RESEARCH ARTICLE OPEN ACCESS

Study of Adsorption Isotherm Model and Kinetics on Removal of Zinc Ion from Industrial waste water by Using Novel Biosorbent (Phyllanthus Emblica)

Mr.P.Muthusamy* Hannah.A
Assistant Professor(S.G), Department Of Biotech, Karunya University, Coimbatore. Tamil Nadu – 641114 India.

ABSTRACT
The removal of Zinc (Zn) metal ion from aqueous solution by using novel bioadsornbent. The impact of beginning metal particle fixation and adsorbent measurements on the adsorption of Zinc (zn) by waste water was researched. The leftover zinc ions was then broke down utilizing Atomic Absorption Spectrophotometer (AAS) (240AA). The adsorption harmony was accomplished when zinc arrangement was 800mg/L. The rate of metal evacuation is of most prominent criticalness for building up a characteristic adsorbent-based water-treatment innovation. The greatest evacuation rate is to be 95.37%. The harmony was accomplished essentially at pH of 7 at 120 minutes and 250 rpm evacuation effectiveness of zinc at steady beginning fixation with 1.25gm measurement infers the capability of gooseberry seeds to adsorb and recoup substantial metals from watery arrangement was effectively exhibited with zinc (zn) test arrangements. The adsorption isotherm studies was done by using Langmuir, Freundlich, temkin, Hill, Jovanovich models and kinetics reaction was studied by pseudo 1st and 2nd order kinetic reaction. The bioadsorption information fit well with the Temkin isotherm model than the other isotherm model. The kinetics 2nd order reaction was fit to this bioadsorbent than the first order kinetics. Removal of zinc ions from crackers industry waste water was found to be 84%. These outcomes have exhibited the gigantic capability of waste water as an option adsorbent for dangerous metal particles remediation in contaminated wastewater. This paper surveys and investigation the innovative parts of expulsion of zinc from the industrial waste water.

Keywords: Phyllanthus emblica, Atomic absorption spectrophotometer(AAS), cracker industrial , adsorption isotherm and kinetics.

I. INTRODUCTION

Industrialisation and urbanization have resulted in exponential discharge of industrial effluents and toxic heavy metals into water bodies. Heavy metals like zinc, iron, chromium, lead etc., which is considered as a toxic pollutant for living organisms. Zinc metal, which is as of now investigated in this exploration work, is available basically in cowhide tanning, valuable metal mining and electroplating modern effluents, as indicated by US EPA, Zinc is thought to be the highest need poisonous toxin. Due to the non-biodegradability they tend to accumulate in vital organs of living organisms and causes various diseases as well as deleterious ecological effects. The acceptable and permissible limit for zinc in surface and portable water is 2mg/m3. Zinc is the topmost priority for toxic pollutant and it is called as essential trace element because very small amounts of zinc are used for human health it causes kidney disorder, nausea, stomach disorder to human bodies.

Along these lines, it gets to be best need to make effluents free from Zn before discharging into the earth. There are a numerous techniques to remove heavy metal from various industrial waste water. Basic strategy included in the treatment of substantial metal remediation incorporates, precipitation (both physical and synthetic), particle trade (tar based), filtration accomplished through physical means, compound based coagulation, flocculation, and other electrochemical strategies. The real obstacles in adjusting these procedures incorporates high operational cost combined with higher vitality necessities, further, era of tremendous slime statement lastly operational complexities. Subsequently, the option of adsorption as a remediation device has been viewed as the best and it is further enlarged with it being practical and ecological benevolent procedure (Salman et al., (2014). Numerous agrarian waste deposits had been broadly contemplated in the past to decide their adsorption productivity. Bioresource material like agribusiness waste residuals, indicating maximal adsorption abilities and metal selectivity had been proposed as suitable biosorbent for overwhelming metal sequestration (Nguyen, 2013). Right now locally accessible farming waste build ups are a programmed decision for remediation of overwhelming metals, they are additionally being considered as an imperative wellspring of biosorbents because of the vicinity of certain practical gatherings, for example, hydroxyl, ester, amino, carboxyl, carbonyl, sulphydryl, and phosphor gathering to which substantial metal tie. In this connection, Gooseberry seed powder (Phyllanthus emblica), a novel biosorbent was analyzed for Zn tying effectiveness. In the present study, different parameters which impact Zn evacuation, for example, pH, beginning metal particle fixation, contact time and adsorbent dose were researched in a clump mode. Scientific strategies, for example, FTIR, XRD and SEM were utilized for biosorbent portrayal. FTIR investigation was utilized to decide the dynamic site in charge of biosorption taking into account the progressions in vibrational frequencies of the utilitarian gatherings. The surface morphology and the porosity of the biosorbent were researched by SEM investigation. Examinations on harmony isotherm and adsorption energy were likewise completed to comprehend the adsorption system.

II. MATERIALS AND METHODS

2.1 Preparation Of Biosorbent Material And Metal Solution:

Gooseberry seeds were obtained locally (Coimbatore, India). The seeds were washed under running faucet water and were subjected to drying in hot air oven at an ideal temperature of 67°C for 24h and it was grinded and sieved to acquire molecule size under 200Mesh size. Stock solution is prepared using 0.5g of zinc sulphate in 1000mL double distilled water. Working solution is prepared by adding 5 mL of stock solution and it is made upto 250 mL by using double distilled water.

III. RESULTS AND DISCUSSION

3.1 Batch Adsorbtion:

The maximal adsorption proficiency of biosorbent was dictated by fluctuating a few parameters which impact the adsorption , for example, pH, contact time, adsorbent measurement and beginning metal focus by altering the volume of metal answer for 100ml. The concentration decay curves and equilibrium sorption limits were resolved in group tests by shaking fixed test tubes containing 0.5g of sorbent and 50mL of Zn arrangement at foreordained times. The Zn ion concentration in the original arrangement and the metal particles left in mass arrangement were dictated by AAS. Time subordinate tests were done by shaking the adsorption mixture at various predetermined intervals and analyzing the Zn particle content toward the end of the contact time.

3.1.1 Removal Efficency:

The percentage of zinc removal (%) was determined using the below equation:

Removal efficiency = {Ci-Co / Ci} x 100 and Ci, Co are represents the initial and final concentration of zinc metal in mg/L.

3.1a) Effect Of Initial Metal Concentration.

The trials were performed by differing the starting metal focus from 100 to 1000 ppm, while the contact time was kept constant for 30 minutes at a consistent adsorbent and pH 4 and a disturbance velocity of 100 rpm. The adsorbent dosage was taken as 0.5 g. Zn evacuation as an element of contact time and starting metal focus is given in the Fig.1. From the Fig. 1, it is clear that with an expansion in metal focus from 10 to 50 mg/L. After which there was negligible removal since the surface of the sorbent gets exhausted after the formation of one layer thickness of metal ions and then metal uptake rate is controlled due to the transport of ions from exterior to interior site of the adsorbent. Similar trend was observed with ternary biopolymeric microspheres (Bajpai and Rai, 2010). The information created because of impact of starting metal focus helps in deciding the balance concentration (Ce), adsorption capacity(qe), metal uptake rate and motor attributes.

3.1b) Effect Of Adsorbent Dosage:

Adsorbent dose assumes a noteworthy part in adsorption process. From the outcome, as appeared in the Fig. 1a), it is comprehended that, with an expansion in adsorbent measurement from 0.5 to 2.0 g, and kept the other parameters constant as 30 minutes,100 rpm and pH 4 .Optimized values obtained from initial concentration was 20 ppm or 800 mg/L from Fig 1a). The most extreme evacuation was achieved at the adsorbent measurement was obtained at 1.5 g through AAS analysis. The watched pattern might be because of more noteworthy accessibility of surface range and useful bunches at higher adsorbent dose (Suresh and Babu, 2008). Thus, electrostatic association happens between the utilitarian gatherings present in the dynamic site of the adsorbent and the metal particles present in the arrangement.

3.1c) Effect Of Time:

Rate evacuation of Zn particles was measured as a component of time to set up a proper contact time in the middle of adsorbent and adsorbate. Effect of adsorbent measurements with metal grouping of 20 ppm with contact time was differed from 30 to 180 minutes furthermore, speed of 100 rpm at pH 4 particles from the arrangement is higher toward the starting because of more prominent accessibility of surface territory and practical gatherings. With an expansion in time, it was found that there exists a control in metal uptake rate, subsequent to the utilitarian gatherings present in the surface of the sorbent gets depleted. It was found that most extreme evacuation was acquired inside of 120 minutes and balance was accomplished inside of minutes in Fig 1b). The outcomes got were in understanding with Talokar, (2011) where most extreme evacuation was portrayed at a contact time of 30 minutes. Along these lines balance time of a hour was chosen for further studies.

3.1d) Effect Of Ph:

pH is the most imperative parameter in substantial metal biosorption. At fluid stage, Zn exist in a few anionic structures. It is watched from Fig. 1c) that the evacuation rate diminishes with an expansion in pH from 2 to 8. Most extreme evacuation was acquired at pH 7 demonstrating the impact of pH in protonation and deprotonation of adsorbent. As the pH is brought down, the surface of the adsorbent gets to be protonated and the vast majority of the zinc exists as anionic species. Hence extensive number of protons in the adsorbent could undoubtedly arrange with the metal particles present in the arrangement through electrostatic cooperation, while the evacuation rate strongly diminishes with an expansion in pH from 2 to 8 because of the deprotonation of adsorbent.

The adsorbent surface gets to be contrarily charged and there exists electrostatic aversion between anionic type of zinc and adsorbent. Comparable results were gotten with Eucalyptus bark (Sarin and Pant, 2006).

3.1e) Effect Of Agitation:

The agitation speed was differ from 100 to 300 rpm and kept the other parameters as optimized values like 20 ppm of initial concentration, 120 minutes, 1.5 g of dosage and pH7. The solution was filtered from whatman filter papers.The solution was given to AAS analysis. The optimized value was obtained as agitation speed of 250 rpm in Fig 1d).

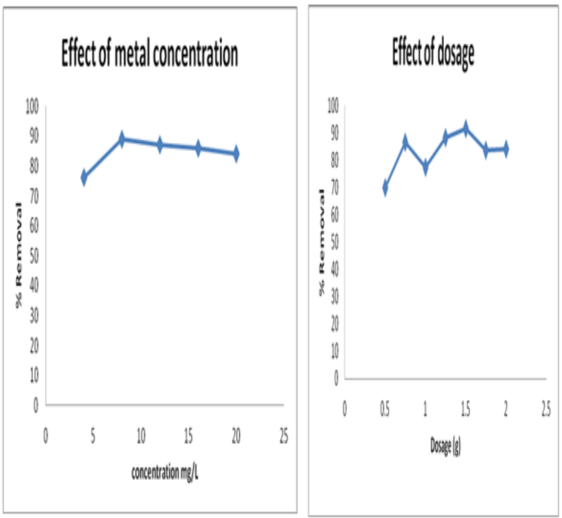


Fig:1a Effect of concentration on removal of Zn
Fig.1.b Effect of dosage on removal of Zn

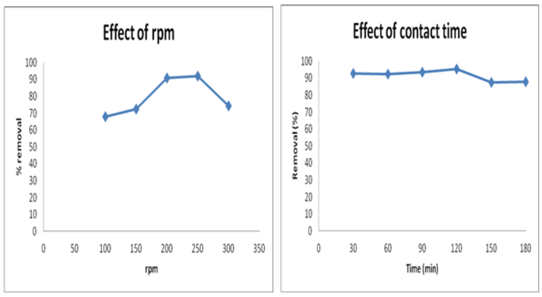


Fig:1.c Effect of agitation on removal of Zn
Fig.1.d Effect of contact time on removal of Zn

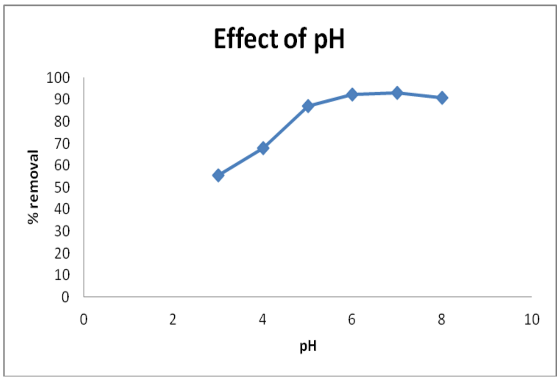


Fig:1 d)

3.2 ft-ir analysis:

To figure out which practical gatherings were responsible for metal sorption, a Fourier transform infrared (FTIR) analyzing strong stage FTIR Spectrometer was performed . FTIR spectra were obtained for gooseberry seed powder before and after the biosorption process. As appeared in Fig. 2(a) and (b), the spectra show various adsorption tops, demonstrating the mind boggling nature of the materials examined.

The broadpeakbetween3412and3444 cm^{-1} is indicative of the existence of bounded hydroxyl groups of macromolecular affiliation (cellulose, pectin, and so forth.). The tops saw at 2920 and 3930 cm^{-1} can be allotted to the C–H bunch. Groups around1650and1750 cm^{-1} are indicative offered esterified carboxyl groups. Moreover, thepeakthatappearsataround1616 cm^{-1} is because of CO extending vibration of a carboxylic corrosive and reinforcing of this crest, on account of gooseberry seed powder, might be demonstrative for increasing number of carboxyl groups on cellulose or pectin chains. The tops around 1596–1616 cm^{-1} are because of the C–C extending that can be ascribed to the sweet-smelling C–C bond. The IR spectra demonstrate that the carbons have distinctive surface structures, e.g., aliphatic, aromatic, cyclic as one can observe at 1457and 1467cm−1 and over the 1374–1250cm−1 territory. The exceptional band at1030–1046cm−1 can be assigned to the C–O of alcohol sand carboxylic acids. Truth be told, it was appeared in the FTIR investigation of the gooseberry seed powder that these materials give a heterogeneous surface diverse useful gatherings accessible to adsorb Zn particle.

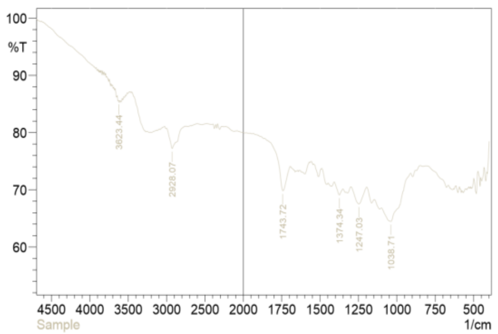


Fig.1 FTIR spectrum analysis on removal of Zinc metal ion Before adsorption

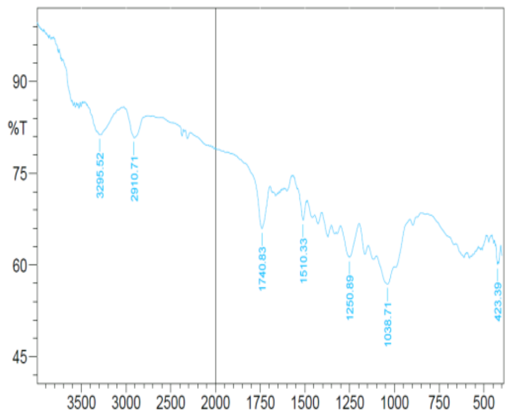


Fig: 2- FTIR spectrum analysis on removal of Zinc metal ion after adsorption

3.3 Sem Analysis

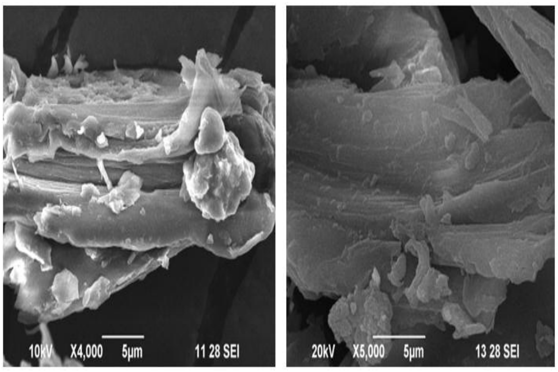


Fig: 2 a) Sem Analysis on Zinc Removal (Before and after adsorption)

SEM analysis was done and it was found that the pore size decreased after absorption. This is due to the binding of zinc ions on the surface of the adsorbent. The layer formed on the adsorbent as shown in fig: 2a) after adsorption shows the zinc ions bound on to the surface of the adsorbent. The morphology of the seed powder before and after adsorption changes and this shows that gooseberry seed powder facilitates the binding of zinc ions effectively.

3.4 Adsorption isotherms:

Adsorption isotherm helps in the assessment of adsorption proficiency of any adsorbent furthermore facilitate in quantifying the correlate particle of harmony with the measure of adsorbate present in the arrangement and relate the quantum of adsorbate adsorbed into any bio resource material at a given temperature. Adsorption limit is given by the observational relations :

$$qe = \frac{(ci - co)}{m} \times v$$

Where qe is the adsorption limit (mg/g), C_i and C_0 are introductory and last metal fixation (mg/L), m is the mass of the adsorbent (g) and V is the volume of the metal arrangement (L). In the present study, adsorption of Zn with the assistance of gooseberry seed powder was
examined by utilizing different adsorption isotherms.

3.4.1 langmuir isotherm model:

This model depends on the suspicion that metal uptake happens on the homogeneous surface by monolayer adsorption. It includes uniform energies of adsorption. Langmuir adsorption isotherm is spoken to by the exact mathematical statement: Fig 3 a)

$$qe = 1/ Qo + 1/ bQoCe$$

Where q is the amount of solute adsorbed per amount of adsorbent (mg/g), K (L/mg) and q0 (mg/g) are the Langmuir constants related to energy of adsorption and maximum monolayer capacity and y is the solution concentration in the solution (mg/L). By plotting 1/q versus 1/y, Langmuir parameters were obtained

3.4.2 Freundlich Isotherm Model:

Freundlich adsorption isotherm is estimated, that metal uptake happens on the heterogeneous surface of an adsorbent by multilayer adsorption. It includes non uniform energies of adsorption from Fig 3 b). Freundlich adsorption isotherm is given by the empirical equation:

$$\log qe = \log KF + 1/ n \log Ce$$

3.4.3 temkin adsorption isotherm model.

Temkin model depends on the idea that the warmth of adsorption of all particles diminishes straightly with scope because of adsorbate-adsorbent association. It includes uniform dissemination of tying energies upto some greatest tying vitality from Fig 3c). Temkin adsorption isotherm model is spoken to by the linearized type of comparison:

qe= Bt lnA+ Bt lnCeq

3.4.4 Hill Isotherm Model:

Slope's comparison was hypothesized to clarify the coupling of different species onto homogeneous substrates. The model accept that adsorption is a helpful marvel, with the ligand tying capacity at one site on the macromolecule, might impact distinctive tying destinations on the same macromolecule.Fig 3d)

$$qe = Qh\frac{Ce^{nH}}{Kd + Ce^{nH}}$$

whereKD, nH, and qHare constants.

3.4.5 Jovanovic Adsorption Isotherm:

Likewise the same presumptions contained inside of the Langmuir display, the Jovanovic model considers the likelihood of some mechanical contacts between the adsorbing and desorbing molecules from Fig 3e). exhibited the steady's estimation for the Jovanovic model

qe= qm(1 − exp (−KJCe))

where qm and KJ are constants.

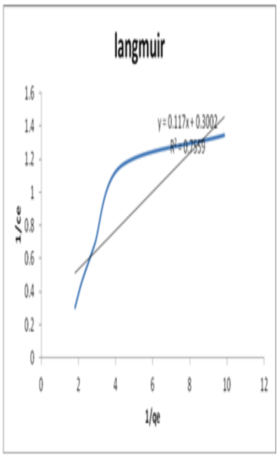


Figure: 3(a)

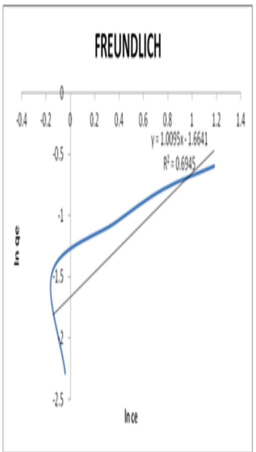
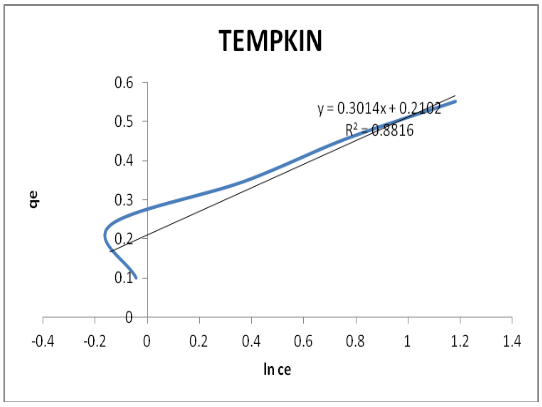


Figure:3 (b)



Figgure;3(c)

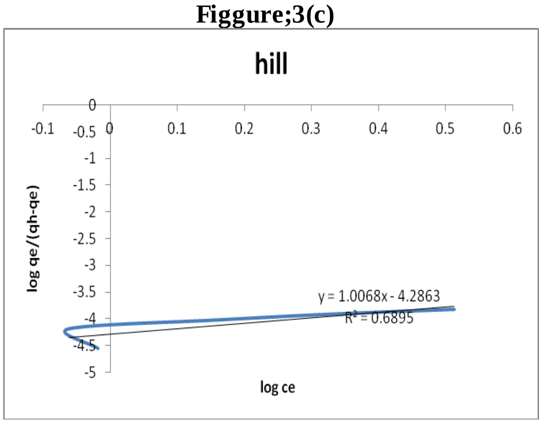


Figure: 3(d)

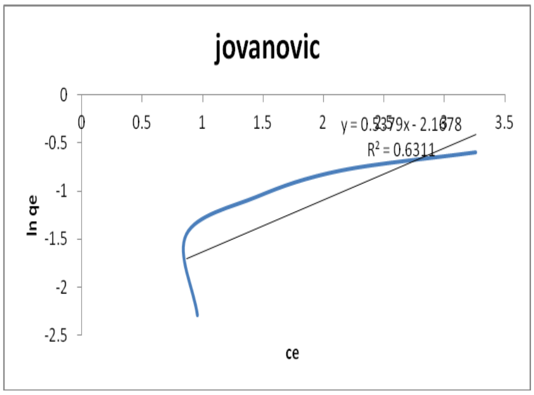


Figure: 3 e)

Isotherm model	Langmuir isotherm model	Freundlich isotherm model	Temkin isotherm model	Hill isotherm model	Jovanovic isotherm model
R^2	0.7559	0.6945	0.8816	0.6895	0.6311

Table : 1 Adsorption isotherm model

3.5 Adsorption Kinetics:

Thinks about on adsorption energy were completed with a specific end goal to decide the metal uptake rate. The impact of beginning metal focus was explored to decide the best dynamic model. Pseudo first request energy model were connected by plotting log (qe-qt) R2 worth was observed to be 0.994 and the outcomes forgotten were observed to be in concurrence with the results got from the biosorption of Zn utilizing the husk of Bengal gram (Ahalya et al., 2005). Pseudo second request energy model were connected by plotting t/qt versus time.

From the Fig. 4 a & b. B,R2Worth was seen to be high (0.999) which suggests adsorption component obeys Pseudo Second request. Different constants decided from energy study are studied. The outcomes got were comparable when granular initiated carbon was utilized as an adsorbent (Gholipour et al., 2011).

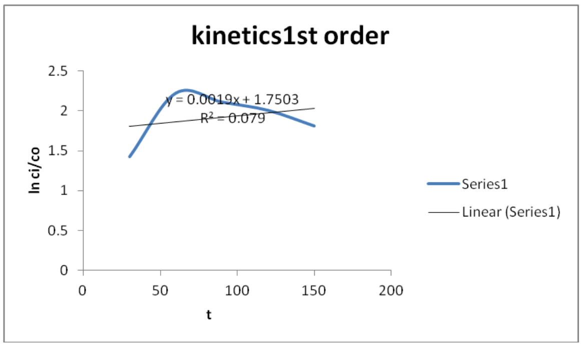


Figure :4 (a)

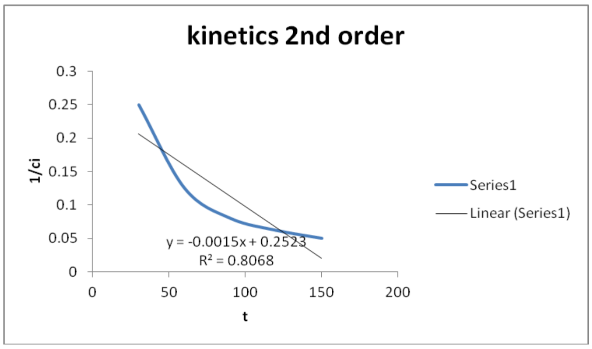


Figure: 4(b)

Kinetics model	Kinetics 1st order	Kinetics 2nd order
R^2	0.079	0.8068

Table : 2 Adsorption kinectics reaction readings

3.6 Treatment Of Industrial Waste Water.

Waste water was collected from Sivakasi crackers industry to study the removal of zinc from it. Under the optimized conditions, the waste water contain zinc is 6.82mg/liter, these polluted waste water was treated to with gooseberry seeds as bioadsorbent to check the amount of zinc present in the adsorbate is 1.08 mg/lit. So the removal of zinc was found to be 84 % which shows the effectiveness of gooseberry seeds.

IV. CONCLUSION

The gooseberry seed powder was found to be better adsorbent based on its efficiency in the removal of zinc, with 96% efficiency, under optimum condition like pH of 7, dosage of 1.5g and equilibrium attained within 120 minutes. Temkin > Langmuir> Freundlich >Hill >Jovanovic. Tempkin isotherm was found to be the best fit and the adsorption mechanism observed. Kinetics 2nd order> kinetics 1st order Pseudo second order kinetics was found best fit to this adsorption kinetics. Removal of zinc from industrial waste water is 84%. Hence the g ooseberry seed powder can be claimed as good for removal of zinc from industrial effluents. This system can be engineered on large scale with low operational and maintenance cost. It is found that spent gooseberry seed powder which is cheap, abundantly available locally and reusable is the most economical among all the developed low cost adsorbents and alternatives to current purification.

REFERENCES

[1]. Ahalya, N.; Kanamadi, R.D.; Ramachandra, T.V., (2005).Biosorption of chromium from aqueous solution by the husk of Bengal gram, E.J.Biotechnol., 8 (3): 258-267**).**

[2]. APHA, AWWA, WEF, (2005). ‘Chromium 3500-Cr DCalorimetric examination of water and wastewater, 17th ed.American Public Health Association, Washington DC.

[3]. A. Saeed, A.M. Waheed, M. Iqbal, Removal and recovery of heavy metals from

[4]. aqueous solution using papaya wood as a new biosorbents, Sep. Purif. Technol.

[5]. 45 (2005) 25–31.

[6]. Baral, S.S.; Das, S.N.; Rath, P., (2006). Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, Biochem. Eng. J., 31(3): 216-222**.**

[7]. B.G. Lee, R.M. Rowell, Removal of heavymetal ions fromaqueous solutions using

[8]. lignocellulosicfibers, J. Nat. Fibers 1 (2004) 97–108.

[9]. Calace, N.; Nardi, E.; Petronio, B.M.; Pietroletti, M.; Tosti, G., (2003). Metal ion removal from water by sorption on paper mill sludge, Chemosphere, (51): 797–803 .

[10]. Cimino, G.; Passerini, A.; Toscano, G., (2000). Removal of toxiccations and Cr(VI) from aqueous solution by hazelnut shell, Water Res., 34(11): 2955-2962**).**

[11]. Gholipour, M.; Hashmipour, H.; Mollashahi, M., (2011). Hexavalent chromium removal from aqueous solution via adsorption on granular activated carbon – Adsorption,Desorption, Modeling and Simulation studies, ARPN J.Eng. Appl. Sci., 6(9).

[12]. Ho, Y.S.; McKay, G., (1999). Pseudo-second order model for sorption processes, Process Biochem., (34): 451-465.

[13]. H. Pino, L.M.S. de Mesquita, M.L. Torem, Biosorption of heavy metals by powder
[14]. of green coconut straw, Sep. Sci. Technol. 41 (2006) 3141–3153.
[15]. I. Gaballah, G. Kilbertus, Recovery of heavymetal ions through decontamination
[16]. of synthetic solutions and industrial effluents using modified barks, J. Geochem.
[17]. Explor. 63 (1998) 241–286.
[18]. Karthikeyan, T.; Rajgopal, S.; Miranda, L.R., (2005).Cr(VI) adsorption from aqueous solution by HeveaBrasilinesis sawdust activated carbon, J. Hazard. Mater., 124(1-3): 192-199
[19]. K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions
[20]. by spent grain, Process Biochem. 36 (2000) 59–64.
[21]. M. Kobya, Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut
[22]. stactivated carbon: kinetic and equilibrium studies, Bioresour. Technol.
[23]. 92004) 317–321.
[24]. Muthukumaran, K.; Beulah, S.S., (2010). SEM and FT-IR studies on nature of adsorpt ion of Mercury(II) and Chromium(VI) from waste water using chemically activated Syzygium jambolanum nut carbon, Asian J.Chem., 22(10): 7857-7864
[25]. N.A.A. Babarinde, J.O. Babalola, R.A. Sanni, Biosorption of lead ions fromaqueous
[26]. solution by maize leaf, Int. J. Phys. Sci. 1 (2006) 23–26.
[27]. Nguyen, T.A.H.; Ngo, H.H.; Guo, W.S.; Zhang, J.; Liang, S.; Yue, Q.Y.; Li, Q.; NguyenT.V., (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater, Bioresour. Tech., (148):574-585**.**
[28]. N. Meunier, J. Laroulandie, J.F. Blais, R.D. Tyagi, Cocoa shells for heavy metal
[29]. removal from acidic solutions, Bioresour. Technol. 90 (2003) 255–263.
[30]. Orhan, Y.; Buyukgungur, H., (1993). The removal of heavy metals by using agricultural wastes, Wat. Sci. Technol.,28(2): 247-255**.**
[31]. P. Madoni, D. Davoli, G. Gorbi, L. Vescovi, Toxic effect of heavy metals on the
[32]. activated sludge protozoan community,Water Res. 30 (1996) 135–142.
[33]. Salman, H.A.; Ibrahim, M.I.; Tarek, M.M.; Abbas, H.S., (2014). Biosorption of heavy metals – a review, J. Chem.Sci. Tech., 3(4): 74-102 **.**
[34]. Sarin, V.; Pant, K.K., (2006). Removal of chromium from industrial waste using eucalyptus bark, Bioresour. Technol.,(97): 15-20 .
[35]. S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low cost
[36]. sorbents for heavy metals,Water Res. 33 (11) (1999) 2469–2479.
[37]. Singha, B.; Naiya, T.K.; Bhattacharya, A.K.; Das, S.K.,(2011). Cr(VI) Ions Removal from Aqueous Solutions Using Natural Adsorbents-FTIR Studies, J. Environ.Protec., (2): 729-735**.**
[38]. Suresh, G.; Babu, B.V., (2008). Adsorption of Chromium (VI) by a Low-Cost Adsorbent Prepared from Tamarind Seeds**,** J. Environ. Eng. Sci., 7(5): 553-557.
[39]. Talokar, A.Y., (2011). Studies on removal of chromium from waste water by adsorption using low cost agricultural biomass as adsorbents, Int. J. Adv. Biotechnol. Res., 2(4):
[40]. 452-456 **.**
[41]. Temkin, M.J.; Pyzhev, V., (1940). Recent modifications to Langmuir isotherms, ActaPhysiochim USSR, (12): 217-222.
[42]. Y. Orhan, H. Buyukgungor, The removal of heavy metals by using agricultural
[43]. wastes,Water Sci. Technol. 28 (2) (1993) 247–255.