE:

**Fe(II) ions:** Ferrous ammonium sulphate with molecular weight 392.12 supplied by S.D. Fine Chemicals, Mumbai, is used for generation of Ferrous ions in aqueous solution.

**Synthetic Wastewater Preparation:** An aqueous stock solution (1000mg/l) of Fe (II) ions is prepared using ferrous ammonium salt. 7.022 g of crystallized ferrous ammonium sulphate is dissolved in 500 ml of water and 50 ml of 1:1 H<sub>2</sub>SO<sub>4</sub> is added. The solution is diluted and made up to 1litre.

During batch mode studies fresh dilutions are used every time.

Concentration of Fe (II) in the supernatant after batch mode adsorption studies is determined spectrophotometrically by 1,10 – Phenanthroline method.

### 2.3. BATCH MODE ADSORPTION STUDIES:

#### 2.3.1 EFFECT OF AGITATION TIME

25 mg adsorbents are shaken with 25 ml Fe(II) ion solution of initial concentration 10 mg/l on an oscillator for 5, 10, 15, 20, 30, 40, 50 and 60 minutes time intervals.

Other parameters: Particle size of adsorbents  $\geq$  120 mesh, Agitation speed = 230 rpm, pH = 2.5, Temperature  $\approx$  303K.

Optimum agitation time is identified and then used for further batch mode studies.

#### 2.3.2 EFFECT OF DOSE OF ADSORBENT

Initial Fe(II) ion concentration of 25 mg/l is used in conjunction with adsorbent doses of 1, 2, 3, 4, 5, and 6 g/l.

Other parameters: Particle size of adsorbents  $\geq$  120 mesh, Agitation time = 40 minutes, Agitation speed = 230 rpm, pH = 2.5, Temperature  $\approx$  303K.

#### 2.3.3 EFFECT OF INITIAL FE(II) ION CONCENTRATION

Initial Fe(II) ion concentrations of 4, 6, 8, 10, 12 and 14 mg/l are used in conjunction with adsorbent dose of 1 g/l.

Other parameters: Particle size of adsorbents  $\geq$  120 mesh, Agitation time = 40 minutes, Agitation speed = 230 rpm, pH = 2.5, Temperature  $\approx$  303K.

#### 2.3.4 EFFECT OF pH

Initial pH of Fe(II) ion solutions are adjusted to 1, 1.5, 2, 2.5 and 3 for 10 mg/l concentration.

Other parameters: Particle size of adsorbents  $\geq$  120 mesh, Adsorbent dose = 1 g/l, Agitation time = 40 minutes, Agitation speed = 230 rpm, Temperature  $\approx$  303K.

#### 2.3.5 EFFECT OF PARTICLE SIZE

Three different sized particles of  $\geq$  120,  $120 \leq 85$  and  $85 \leq 60$  meshes are used in conjunction with 6 mg/l Fe(II) ion concentration.

Other parameters: Adsorbent dose = 1 g/l, Agitation time = 40 minutes, Agitation speed = 230 rpm, pH = 2.5, Temperature  $\approx$  303K.

### 2.3.6 EFFECT OF AGITATION SPEED

100, 170 and 230 rpm agitation speeds are used in conjunction with initial Fe(II) ion concentration of 10 mg/l.

Other parameters: Particle size of adsorbents  $\geq$  120 mesh, Adsorbent dose = 1 g/l, Agitation time = 40 minutes, pH = 2.5, Temperature  $\approx$  303K.

### 2.3.7 EFFECT OF TEMPERATURE

303K, 313K and 323K temperatures are used in conjunction with 8 mg/l Fe(II) ion concentration.

Other parameters: Particle size of adsorbents  $\geq$  120 mesh, Adsorbent dose = 1 g/l, Agitation time = 40 minutes, Agitation speed = 230 rpm, pH = 2.5.

### 2.4 COD REDUCTION STUDIES:

COD of Fe(II) ion solution before and after adsorption is determined for 10 mg/l initial Fe(II) ion concentration for an adsorbent with highest adsorbent capacity. Reduction in COD due to removal of Fe(II) ion after adsorption is then tabulated.

## III. RESULTS AND DISCUSSION

### 3.1 EFFECT OF AGITATION TIME

Effect of Agitation time on adsorption of Fe (II) ions is presented in **Figure 1**. In first 5 minutes the adsorption of Fe(II) ions is rapid and adsorption equilibrium is attended after 30 to 40 minutes. Therefore, 40 minutes optimum agitation time is taken for further batch mode studies.

The rapid adsorption at initial stage is due to more number of active sites on the surface of adsorbent, followed by slower adsorption due to intra particle diffusion.

At adsorption equilibrium 32 to 86 % removal of Fe (II) ions is observed depending upon the adsorption capacities of adsorbents under study.

Order of adsorption capacities of adsorbents is TFSP > CCP > TPLP > MLP > PPP > MPFP.

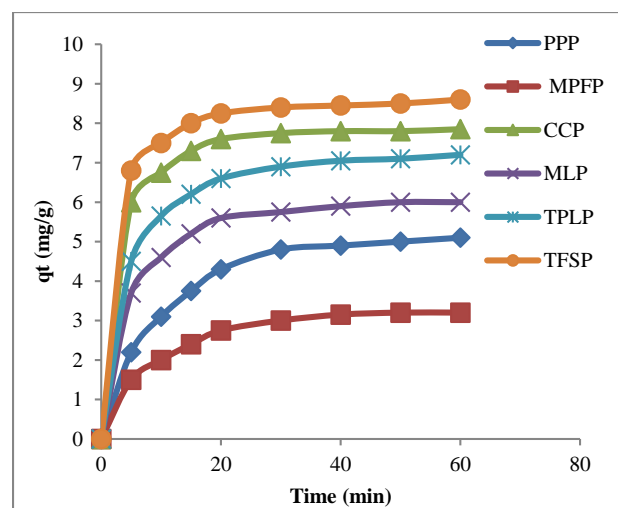


Figure 1: Effect of agitation time on adsorption of Fe (II) ions.

The mechanism of adsorption is investigated by pseudo - first order, pseudo- second order, Natarajan and Khalaf first order, Bhattacharya and Venkobachar first order, intraparticle diffusion and Elovich kinetic models.

Langergen pseudo first order kinetic model plot of  $\log (q_e - q_t)$  versus  $t$  (Figure 2) appears linear but  $q_{e(\text{exp})}$  values differ from the corresponding  $q_{e(\text{the})}$  showed that adsorption of Fe(II) ions on adsorbents CCP, MLP, TPLP and TFSP is not a first order kinetics. But adsorption of Fe (II) ions on PPP and MPFP,  $q_{e(\text{exp})} \approx q_{e(\text{the})}$  showed first order kinetics and here weaker forces overcame the stronger chemisorptions during adsorption. (Table 1)

Langergen pseudo second order kinetic model plot of  $t/q_t$  versus  $t$  (Figure 3) is highly linear and thus chemisorption playing a significant role in the rate determining step. The correlation coefficient  $R^2$  lie between 0.995 to 0.999 and  $q_{e(\text{exp})} \approx q_{e(\text{the})}$  showed that pseudo second order adsorption equation of Langergen fit well with whole range of agitation time. This shows that the adsorptions of the Fe(II) ions onto adsorbents under study follow second order kinetics. (Table 1) and rate of adsorption depends on nature of adsorbate as well as adsorbents under study.

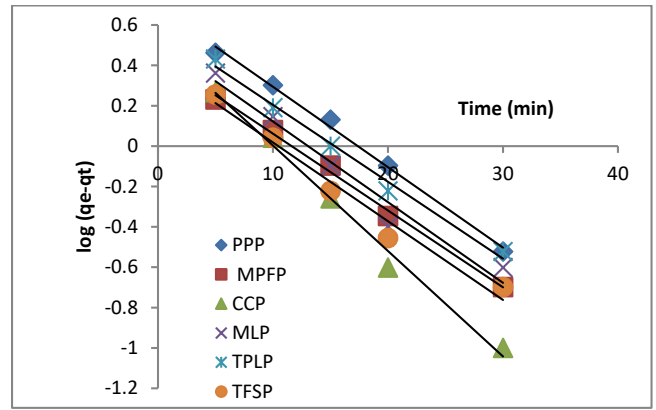


Figure 2: Pseudo first order plot

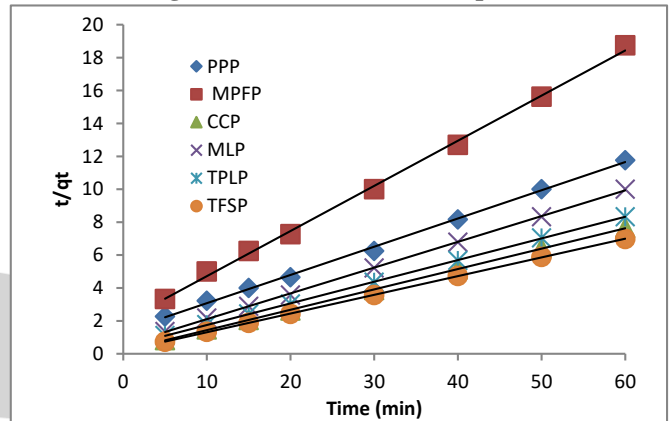


Figure 3: Pseudo second order plot

Table1: Effect of agitation time on adsorption of Fe (II) ions

Adsorbent	Initial Fe (II) ion Conc. (mg/l)	Pseudo -first order model				Pseudo -second order model				
		$q_{e(\text{exp})}$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$q_{e(\text{the})}$ (mg/g)	$R^2$	$q_{e(\text{exp})}$ (mg/g)	$K_2$ (g/mg/min)	$q_{e(\text{the})}$ (mg/g)	$h$ (mg/g .min)	$R^2$
PPP	10	5.1	0.08982	4.90908	0.995	5.1	0.02153	5.84795	0.73638	0.998
MPFP	10	3.2	0.08751	2.76694	0.995	3.2	0.03792	3.64964	0.50505	0.998
CCP	10	7.85	0.11976	3.34965	0.99	7.85	0.08233	7.8125	5.02513	0.999
MLP	10	6	0.08982	3.31894	0.963	6	0.04532	6.41026	1.8622	0.999
TPLP	10	7.2	0.87514	3.83707	0.99	7.2	0.03945	7.63359	2.29885	0.999
TFSP	10	8.6	0.08982	2.55859	0.973	8.6	0.07424	8.84956	5.81395	0.999

$K_{ad}$  is first order adsorption rate constant ( $\text{min}^{-1}$ ) calculated from slope of the Natarajan and Khalaf first order kinetic linear plot  $\log(C_0/C_t)$  against  $t$ , Figure 4, Table 2. Correlation coefficient values ( $R^2$ ) showed that Natarajan and Khalaf first order kinetic equation does not fit well with whole range of agitation time. If the forward rate constant ( $K_1$ ) is much higher than the reverse rate constant ( $K_2$ ), i.e.  $K_1/K_2 > 1$  indicating the rate of adsorption is dominant and the adsorbent have better adsorption capacity. But if  $K_1/K_2 < 1$ , rate of desorption is dominant and the adsorbent have weaker adsorption capacity.  $K$  is first order adsorption rate constant Bhattacharya and Venkobachar first order kinetic equation ( $\text{min}^{-1}$ ) which is calculated from slope of the linear plot  $\log [1 - U(T)]$  against  $t$ , Figure 5, Table 2. Quiet good linearity with respect to  $R^2$  value is observed for

Bhattacharya and Venkobachar first order equation for adsorption of Fe(II) ion on these adsorbents till equilibrium time.

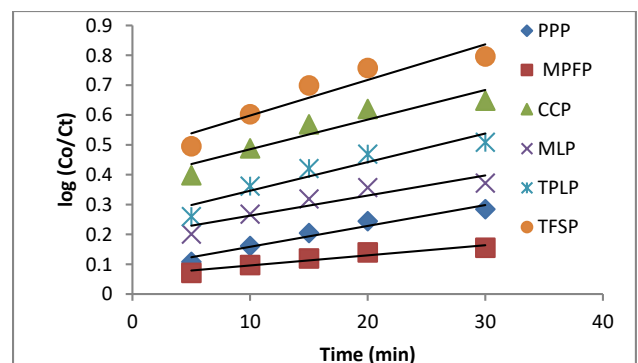


Figure 4: Natarajan and Khalaf first order plot

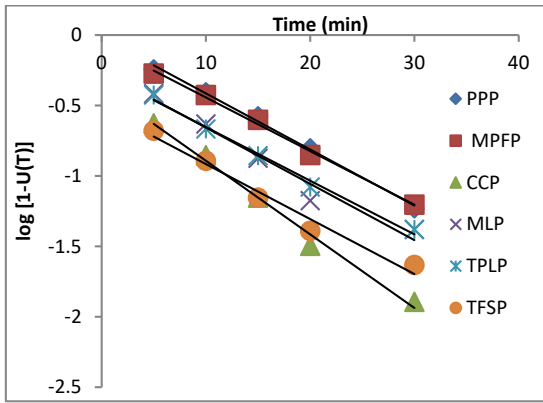


Figure 5: Bhattacharya and Venkobachar first order plot

The intra particle diffusion rate constant  $K_i$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) values are determined from the slope of the plot  $q_t$  against  $t^{1/2}$ , Figure 6, Table 2 showed a linear relationship only after certain time but they do not pass through origin due to boundary layer effect. Higher values of  $K_i$  and intercepts means an enhancement in the rate of adsorption. The larger value of intercepts means greater the contribution of surface sorption in rate determining step.

Elovich kinetic model constants  $\alpha$  and  $\beta$  are calculated, from the intercept and slope of plot  $q_t$  against  $\ln t$ , Figure 7, Table 2. This Elovich kinetic model gave quiet linear relationship with respect to Correlation coefficient values ( $R^2$ ). The Elovich model describes second-order kinetic, assuming that the actual solid surface is energetically heterogeneous. Constant  $\alpha$  depends on initial rate of adsorption which is high

for an adsorbent which has high adsorption capacity but constant  $\beta$  which is desorption constant has the low value for the same adsorbent and vice versa. This showed that Elovich kinetic model fit reasonably well for the adsorbents under

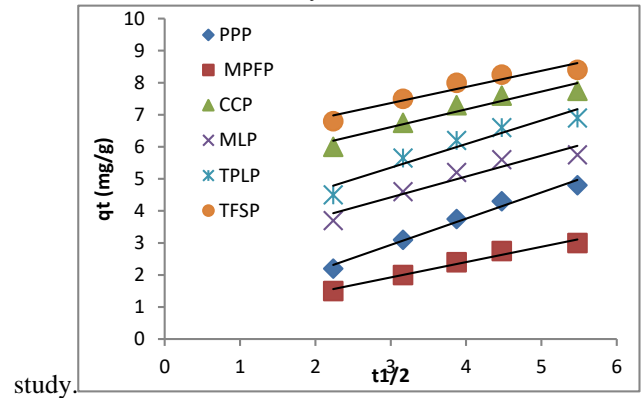


Figure 6: Intra particle diffusion plot

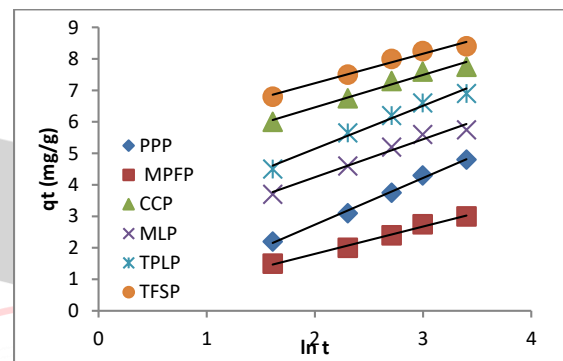


Figure 7: Elovich plot

Table 2: Effect of Agitation time on adsorption of Fe (II) ions

Adsorbent	Initial Fe (II) ion Conc. (mg/l)	Intra particle diffusion model			Elovich Model			Natarajan and Khalaf model		Bhattacharya and Venkobachar model	
		$K_i$ ( $\text{mg/g/min}^{1/2}$ )	A (mg/g)	$R^2$	$\alpha$ ( $\text{mg/g/min}$ )	$\beta$ ( $\text{g.mg}^{-1}$ )	$R^2$	K ( $\text{min}^{-1}$ )	$R^2$	K ( $\text{min}^{-1}$ )	$R^2$
PPP	10	0.817	0.488	0.981	0.0025	0.673	0.995	0.016	0.957	0.089	0.995
MPFP	10	0.477	0.494	0.975	174303	1.153	0.99	0.006	0.936	0.087	0.995
CCP	10	0.554	4.949	0.919	1.30004	0.971	0.974	0.020	0.877	0.119	0.99
MLP	10	0.649	2.473	0.918	2.33107	0.829	0.973	0.013	0.862	0.089	0.963
TPLP	10	0.736	3.138	0.927	2.4110	0.731	0.982	0.020	0.895	0.087	0.99
TFSP	10	0.504	5.852	0.917	1.1148	1.068	0.974	0.025	0.885	0.089	0.973

### 3.2 EFFECT OF DOSE OF ADSORBENT

The adsorption studies of Fe (II) ions were carried out by varying the Dose of Adsorbents. It was found that % removal of Fe(II) ions increased (Figure 8) but amount of Fe(II) ions adsorbed per unit mass of adsorbents decreased (Figure 9) with increase in dose of adsorbents from 1 to 6 g/l. With increase in amount of adsorbent, number of active sites available for adsorption also increases thus percentage removal of Fe(II) ions also increases. But all active sites may not be available during adsorption due to overlapping between the active sites and thus amount adsorbed mg/g of adsorbent decreases. Thus, the adsorption equilibrium stage

is reached where amount of Fe(II) ions adsorbed remains constant even after increase in dosage of adsorbents. Adsorbent doses of 3 to 5 g/l are required to attend equilibrium. Adsorbent which has more adsorption capacity required lowest adsorbent dose to attend the equilibrium and vice versa. Therefore, depending upon the adsorption capacities of the adsorbents the amount of Fe(II) ions adsorbed after equilibrium per unit mass of adsorbent is different. For above 90% removal of Fe(II) ions about 3 g/l of TFSP doses is required. But for other adsorbents even 6 g/l dose also is not enough to remove 90% of Fe(II) ions.

Thus TFSP is found to be the excellent adsorbent for removal of Fe (II) from the aqueous solutions.

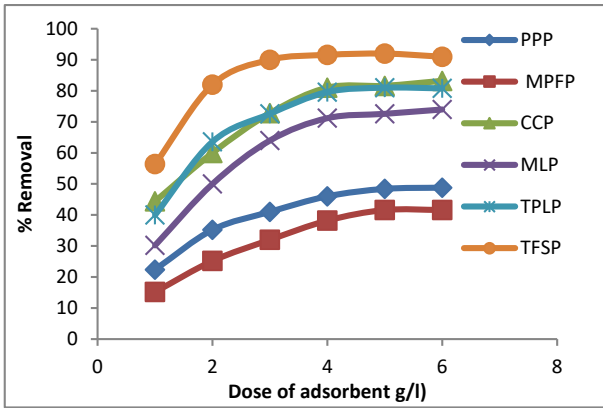


Figure 8: Effect of Dose of Adsorbent on % Removal of Fe (II).

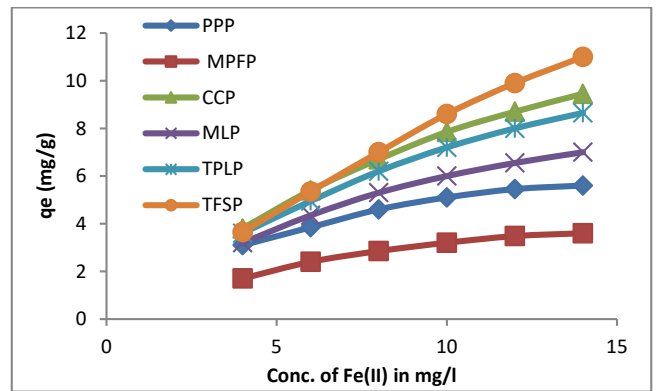


Figure 10: Effect of initial Fe(II) ion concentration on adsorption of Fe (II).

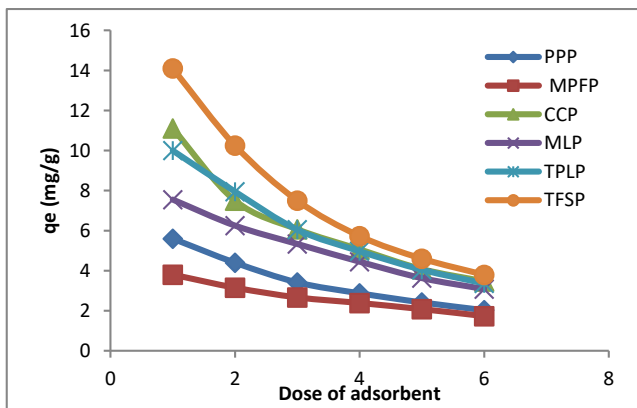


Figure 9: Effect of Dose of Adsorbent on amount of Fe (II) adsorbed in mg/g of adsorbent

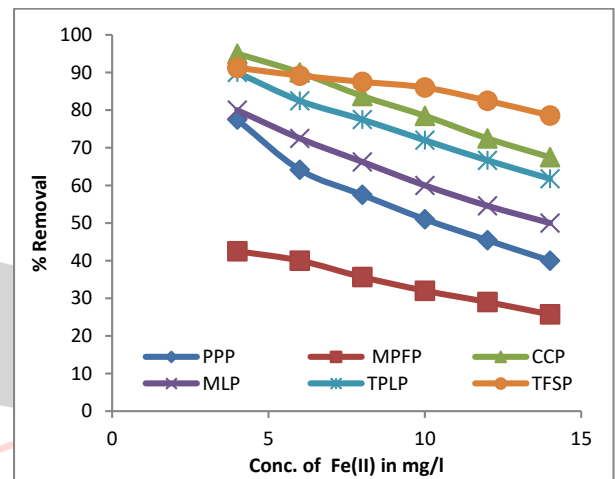


Figure 11: Effect of initial Fe(II) ion concentration on % removal of Fe (II).

### 3.3 EFFECT OF INITIAL Fe(II) ION CONCENTRATION

Amount of Fe(II) ions adsorbed per unit mass of adsorbent increased **Figure 10** but % removal decreased **Figure 11** with increase in initial Fe(II) ion concentration from 4 to 14 mg/l.

With increase in Fe(II) ions concentration from 4 to 14 mg/l, percentage sorption decreased from 77.5 to 40 % Fe (II) for PPP, 42.5 to 25.71 % Fe (II) for MPFP, 95 to 67.5 % Fe (II) for CCP, 80 to 50 % Fe (II) for MLP, 90 to 61.79 % Fe (II) for TPLP, 91.25 to 78.57 % Fe (II) for TFSP but amount of Fe(II) ions adsorbed per unit mass of adsorbent increased from 3.1 to 5.6 mg/g Fe (II) for PPP, 1.7 to 3.6 mg/g Fe (II) for MPFP, 3.8 to 9.45 mg/g Fe (II) for CCP, 3.2 to 7 mg/g Fe (II) for MLP, 3.6 to 8.65 mg/g Fe (II) for TPLP, 3.65 to 11 mg/g Fe (II) for TFSP,.

At any agitation time, increase in initial Fe(II) ion concentration decreased the percent adsorption and increased the amount of Fe(II) ion uptake ( $q_1$ ) per unit weight of the adsorbent. At low initial Fe(II) ion concentration, the percent uptake of the Fe(II) ion is high but the actual amount of the Fe(II) ions adsorbed ( $q_1$ ) is low and vice versa.

The plot of  $\log q_e$  against  $\log C_e$  shows good linearity ( $R^2 = 0.962$  to  $0.998$ ) indicating the adsorption of Fe(II) ions obeys the Freundlich adsorption isotherm, **Figure 12**. The values of  $K_f$  and  $n$  are given in the **Table 3**. The adsorbent which has greater adsorbent capacity has higher value of  $K_f$  and vice versa. Values of 'n' are between 1 to 10 indicate an effective adsorption. Thus, Freundlich adsorption isotherm fit well for these adsorption studies.

Plot of  $C_e/q_e$  against  $C_e$  is linear ( $R^2 = 0.992$  to  $0.998$ ) that suggest the applicability of the Langmuir adsorption isotherm **Figure 13**. The values of  $q_m$  and  $b$  are determined slope and intercepts of the plot and are listed in **Table 3**. Monolayer (maximum) adsorption capacities ( $q_m$ ) obtained from Langmuir plot gives an idea of effectiveness of adsorbents towards Fe(II) ions. These  $q_m$  values varies from adsorbent to adsorbent and are depend upon available active sites on the surface of adsorbent.  $R_L$  values lie between 0 to 1 indicates favourable adsorption **Table 4**. Thus, Langmuir adsorption isotherm fit well to these adsorption studies.

$q_m$  values are found to be order of TFSP > CCP > TPLP > MLP > PPP > MPFP.

Plot of  $q_e$  against  $\ln C_e$  is linear ( $R^2= 0.986$  to  $0.999$ ) **Figure 14**. Temkin constants B and A are calculated from the slope and intercept of the plot. The results of the plot are listed in **Table 3**. Constant A (equilibrium binding constant) and B related to heat of adsorption are in good agreement with the adsorption capacities of the adsorbents. Heat of adsorption values are greater for the adsorbent which has greater adsorption capacities indicates endothermic adsorption. Thus, Temkin adsorption isotherm also fit well to these adsorption studies.

All the adsorption isotherms fit well for adsorption of Fe(II) ions on the adsorbents under study.

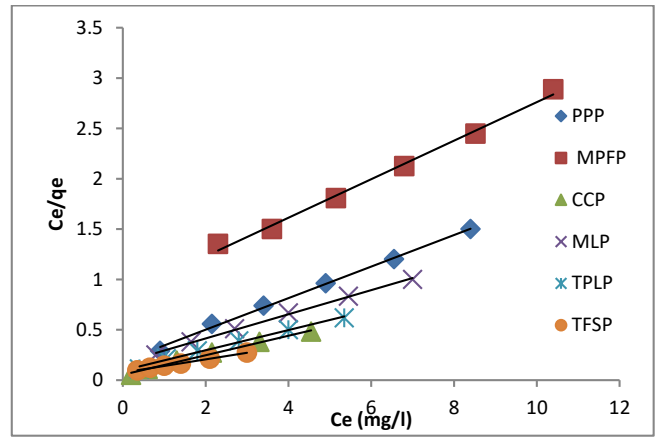


Figure 13: Langmuir adsorption isotherm plot

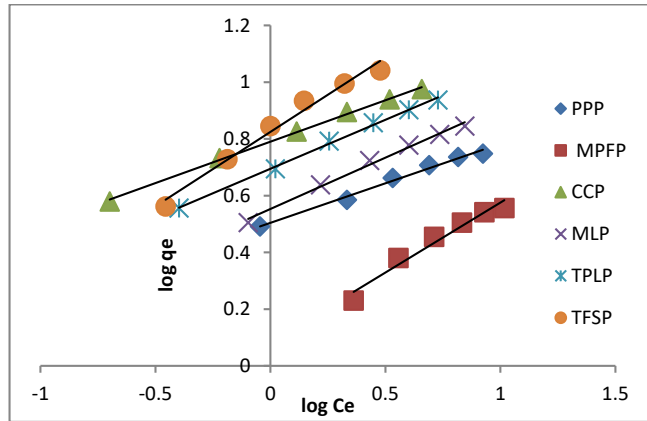


Figure 12: Freundlich adsorption isotherm plot

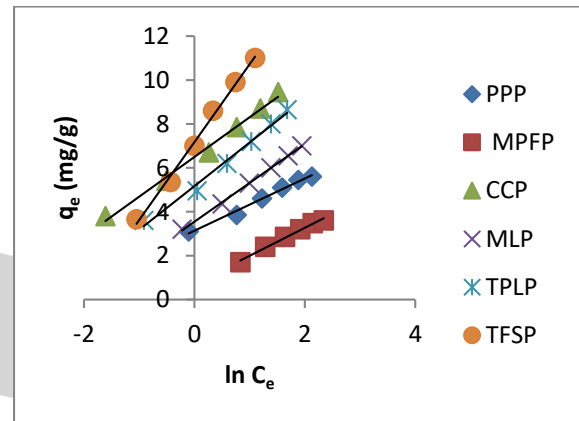


Figure 14: Temkin adsorption isotherm plot

Table 3: Effect of initial Fe(II) ion concentration on adsorption of Fe (II) ions

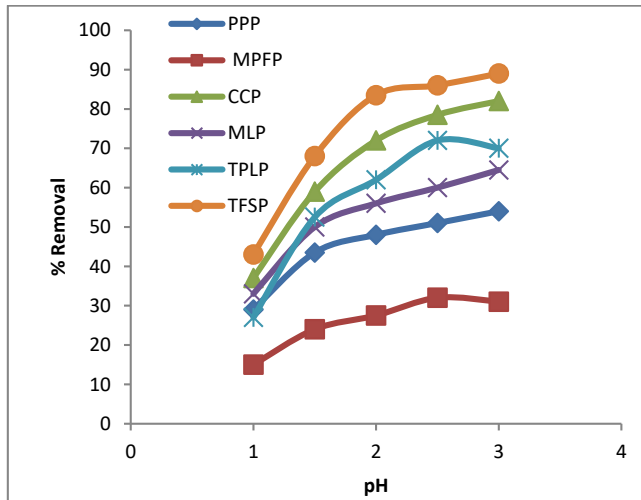
Adsorbent	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	$K_f$	$n$	$R^2$	$q_m$	$b$	$R^2$	A	B	$R^2$
PPP	3.1915	3.5971	0.988	6.41	0.8298	0.996	14.0838	1.186	0.986
MPFP	1.2078	2.0284	0.962	5.236	0.2255	0.994	1.7479	1.275	0.99
CCP	6.1659	3.4364	0.998	10.309	1.8654	0.992	36.0331	1.812	0.991
MLP	3.5727	2.77	0.991	8.403	0.6839	0.997	7.4268	1.768	0.999
TPLP	4.9431	2.8986	0.997	10	1.0417	0.992	13.4651	1.988	0.988
TFSP	6.6681	1.9084	0.98	15.385	0.8667	0.998	7.5706	3.543	0.994

Table 4: Dimensionless separation factor ( $R_L$ ) calculated from Langmuir constant (b)

Initial Fe (II) ion Conc.(mg/l)	PPP	MPFP	CCP	MLP	TPLP	TFSP
4	0.23153	0.52576	0.11818	0.26769	0.19355	0.22388
6	0.16726	0.42499	0.08202	0.19595	0.13793	0.16129
8	0.13092	0.35663	0.0628	0.15453	0.10714	0.12605
10	0.10755	0.30722	0.05088	0.12757	0.08759	0.10345
12	0.09126	0.26983	0.04276	0.10861	0.07407	0.08772
14	0.07926	0.24056	0.03688	0.09456	0.06417	0.07614

### 3.4 EFFECT OF pH

The adsorption of Fe (II) ions from 5 mg/l concentration are carried out on different adsorbents by varying the pH from 1 to 3. The amount of Fe(II) ions adsorbed per unit mass of adsorbent at equilibrium ( $q_e$ ) increases with increase in pH **Figure 15**. But for adsorbents TPLP and MPFP, adsorption is less for pH 3 than pH 2.5. Thus, adsorption batch mode studies of Fe(II) ions are carried out at pH 2.5.

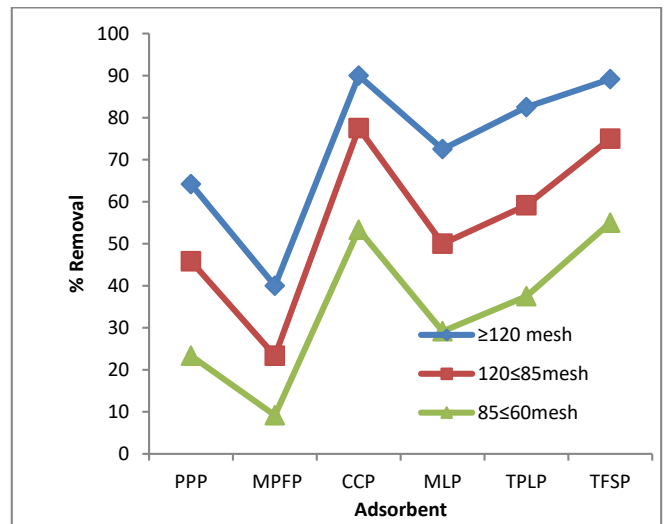


**Figure 15: Effect of pH on adsorption of Fe (II) from initial concentration of 5 mg/l**

The optimum pH for adsorption of ferrous ions on to the adsorbents is observed at pH 2.5. The lower uptake at higher pH is probably due to the formation of anionic hydroxide complexes. To avoid precipitation of ferric ions as their hydroxides, all batch mode studies are carried below pH 3.5.

### 3.5 EFFECT OF PARTICLE SIZE

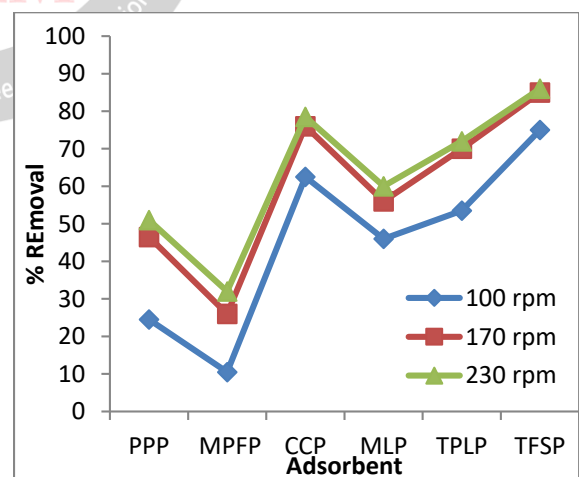
Adsorption of Fe(II) on three sized particles  $\geq 120$ ,  $120 \leq 85$  and  $85 \leq 60$  mesh of adsorbent is studied for 4 mg/l Fe(II) ion concentrations. The results of variation of these particle sizes on Fe(II) ion adsorption are shown in **Figure 16**. It can be observed that as the particle size increases the adsorption of Fe(II) ion decreases and hence the percentage removal of Fe(II) ion also decreases. This is because the smaller particles have more surface area and access to the particle pores is facilitated when their size is small. For larger particles, the diffusion resistance to mass transfer is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently amount of Fe(II) ion adsorbed is small. It is also believed that the breaking up of large particles to form smaller ones opens some tiny sealed channels, which might then become available for adsorption, and so the sorption by smaller particles is higher than that by larger particles. These observations indicate that Fe(II) ion sorption occurs by a surface mechanism. Thus batch mode studies are carried out with smaller particle size ( $\geq 120$  mesh).



**Figure 16: Effect of particle size on % removal of Fe (II).**

### 3.6 EFFECT OF AGITATION SPEED

**Figure 17** illustrates the adsorption kinetics of Fe (II) ions from 4 mg/l initial concentrations by biosorbents for different agitation speeds. The amount Fe(II) ions adsorbed at equilibrium ( $q_e$ ) in mg/g is found to increase with increase in agitation speed of an oscillator from 100 to 230 rpm. Adsorption is maximum at 230 rpm agitation speed. With increasing the agitation speed, the rate of diffusion of Fe(II) ions from bulk liquid to the liquid boundary layer surrounding the particle become higher because of decrease of thickness of the liquid boundary layer. Thus, uptake of Fe(II) ions increased with increasing agitation speed. Increasing agitation speed decreases the film resistance to mass transfer surrounding the adsorbent particles thus increasing adsorption of Fe(II) ions. Thus, batch mode studies are carried with 230 rpm agitation speed.

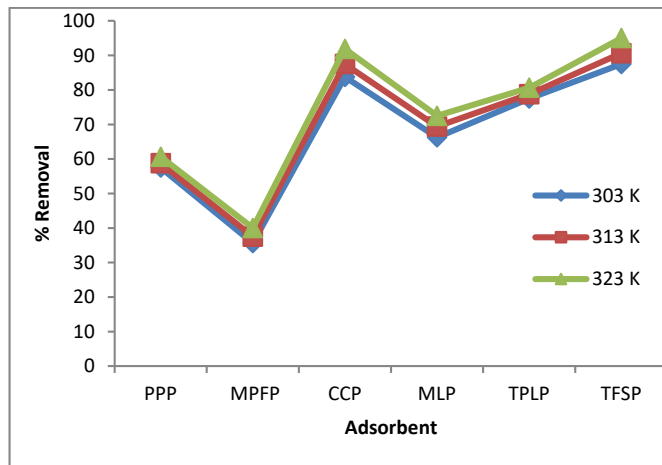


**Figure 17: Effect of agitation speed on adsorption of Fe (II).**

### 3.7 EFFECT OF TEMPERATURE

Results of variations in temperatures on adsorption of Fe(II) ion are shown in **Figure 18**. From plot it is observed that as the increase in experimental temperature from 303K to 323K,

the Fe(II) ion adsorption also increased. This is probably due to increase in temperature leads to an increment in the mobility of the ions and also the enlargement of the pore sizes of the adsorbent particle at higher temperature can also be beneficial towards the Fe(II) ion adsorption.



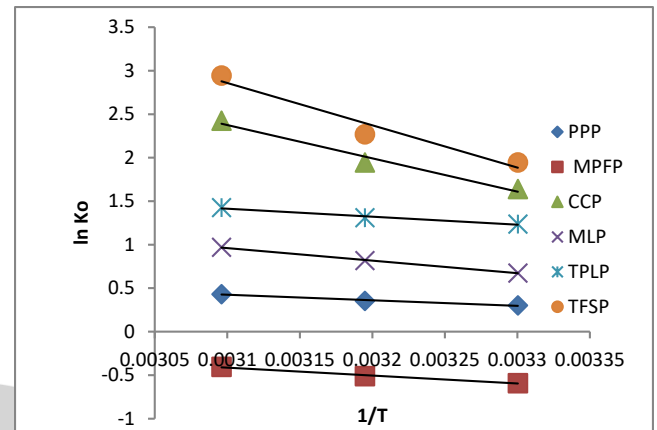
**Figure 18: Effect of temperature on adsorption of Fe (II)**

**Thermodynamic analysis:**

Thermodynamic parameters such as free energy change ( $\Delta G$ ) (J/mole), enthalpy change ( $\Delta H$ ) (J/mole) and entropy change ( $\Delta S$ ) (J/K/mole) are determined.

$\Delta G$  values are obtained from equation  $\Delta G = - RT \ln K_o$

$\Delta H$  and  $\Delta S$  values are obtained from the slope and intercept values of the plot  $\ln K_o$  against  $1/T$  (Figure 19) and are presented in Table 5. Negative  $\Delta G$ , low positive  $\Delta H$  ( $< 40$  KJ/mole) and positive  $\Delta S$  values are obtained for the adsorbent – Fe(II) ions systems indicates favourable, spontaneous, endothermic physisorption. Only for MPFP showed positive values of  $\Delta G$ . TFSP showed  $\Delta H > 40$  KJ/mole indicates possibility of chemisorption.



**Figure 19: Von't Hoff plot of effect of temperature on adsorption of Fe (II)**

**Table 5: Equilibrium constants and thermodynamic parameters**

Adsorbent	Ko			$\Delta G$ (J/mole)			$\Delta H$ (J/mole)	$\Delta S$ (J/K/mole)
	303K	313K	323K	303K	313K	323K		
PPP	1.3529	1.4242	1.5397	-761.49	-920.27	-1159	5246.97	19.787
MPFP	0.5534	0.6	0.6667	1490.52	1329.31	1088.84	7562.41	19.995
CCP	5.1539	7	11.308	-4130.7	-5063.8	-6513.4	31875.9	118.56
MLP	1.963	2.2653	2.6364	-1699	-2127.9	-2603.2	11988.8	45.153
TPLP	3.4444	3.7059	4.1613	-3115.6	-3408.8	-3828.9	7670.5	35.526
TFSP	7	9.6667	19	-4902	-5903.8	-7907.1	40455.9	149.4

**COD REDUCTION STUDIES:**

**Table 6: % Reduction in COD after adsorption**

Adsorbent	Fe(II) ion Conc.(mg/l)		COD (mg/l)		% Reduction in COD
	Before adsorption	After adsorption	Before adsorption	After adsorption	
TFSP	10	1.4	620	180	70.97

Reduction in COD up to 70 – 80 % [Table 6] indicates sorption of Fe(II) on natural adsorbents under study is found to be the better technique for wastewater management.

**IV. CONCLUSION**

Bio sorption technology, utilizing natural materials to passively remove Fe(II) ions from aqueous solutions, offers an efficient and cost effective alternative compared to traditional chemical and physical remediation and decontamination techniques. Equilibrium attains faster

within 20 to 40 minutes for the Fe(II) ions and adsorbents under study showed the effectiveness of adsorbents towards Fe(II).

The best fitting isotherm models are found to be Langmuir and Freundlich. Temkin isotherm also fit reasonably well. Freundlich constants  $K_f$  and  $n$ , Langmuir constants  $b$ ,  $q_m$  and



$R_L$ , and Temkin constants proved that adsorption of basic Fe(II) ions on to natural materials are favourable. Monolayer maximum adsorption capacities ( $q_m$ ) of the adsorbents under study towards these basic Fe(II) ions are found to be greater than the adsorbents used in the previous studies showed the relevance of these low cost adsorbents. Monolayer adsorption capacities for the adsorbents are found to be in order of TFSP > CCP > TPLP > MLP > PPP > MPFP.

Lagergen pseudo -second order model best fits the kinetics of adsorption as  $R^2 \approx 1$  and  $q_{e(\text{the})} \approx q_{e(\text{exp})}$  indicating possibility of chemisorption. Charges on surface of adsorbent and Fe(II) ion are found to be responsible for adsorption. Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step. Elovich second order model also fit reasonably well. The initial rate of adsorption constant and desorption constant is found to be in consistent with the adsorption studies. Only for PPP and MPFP,  $q_{e(\text{exp})} \approx q_{e(\text{the})}$  showed first order kinetics and here weaker forces overcomes the stronger chemisorptions during adsorption

Adsorption is found to increase with increasing pH, increasing temperature and decreasing particle size.

Thermodynamic analysis showed negative values of  $\Delta G$  indicating adsorption is favourable and spontaneous, positive values of  $\Delta H$  indicating endothermic physisorption and positive values of  $\Delta S$  indicating increased disorder and randomness at the solid- solution interface of Fe(II) ion with the adsorbents. Only MPFP showed positive values of  $\Delta G$ . TFSP showed  $\Delta H > 40$  KJ/mole for Fe (II) adsorption.

Thus, natural adsorbents found to have very good adsorption capacities towards ferrous ions.

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