



REMOVAL OF IRON FROM AQUEOUS SOLUTION USING *Meretrix casta* SEASHELLS AS AN ADSORBENT

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ABSTRACT

The present study aims to investigate the adsorption efficiency of seashell powder derived particularly from *Meretrix casta* species on the removal of iron from synthetic water under laboratory conditions. In batch experiments the parameters such as initial concentration, pH, adsorbent dosage and contact time were studied. Physical characteristics such as XRD, FTIR and SEM analysis of sea shell powdered were studied. From XRD it is clearly shows that the main constituent of sea shell adsorbent is calcite. SEM analysis clearly shows how the morphology changes before and after adsorption. From the results of batch experiment optimum values of each parameter are obtained. From the optimum values, the effect of initial concentration, pH, adsorbent dosage and contact time were studied. Thus, it was concluded that seashell has potential for application as adsorbent for removal of iron from aqueous solution.

Keywords— Adsorption, Seashells, *Meretrix casta*, FTIR, XRD, SEM

I. INTRODUCTION

It is found that almost 70% of India's surface water and a ground water are contaminated by toxic, biologic, inorganic, organic and pollutants. India's major rivers are polluted badly and in every year 50 million cubic meters of untreated sewage were transported into India's coastal waters. Adsorption technique for wastewater treatment has become more popular in recent years owing to their efficiency in the removal of pollutants too stable for biological methods [3].

Ground water commonly contains iron which the 4th abundant element and 2nd most abundant metal present in earth's crust. Sulphide, magnetite, pyrite, siderite or carbonates, silicates, olivine, pyroxenes are present in water under anaerobic conditions in the existence of reducing agents like hydrogen sulphide and organic matter [12]. Iron usually exists in natural water in reduced soluble divalent ferrous FE (II) and oxidized trivalent ferric FE (III) forms. Iron (as Fe²⁺) concentrations of 40 µg/L can be detected by taste in distilled water. In well-water, iron concentrations below 0.3 mg/L were characterized as unnoticeable, whereas levels of 0.3–3 mg/L were found acceptable. The interactions of corroded iron pipe surfaces with water are of importance because they can lead to serious water quality degradation and material deterioration [9].

The first quantitative observation on adsorption was reported by C.W.Sheelee in 1773 and Fontana in 1777 on uptake of gases by charcoal and clays [3]. However the term adsorption was proposed by Bois Reymond but introduced in to literature by kayser. Ever since then adsorption process has been widely used for the removal of solutes from solutions and gases from air atmosphere.

Agricultural and industrial wastes such as rice husk and fly ash for the removal of heavy metals viz Fe, Pb, Ni, Cd and Cu. it was found that low cost adsorbents can be fruitfully used for the removal of heavy metals [4]. Iron removal by adsorption using ash from oil palm industry, capable of removing over 99 % of Fe from aqueous solution, is an effective adsorbent for Fe [7]. Sugarcane bagasse, Coconut coir exhibits remarkable binding characteristics for removal total iron, so special interest was devoted for optimizing its uptake and studying its selectivity properties under static and dynamic conditions [10].

Meretrix casta, an edible bivalve mollusc, is a backwater clam species [2]. It has considerable commercial importance and occurs abundantly in estuaries and backwaters of both the east and west coast of India. For protecting itself from environmental fluctuations and predation, these clams burrow itself into bottom

sediment. Along west coast, it occurs in Goa, Uppunda, Coondapur, Udyavara and Mulki estuaries in Karnataka and Ashtamudi, Chettuva, Beypore, Korapuzha, Moorad and Chaliyar estuaries in Kerala. This species contributes to livelihood of large number of fishers living along these estuaries.

The feasibility of sea shell powder to remove Basic Green 4 (BG 4), which is a cationic dye obtained from aqueous solutions [11]. Acid mine waste (AMD) treatment remains a virgin region for broad research attributable to the constraints of the current and proposed AMD treatment advances [8].

The Taguchi method was developed to improve the implementation of off-line total quality control. The method is related to finding the best values of the controllable factors to make the problem less sensitive to the variations in uncontrollable factors. This kind of problem was called by Taguchi robust parameter design problem.

The present study focuses on adsorption characteristics of seashell on removal of iron from water. The reason for this study is because the iron content in groundwater of surathkal is more than permissible limit. My concept is that surathkal is in coastal area, so that seashell is available in large quantity. These seashells can be used as adsorbents for removal of iron content in ground water. No detailed studies were done on adsorption removal of heavy metals by seashell. In this context the present study is significant as it studies the removal efficiency of iron on seashell. For the powder shells characterization, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform IR spectroscopy (FT-IR) were performed.

II. Materials and methods

A. Adsorbent collection and preparation

The seashells collected from NITK beach were used for this study. The seashells were first thoroughly washed with tap water and then with distilled water to remove sand, dirt and other unwanted particles. Then these are dried at 373K for 24 hours in a hot air oven. Then the dried adsorbents are crushed and powdered by using ball mill. These powdered adsorbents are then sieved using 100 μ m sieve. The particles which are not passed into the sieve are again put into the ball mill and powdered again. Finally, the powdered adsorbent was stored in an air tight container. These adsorbents are used without any pre-treatment for iron adsorption.



Figure 1: seashell

B. Preparation of adsorbate solutions

Synthetically prepared metal solution was used for evaluating the adsorption efficiency of seashell. The iron synthetic solution was prepared as such:

Analytical grade ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used to prepare a stock solution. 49.78mg was measured exactly and make it up to 1000ml. 1 ml of this solution contains 0.1mg of Fe. Adsorbate sample solutions for the study were prepared by diluting the stock solution to corresponding concentrations. Stock iron solution and samples were prepared on each day of study.

B.1 Adsorbate analysis

Total iron concentrations of iron samples before and after adsorption were analysed by standard 1, 10-phenanthroline method.

B.2 Preparation of standard calibration curve.

Standard calibration curve was plotted by preparing working standards of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.8, 2.0 mg/l from stock iron solution. 50 ml of standards was measured; 2 ml of concentrated HCL and 1 ml of hydroxylamine hydrochloride solution were added to this. The sample was heated to reduce the volume to 15-20 ml. the boiled sample was cooled to room temperature and transferred to 100 ml nester's tube. 10 ml of ammonium acetate buffer and 4 ml of phenanthroline solution were added and diluted to the mark. The solution was left for 10 minutes for colour development and tested in a UV spectrophotometer at 510 nm.

The metal ion concentrations of adsorbate samples before and after adsorption were analysed in UV spectrometer by standard phenanthroline method using the plotted standard calibration curve.

C. Adsorbent characterization

C.1 SEM analysis

The surface morphology of seashell was visualized in JOEL analytical scanning electron microscope (SEM). The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). The SEM is widely used to identify phases based on qualitative chemical analysis and/or crystalline structure.

C.2 FTIR analysis

The functional groups of the seashell were observed by a Bruker (alpha) KBr/ATR Fourier Transform Infrared Spectroscopy (FTIR) system. FTIR spectra were recorded in the 600-4000 cm⁻¹ region. FT-IR stands for Fourier Transform Infrared. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. The wavenumbers of the absorption band are characteristic chemical identity of the substance in question. The intensity of the absorption bands allows quantitative analysis of the samples [1].

C.3 XRD analysis

The X-Ray Diffraction crystallographic analysis was done by Bruker(Alpha) Diffractometer. The scanning was made between 2 θ and 80 θ in 2 θ with a step size of 0.010 and a count time of 0.5 s step-1. As per the reference, the values of 2 θ for Calcite are 23.04, 29.43, 31.45, 36.00, 39.44, 43.18, 47.17, 47.53, 48.56, 57.45 and 60.73 [5].

D. Batch experiments

Batch experiments were designed to investigate the efficiency of iron removal with different initial adsorbate concentration (1.5, 2, 2.5, 3 mg/l), dosages of seashell (15, 20, 25, 30mg), Ph (4,5,6,7) and contact time(30, 45, 60, 90min). BOD bottles (300ml capacity) containing a fixed dosage of seashell with 100 ml of iron solution corrected to pH was placed in a mechanical rotary shaker for a fixed time period. The bottles were then removed and samples were filtered through Whatman filter paper No 42. Final Iron concentration was determined using 1, 10 phenanthroline method in a UV spectrophotometer. Removal efficiency of the adsorbent was calculated as

$$\text{Removal efficiency \%} = [(Co-Ce)/Co] \times 100$$

Where,

Co: Initial concentration, mg/l

Ce: final concentration, mg/l

The optimum value for each selected parameter was found out by conducting DOE trails. The process parameter combinations were done according to the design matrix of Taguchi 4 level design. A total of 16 trials were done using different combination of parameter values. The optimum value was found out by analysing the experimental data obtained from batch studies in Minitab DOE software. The resulted graph showed the optimum value of each process parameter. The optimum value of parameters was further used for the study of trend in effect of each parameter.

III. RESULTS AND DISCUSSION

A. Adsorbent characterization

The X-Ray Diffraction crystallographic analysis was done by Bruker(Alpha) Diffractometer. The scanning was made between 2θ and 80° in 2θ with a step size of 0.01° and a count time of 0.5 s step-1. As per the reference, the values of 2θ for Calcite are $23.04, 29.43, 31.45, 36.00, 39.44, 43.18, 47.17, 47.53, 48.56, 57.45$ and 60.73 (Helen E. A. Tudor et al. 2005). The peaks obtained here are nearly to these values. So, it is clear that the main constituent of the seashell powder adsorbent is Calcite (CaCO_3). Here well defined peaks are observed, hence the material under investigation is crystalline.

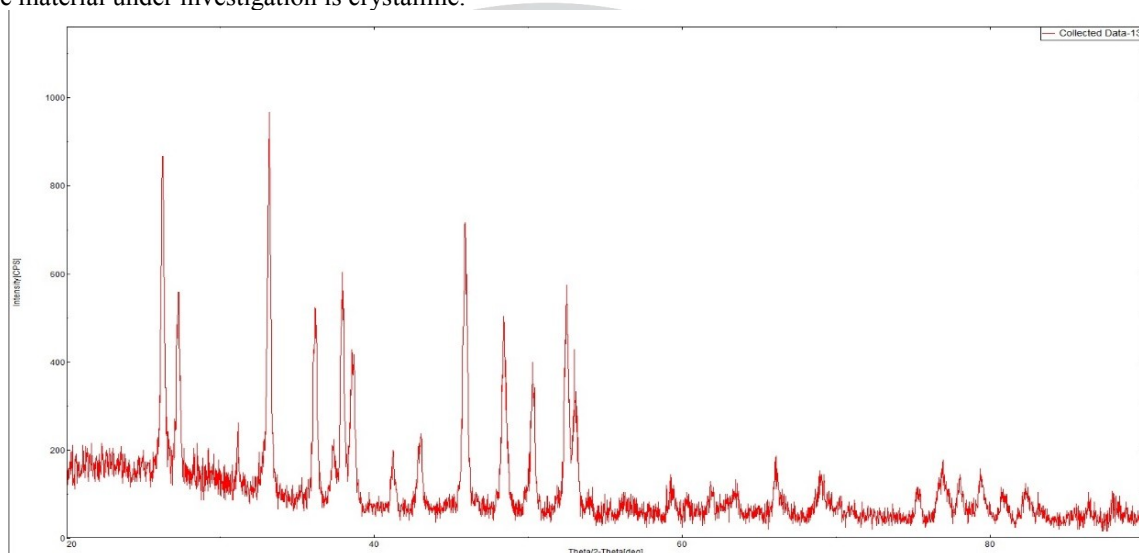


Figure 2: XRD

IR analysis were performed by a Bruker (Alpha) spectrometer. The spectra over the range of $600\text{--}4000\text{cm}^{-1}$ were recorded by using the KBr pellets. The FTIR spectra confirms the presence of Calcium Carbonate in the adsorbent composition in high amount.

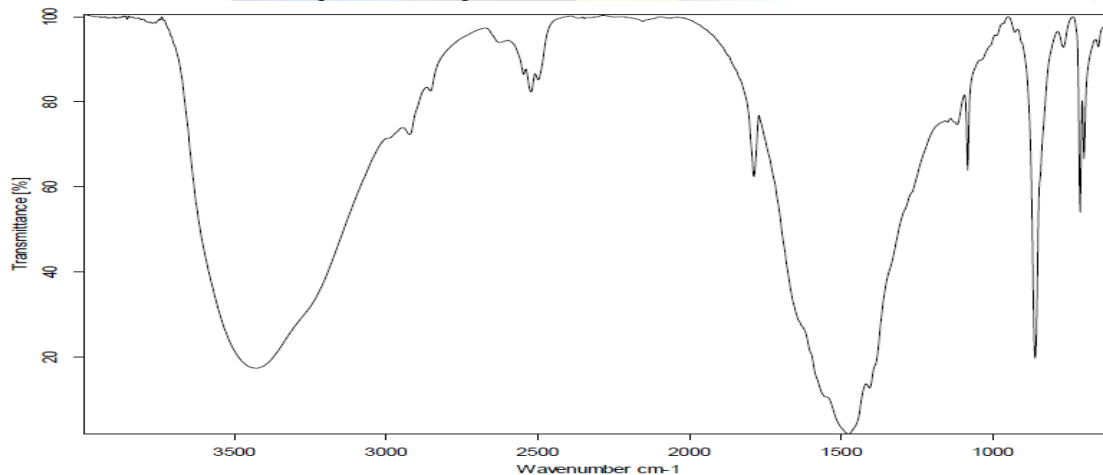


Figure 3: FTIR

The major absorption bands of carbonate spectra are accredited to the fundamental vibrations of the carbonate radical CO_3^{2-} . The spectrum of pure calcite shows characteristic absorption bands at 714, 872, 1449, 1780, and 2518cm^{-1} ; the characteristic bands of pure aragonite are situated at 691, 709, 852, 1079, 1478, 1798, and 2529cm^{-1} .

The surface morphology of seashell was observed under different magnification with the help of a Scanning Electron Microscope (SEM).

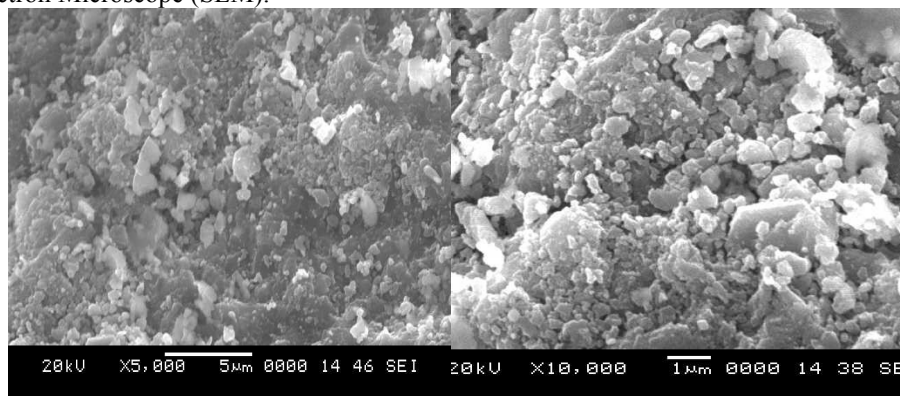


Figure 4: SEM before adsorption

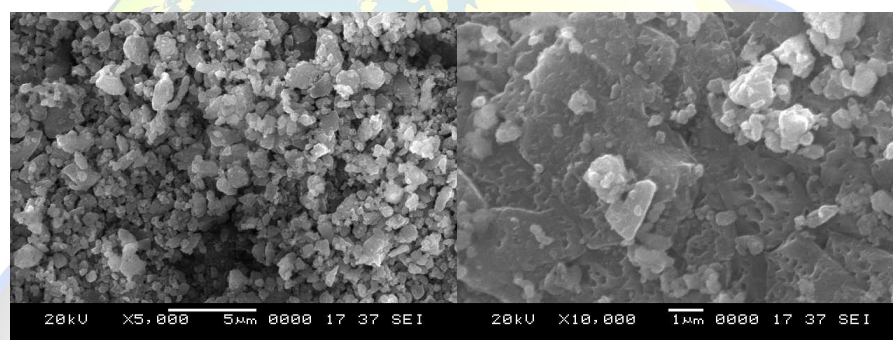


Figure 5: SEM after adsorption

B. Effect of initial adsorbate concentration

Initial concentration of iron was varied from 1.5mg/L to 3mg/L . Figure 3.5 shows the trend of removal efficiency of iron with initial concentration. It is observed that the removal efficiency was increasing with increase in initial concentration of iron. This may be because at higher concentration there is higher driving force for mass transfer. In addition to that with increase in metal ion concentration the active sites of adsorbent are surrounded by higher number of metal ion molecules which leads to more efficient adsorption within a period of time. As the concentration of metals increases, the adsorption by the seashell also increases, which indicates that the material used has a good adsorption capacity for this metal. The equation of the trend line explains the effect of any values of initial adsorbate concentration on removal efficiency of iron. This may be because of the start of the desorption process. The optimum value of initial concentration is 2.5mg/L . The R^2 value of 0.9865 indicates a good fit of trendline to the experimental data.

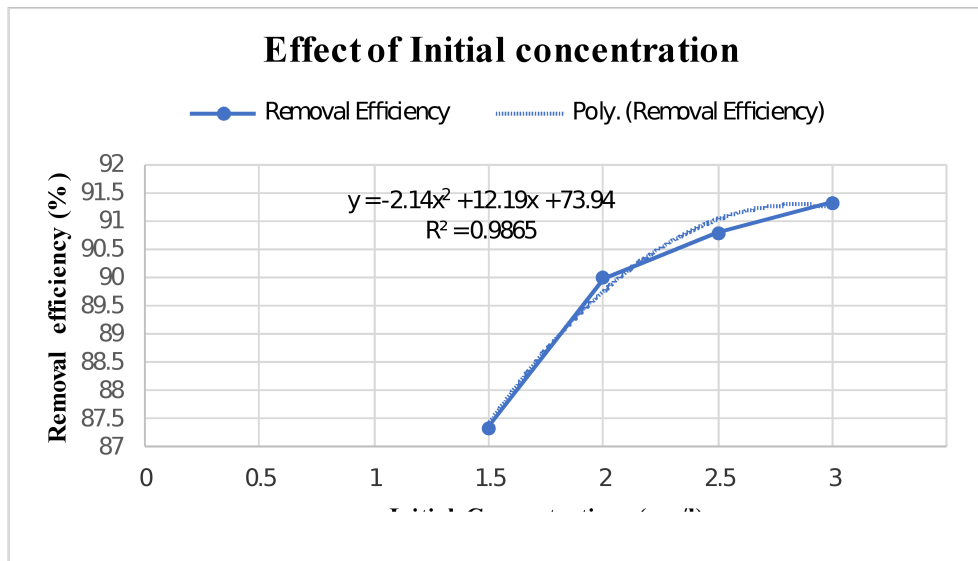


Figure 6: Effect of initial concentration

C. Effect of adsorbent dosage

Figure 7 shows the effect of seashell dosage on iron removal. It was found that iron removal increased with increase in dosage of adsorbent dosage from 15mg to 30mg. The optimum dosage was found to be 25mg. The increase in removal efficiency may be due to the availability of more active adsorption sites. The equation of the trendline explains the effect of any values of adsorbent dosage on the removal efficiency of iron. The R² value of 0.9995 indicates a good fit of trendline to the experimental data obtained.

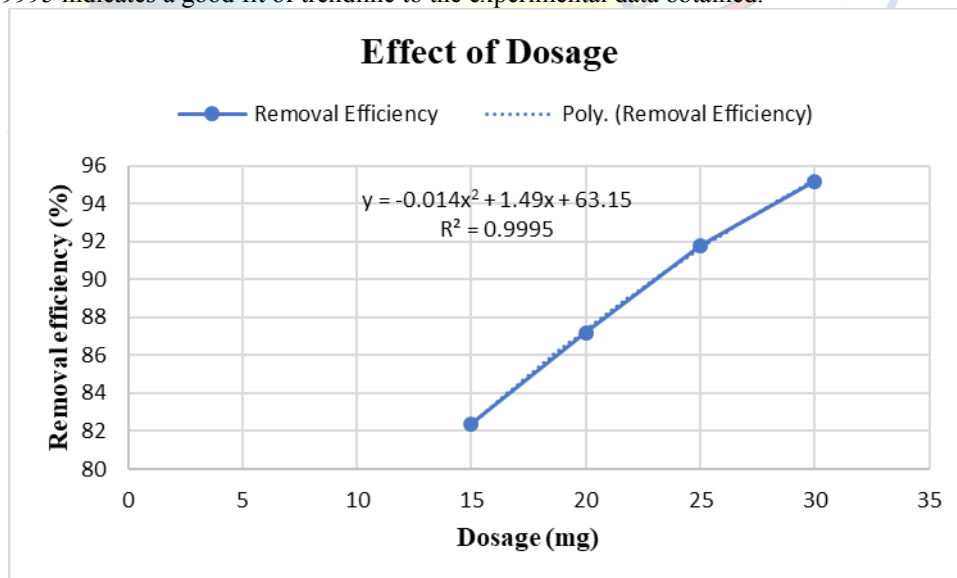


Figure 7: Effect of adsorbent dosage

D. Effect of pH

Figure 8 shows the effect of pH on iron adsorption by the are seashell powder. pH was varied from 4 to 7 with an initial adsorbate concentration of 2.5mg/L, adsorbent dosage of 25mg and a contact time of 60 minutes. The rotation speed was maintained as 150 rpm for all runs. Graph shows that at lower pH value, the removal of iron was very low. It increased with increase in pH. The lesser value of pH in the acidic range may be because of the H⁺ ion concentration with the metal ions for the binding sites. The optimum value was

observed at a pH of 6, after which the efficiency decreased. This may be due to the formation of soluble hydroxyl complexes.

The equation of the trendline explains the effect of any values of pH on removal efficiency of iron. The R² value of 0.9618 indicates a good fit of trendline to the experimental data obtained.

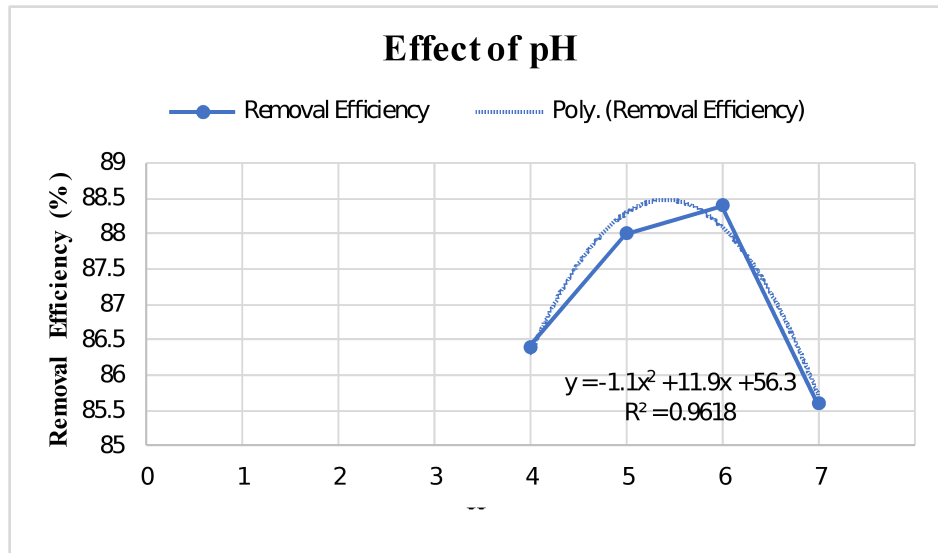
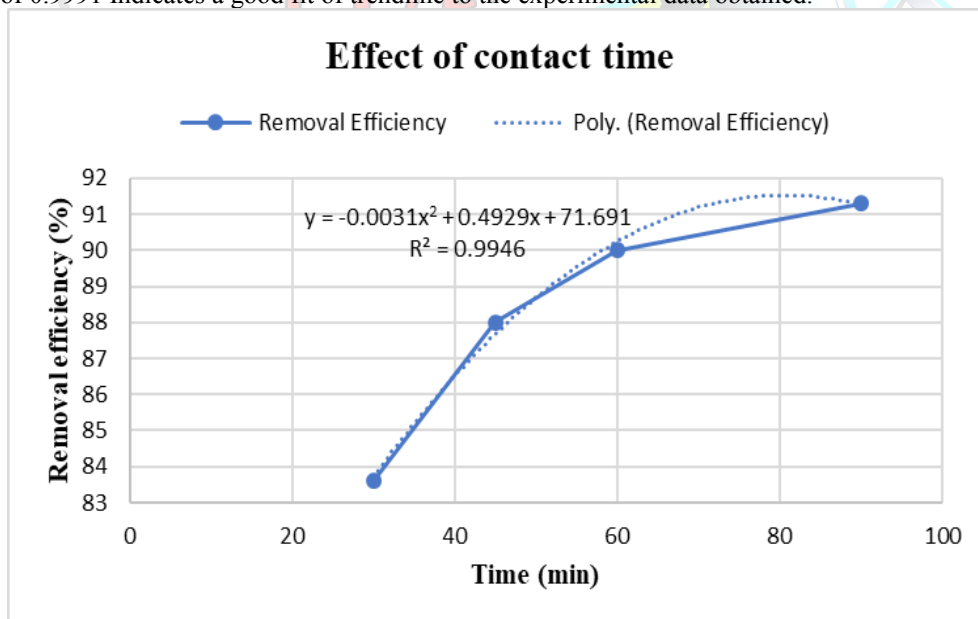


Figure 8: Effect of pH

E. Effect of Contact time

Batch study was conducted with four different contact time varying from 30 minutes to 90 minutes. The change in adsorption efficiency with contact time is shown in the figure 9. The results indicate that the optimum removal efficiency is achieved at a contact time of 60 minutes. After that there is no considerable variation, removal efficiency is almost constant. This may be due to the saturation of active sites on the adsorbent surface and the system reached equilibrium.

The equation of the trendline explains the effect of any values of contact time on removal efficiency of iron. The R² value of 0.9991 Indicates a good fit of trendline to the experimental data obtained.



**Figure 9: Effect of contact time**

IV. CONCLUSION AND WAY FORWARD

In this study the ability of the seashell powder to remove iron from aqueous solution was investigated. The parameter such as initial concentration, adsorbent dosage, pH and contact time were considered as effect on under adsorption efficiency of seashell powder. The adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and X-ray diffraction (XRD) techniques. Seashell was found to be good adsorbent and optimum value of pH was found to be 6. The optimum value of initial concentration of iron is found to be 2.5 mg/l. the optimum of value of dosage of adsorbent is found to be 25 mg. It is observed that when dosage increases, removal efficiency also increases. The optimum value of contact time is found to be 60 minutes. These results may be considered as a starting point for further research on equilibrium, kinetics and thermodynamics of adsorption of iron onto seashell.

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