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## Utility of Shell of *Pisum sativum* as an adsorbent in adsorption study of Iron from aqueous solution.

R K Dandge, S D Rathod<sup>1</sup> and Milind Ubale<sup>2</sup>

<sup>1</sup>Department of Chemistry Milind College of Science, Aurangabad

<sup>2</sup>Post Graduate Department of Chemistry VasantNaikMahavidyalaya Aurangabad  
(M. S.) India

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### ABSTRACT

Shell of *Pisum sativum*. (SPS) (Green Peas) was treated with sulphuric acid and used as a low cost, easily available adsorbent for the removal of Fe (II) from aqueous solution and industrial waste water. Batch experiments were conducted to determine the effects of contact time, pH, and initial concentration of adsorbate, temperature and adsorbent dose. The adsorption of Fe (II) was found maximum (91.773) at 50 min. contact time, (91.209) at 7 pH, (92.28) at 1 ppm metal ion concentration, (86.212) at 313 K and (91.773) at 1 gm. dose. Equilibrium data were well represented by the Freundlich isotherm model for all tested adsorption systems. The thermodynamic study has showed that the Fe (II) adsorption onto (SPS) was favorable and spontaneous. The kinetics study showed that Fe (II) adsorption follows the second order kinetics. Applicability of adsorbent was tested for the removal of Fe (II) from industrial waste water and the results obtained were encouraging.

**Keywords:** Adsorption, Low cost material, (SPS), Freundlich and Langmuir isotherm.

### INTRODUCTION

In an increasingly industrialized world, the need to deal with wastewater and industrial effluents generated by industrial process cannot be ignored. This pollution enters into the environment in various forms and threatens the quality of air, land and water. [1] Industrial and mining waste waters are the major source of pollution of heavy metals. Furthermore in developing countries like India, many industries are operated at small or medium scale or even as a family business



within the residential premises of the owner. These smaller units can generate a considerable pollution load which in many cases is discharge directly into the environment without any facilities for waste-water treatment. This is because the capital investment, turnover and profit for these industries are also small. In India, such a situation exists and the discharge of waste water containing chemicals and metallic ions into nearby water courses. Heavy metals can pose health hazards if their concentration exceeds allowable limits. Even when the concentration of metal does not exceed these limits. [2] There is still a potential for long term contamination since heavy metals are known to be accumulative within biological system [3]. Thus heavy metals such as Nickel (II), Copper, Cadmium, Lead, Zinc and iron have harmful effects on human physiology and other biological systems when they exceed the tolerance level [4], [5]. In water the iron occurs mainly in the divalent and trivalent state. The main source of iron in industrial wastewater is iron, steel, hardening, metal processing and fabrication industries. Iron is an essential element in human nutrition. It is contained in a number of biologically significant proteins, but ingestion in large quantities results hemochromatosis where in tissue damage results from iron accumulation [6-11]

Heavy metal adsorption was studied on various adsorbents such as activated carbon [12], fly ash [13], and bioadsorbents (adsorbents from plant- and animal-origin materials, for example bark/tannin-rich materials, humus, peat moss, modified cotton and wool, chitin, chitosan, seaweed, and biopolymers [14-16]). Activated carbon is the most widely used adsorbent but commercially available activated carbons are very expensive [17]. Many low cost adsorbents have been used for the removal of heavy metals e.g. brick kiln ash, fly ash, bidi leaves, teak leaves, amla dust, wallastonite, peanut hull and Neem leaves [18]. Other such adsorbents are pine cone [19], peels of banana, grape bagasse [20], which were used for removal of particular metals from water.

Literature survey indicates that the use of (SPS) as a low cost adsorbent for removal of heavy metals from aqueous solutions and industrial waste water has not been reported. Thus in the present study the systematic work was carried to investigate the adsorption properties of (SPS) for the removal of Fe (II).



## MATERIALS AND METHODS

### Preparation of adsorbent

The adsorbent selected for the present study was Shell of *Pisum sativum*. (SPS) (Green Peas) which is locally available plant and was collected in Aurangabad District of Maharashtra. The sample Shell of *Pisum sativum* was dried in shadow, avoiding direct sunlight on them. The dried Shell of *Pisum sativum* were grinded into powder and washed with distilled water and filtered. The residue left was treated with very dilute solution of sulphuric acid (0.1 N). It was then stirred for half an hour vigorously using mechanical stirrer at room temperature. Then it was filtered and washed with distilled water repeatedly to remove free acid. After chemical treatment the residue was dried first in air and finally in oven at 90-100<sup>0</sup>C for 8-10 hours and powdered using electric grinder. The homogeneous powder was passed through mesh for desired particle size. The adsorbent once prepared was used throughout the experimental work. The particle size of adsorbent selected for these experiments was on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernatant liquid [21]

### Preparation of Fe (II) metal ion solution

Fe (II) prepared by dissolving ferrous ammonium sulphate in double distilled water. The chemicals used were of analytical grade and used without further purifications. The solutions were prepared in doubly distilled water. A distilled water prepared by using first metal distillation unit and then all quick fit glass assembly in permanganatic condition, wherever necessary the prepared solutions were standardized as per literature [21].

### Adsorption experiments

Each batch adsorption study was carried out by using sulphuric acid treated (SPS) with iron ion solution under different conditions at maximum time 50 minutes. Iron was determined using spectrophotometer (SL-159 ELICO UV-VISIBLE SPECTROPHOTOMETER).

Iron from Industrial waste water was determined using AAS (LABINDIA AA 7000, Atomic Absorption Spectrophotometer) before adsorption experiments and using spectrophotometer (SL-159 ELICO UV-VISIBLE SPECTROPHOTOMETER) after the adsorption experiments.



After batch experiments percentage adsorption of Fe (II) from aqueous solution and industrial waste water were computed[22],

$$\% \text{ Adsorption} = (C_I - C_F) / C_I * 100$$

Where,  $C_I$  and  $C_F$  are the initial and final Fe (II) concentrations respectively.

## RESULTS AND DISCUSSION

The experimental data obtained from the different batch type experiments, in the present investigation was analyzed and interpreted based on the adsorption of Fe (II) on (SPS).

### Effect of contact time

The effect of contact time was studied by keeping adsorbent dose 1 g, initial concentration of adsorbate 25 ppm, pH 2 and room temperature (303 K) and varying time. It was found that the adsorption percentage increases with increase in time from 10 minutes to 50 minutes and after 50 minutes the percentage adsorption remains constant (Fig.1). Time taken for the completion of adsorption was 50 minutes. It was in good agreement with the reported work of Jute and Sun hemp as adsorbent[23 and SJH]. The equilibrium contact time was 50 minutes. Ions diffuse to surface and in to the pores of (SPS) which have very large number of surface area. When the time increased more than 50 minute remaining ions adsorbed or diffused into the pore could be saturated, the affinity of metals adsorbed will decrease. Thus, the affinity of metal adsorbed is depending upon appropriate time. Therefore the contact time 50 minutes was selected in all experiments.

The experimental data was tested by first and second order equations.

In pseudo –first order kinetic model a simple kinetics of adsorption given by Lagergren rate equations[24] were as,

$$dq/dt = k_1 (q_e - q_t) \dots\dots\dots (1)$$

The integrated form is,  $\log (q_e - q_t) = \log q_e - k_1 / 2.303 * t \dots\dots\dots (2)$

Where  $q_e$  and  $q_t$  represent the amount of Fe adsorbed (mg/g) at equilibrium time and at time  $t$ (min) respectively,  $k_1$  represents the first order rate constant ( $\text{min}^{-1}$ ). If plot of  $\log (q_e - q_t)$  versus

It was linear then the adsorption process was followed pseudo –first order kinetics but it was not followed the pseudo –first order kinetics.

In second order adsorption kinetics, the plot of  $t/qt$  versus  $t$  was found to be linear with  $R^2 = 0.991$  (Fig.2). The present studies reveal that adsorption of Fe (II) onto the surface of SPS followed second order kinetic model.

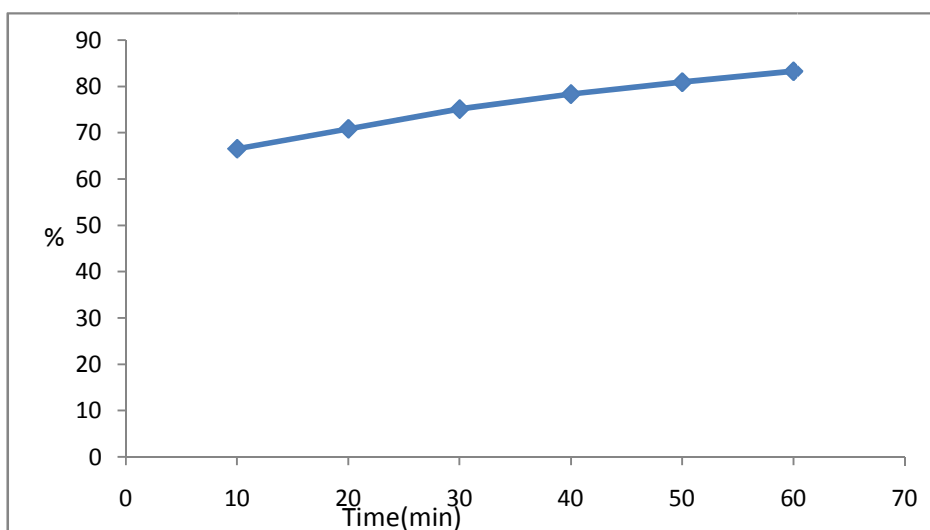


Fig.1: Effect of contact time on removal of Fe (II)

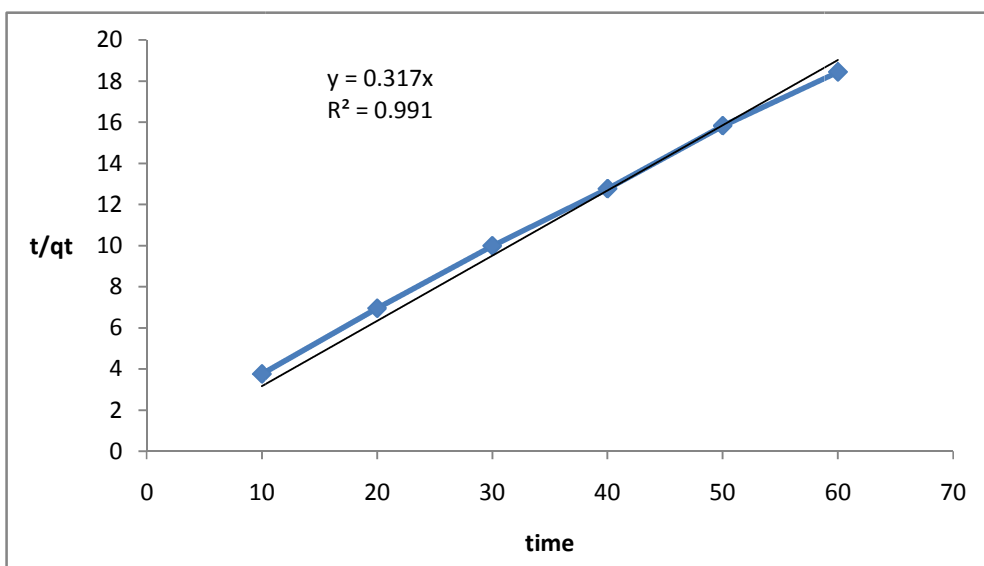


Fig.2: Second order reaction



### Effect of adsorbent dose

Amount of adsorbent plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. In our present study with increase in the amount of (SPS) as adsorbent the Fe(II) removal efficiency increased rapidly (Fig.3) which may be due to the greater availability of the exchangeable sites or surface areas at higher concentration of the adsorbent. Our findings are in good support with the reported work by Srinivas et.al. [25].

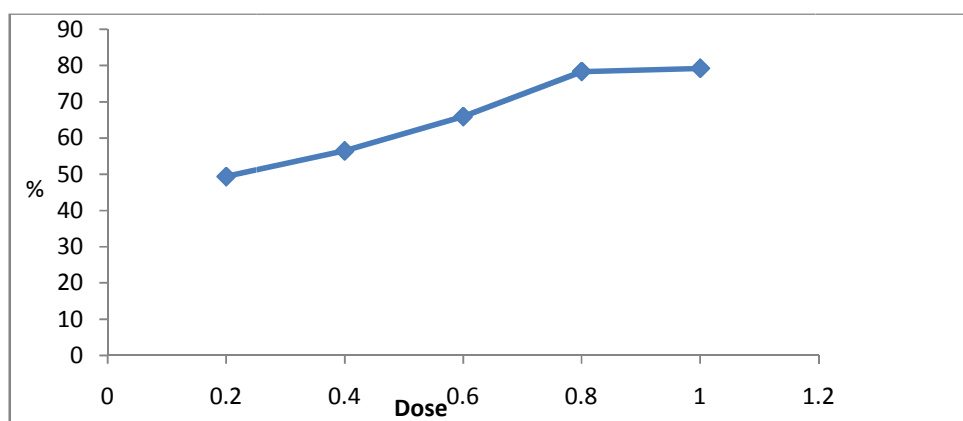


Fig.3: Effect of adsorbent dose on removal of Fe (II)

### Effect of initial concentration of adsorbate

The adsorption of Fe(II) onto the surface of (SPS) was rapid initially, slows down later on and finally reached towards equilibrium indicating saturated adsorption[26]. The increased in adsorption may be attributed to increase in surface activity and due to micelle formation or the aggregation of iron ions in the concentration range studied[26]. In our present investigation the percentage removal of iron decreased with the increased in the initial concentration of adsorbate (Fig.4). Our findings are supported by the reported work of Sureshkumar Halnor et.al. [27] and R.S.Shelke et.al. [28].

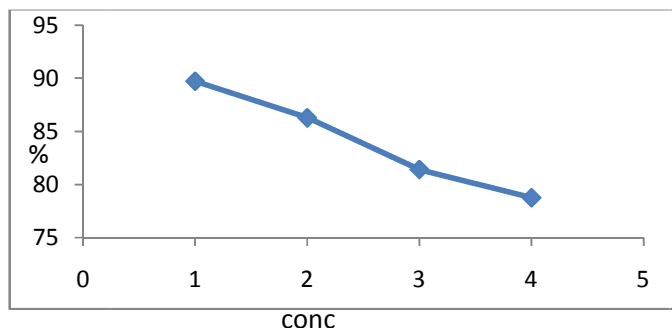


Fig.4: Effect of initial concentration of adsorbate on removal of Fe (II)

### Effect of temperature

Temperature plays a major role in the adsorption of heavy metals on the surface of adsorbent. Adsorption study was carried out in different temperature range (293-333 K) and remaining parameters were kept constant and found that adsorption increases with increase in temperature from 293-313 K and decreases from 323-333 (Fig.5). The increased in adsorption from 293-313 K indicates endothermic adsorption. It has been reported that the increase in uptake with temperature is mainly due to an increase in the number of adsorption sites created by the breaking of some of the internal bonds near the edge of the crystal[29]. The decrease in adsorption with increase in temperature is due to the increase in solubility of the adsorbate with increase in temperature, or the mobility of the large ions increases with increasing temperature [27].

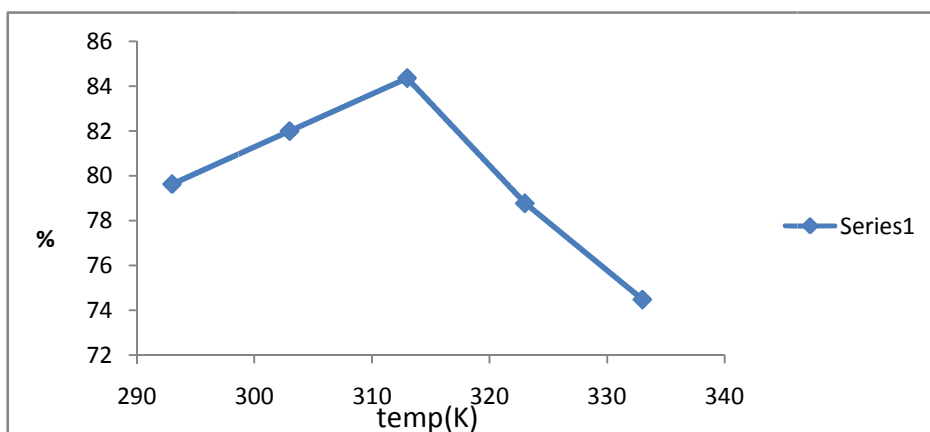


Fig.5: Effect of temperature on removal of Fe (II)

## Effect of pH

Solution pH is one of the most important parameter for adsorption of heavy metals from aqueous solution and industrial wastewater. In order to investigate the effect of pH on the adsorption of Fe (II), the batch equilibrium was studied at different pH values and it was found that the amount of metal adsorbed increases with increasing pH (Fig.6). At a low pH adsorption of iron was less; the  $H^+$  ions are much larger than ions of iron on the surface of the powder which limits the access of iron ions on the surface of grains of the adsorbent. When the pH increases, the effect of competition from  $H^+$  ions decreases and the positive charged ions take their place on the surface[30]-[32].

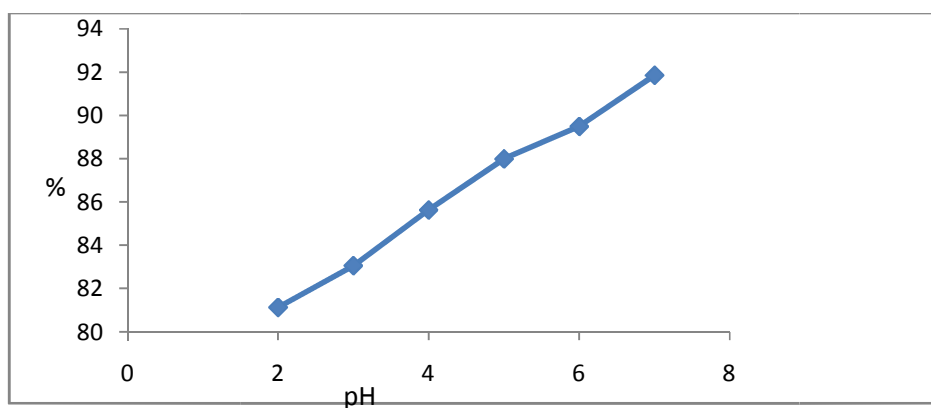


Fig.6: Effect of pH on removal of Fe (II)

## Adsorption Isotherms

The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate and adsorbent doses were analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of (SPS)[22].

### Freundlich Adsorption isotherm

The Freundlich equation was applied to describe the analytical results on adsorption. It was an empirical result agrees quite well with Langmuir equation and experimental data over a moderate range of adsorbate concentration. It is represented by the equation[33],

$$\log x/m = \log k + 1/n \log C_{eq}$$





Where,  $C_{eq}$  is the equilibrium concentration (mg/L) and  $x/m$  is the amount adsorbed per unit mass of adsorbent (mg/g). Plotting  $\log x/m$  vs.  $\log C_{eq}$  a straight line was obtained with a slope of  $1/n$ , and  $\log k$  is the intercept. The  $k$  value was found to be 9.79. The value of 'n' was calculated to be 1.0211. As the value of 'n' is  $1 < n < 10$ , shows favorable adsorption of Fe (II) on (SPS)

### Langmuir Adsorption isotherms

Langmuir equation was also applied for adsorption equilibrium. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate molecules on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface [22].

$$C_e / q_e = 1 / Q_0 b + C_e / Q_0$$

Where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of solute in the bulk solution (mg/L),  $Q_0$  is the monolayer adsorption capacity (mg/g) and  $b$  is a constant related to the free energy of adsorption.

The linear plot of  $C_e / q_e$  vs.  $C_e$  shows that the adsorption obeys Langmuir adsorption model.  $Q_0$  and  $b$  respectively were determined from the Langmuir plots and found to be 51.36 mg/g and 0.15 mg/L. The essential characteristic of Langmuir isotherm were expressed in terms of a dimensionless constant separation factor or equilibrium factor  $R_L$ , which is defined by

$R_L = 1 / (1 + bC_0)$ , Where  $b$  is the Langmuir constant and  $C_0$  is the initial concentration of Fe (II).

$R_L$  is indicative of the nature of the isotherm and is enlisted below as [26],[27],

$R_L$ Value	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In present study  $R_L$  value observed was between 0 and 1 indicate favorable adsorption of Fe (II) on SPS.  $R_L$  value in the present study was 0.00022.



### Thermodynamic Parameters

Thermodynamic parameters such as free energy, enthalpy and entropy of adsorption were calculated and found that  $\Delta G$  was negative and showed spontaneous nature of adsorption process,  $\Delta H$  was negative and showed exothermic nature of adsorption process,  $\Delta S$  was positive and showed the increasing randomness at solid/liquid interface during the adsorption of iron. All these values demonstrate a spontaneous and favorable adsorption process.

### Application to industrial wastewater

The suitability of the SPS adsorbent for the removal of Fe (II) with respect to Industrial waste water was evaluated. Adsorption experiments were conducted with Industrial waste water samples  $S_1$ ,  $S_2$  and  $S_3$  containing Fe(II). Table-1 and 2 gives the details of the Industrial waste water samples applied for this study before and after adsorption experiments. The concentration of Fe (II) in  $S_1$ ,  $S_2$  and  $S_3$  were determined by AAS. The percentage of Fe (II) removal in each sample was determined by usual procedure. The results are shown in Table-2. From which it is evident that Fe (II) removals were 84.045, 83.296 and 83.692% from  $S_1$ ,  $S_2$  and  $S_3$  respectively. It has been observed that 84.045 % removal of Fe (II) could be achieved with an adsorbent dose of 1gm/100ml.

**Table 1 Concentration of iron in industrial waste water before adsorption**

Name of sample/Name of metal ion	$S_1$ Co(ppm)	$S_2$ Co (ppm)	$S_3$ Co (ppm)
Fe	13.58	16.47	14.3

**Table 2: Concentration of iron in industrial waste water after adsorption**

Name of sample	Industrial waste water (ml)	Amt. of adsorbent (gm.)	Time (min)	% Removal
$S_1$	100	1	50	84.045
$S_2$	100	1	50	83.296
$S_3$	100	1	50	83.692



### CONCLUSIONS:

The present study shows that the sulphuric acid treated Shell of *Pisum sativum* is an efficient, low-cost adsorbent for the removal of toxic Fe (II) from aqueous solution. The adsorption of Fe (II) was found to be dependent on contact time, adsorbent dose, initial concentration of adsorbate, temperature and pH. The equilibrium adsorption data showed significant correlation to Langmuir and Freundlich adsorption isotherms and the adsorption was followed second order kinetics. Value of  $R_L$  indicates this adsorption process is favorable. Adsorption with low cost adsorbent is not only cheaper but requires less maintenance and supervision. With the application of very small dose of adsorbent (1gm/100ml), it is possible to remove about 84 % Fe (II) from industrial waste water. It is suggested that the use of this adsorbent for removal of Fe (II) from industrial waste water is an effective and low cost process.

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