Biosorption of Cr, Ni & Cu from industrial dye effluents onto *Kappaphycus alvarezii*: assessment of sorption isotherms and kinetics

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Abstract— Biosorption is considered as one of the most effective treatment technology for the removal of toxic metals from the environment. Biosorption potential of *Kappaphycus alvarezii* was studied for removal of toxic heavy metals such as chromium (Cr), nickel (Ni) and copper (Cu) from industrial dye effluents in batch mode. The experiments were carried out at room temperature ($25 \pm 1°C$) at pH 7. The equilibrium time was observed at 70 to 80 minutes. The study reveals maximum 90.22 % and 68.78 % of Ni and Cr removal respectively in E1 effluent and 81.53 % of Cu removal in E4 effluent. The Freundlich and Langmuir isotherm shows the favorable biosorption of metals and data are well fitted; kinetic study reveals the adsorption reaction follows pseudo-second order model and the data fitted well with the kinetic studies. The SEM and FTIR analysis represents strong cross linkage of the metals and functional groups variation which was occurred due to the potential biosorption capability of the biomass. Thus the red seaweed biomass of *Kappaphycus alvarezii* has considerable potential as biosorbent for the removal of heavy metals from effluent which is eco friendly and low cost material to apply on polluted water contaminated with toxic metals.

Keywords— Biosorption, Heavy metal, FTIR, SEM, Freundlich model, Langmuir model, Kinetics

INTRODUCTION

Presence of heavy metal in water is main concern of water pollution. Various industries contribute in environmental pollution by discharging loads of toxic substances and hazardous material which damages the environment [1]. There are more than 0.7 million tons of synthetic dyes are produced every year and more than 10,000 different types of dyes and pigments produced around the globe. India leads the production of reactive dyes due to accessibility of dyes intermediate such as vinyl sulphone in the country; the other countries such as Taiwan, China and Korea mainly produce scatter dyes [2]. Thus it resulted in increasing demands of dyes in various applications such as pulp & paper, ink & paint, food, cosmetics, pharmaceuticals, textile, electroplating, plastic, tannery & leather industries etc. This excessive demand of applications contributes release of hazardous chemicals and heavy metals in water systems which creates health hazardous for all living organisms [3][4]. During the processing operations approximately 10-20 % of the dye products lost in effluent streams [5]. There are various conventional methods to treat these effluents such as chemical coagulation and flocculation, trickling filter, ion-exchange methods, membrane separation, advanced oxidation process, electrolysis process, photo-degradation available [6][7][8][9][10][11][12] However these processes possess inherent astrictions such as generation of by products, high cost intense power requirements [13]. Biological treatments such as biosorption and biodegradation implied economically low cost and environment friendly methods to be proposed for its potential application in mitigation of dyes from dyes effluent [14][15][16][17]. Biosorption takes place on the surface of biomass. It can be considered that biosorption process indicates passive sorption of pollutants and metals which contributes in reduction of pollutant by allowing the recovery of the products from the effluent by utilizing living and non living biomass [18][19][20][21]. Biosorption acquired from dead microbial cells, seaweed biomass, agricultural waste [22], aquatic ferns, orange peels [23] are used as chelating and complexing biosorbents to appropriately remove metals to contemplate and dyes from effluent [24][25][26][27][28][29][30]. Seaweed biomass is reported to have a tremendous biosorptive performance [31][32]. Seaweeds can to be easily and speedily grown on rocky surface because of its vast abundance in oceanic shores, they are found suitable for the biosorption. Seaweeds have special surface properties to easily bind metallic and organic components from the effluent. They possess characteristic cell wall that binds with pollutants. The algal cell wall comprised of various functional groups such as sulphate, phosphate, amino, carboxylic acid, alginic acid, proteins [30]. Even though large abundance of seaweed species on the globe was found but there are very few reports available to study biosoption of metals and organic components removal application in effluent treatment. Various species of microalgae and macro algae are potential for the waste treatment systems but all the reports were found only on metal removal capabilities from effluents [33][34][35][36]. In the present study red seaweed biomass of *Kappaphycus alvarezii* was used for determination of heavy metal removal. The adsorption procedure studied through kinetics and isotherm perspectives.

MATERIAL AND METHODOLOGY

Effluent Collection with Heavy Metal Analysis

The effluent was collected from different industrial dyes units of Gujarat, India. The collected effluents were entitled as E1, E4 and E6 as they are the effluent of reactive red azo, reactive yellow azo dyes and reactive black azo dyes effluent respectively. These effluents contain mixture of chemical complex structures and heavy metals. The heavy metal concentration in effluents was studied by ICP-OES (Model-Optima 3300 RL, Make-Perkin Elmer) followed by standard methods of APHA-AWWA, 1985. The concentration of Cr, Ni and Cu is indicated in Table-1.

The effluent samples E1, E4 and E6 were digested by aqua-regia of HCL: HNO_3 (1:3 V/V) on hot plate in a beaker for an hour and then diluted with double distilled water. These light yellow colored effluent samples were analyzed for heavy metals Cr, Ni and Cu after digestion using Atomic Absorption Spectroscopy (Make-Shimadzu, Model-AA 7000).

Table-1 Heavy Metal Analysis of Effluent

Heavy Metal	Chromium (Cr) ppm	Nickel (Ni) ppm	Copper (Cu) ppm
E1	0.6573	0.174	-
E4	0.5179	0.2054	16.865
E6	0.1376	0.1754	16.048

(E1 is the effluent of reactive red azo dyes, E4 is the effluent of reactive yellow azo dye and E6 is the effluent of reactive black azo dyes; ppm is parts per million)

Biosorption Study by *Kappaphycus alvarezii*

The biosorption of heavy metal such as Cr, Ni and Cu was studied by using biomass of *Kappaphycus alvarezii*. The experiment was carried out in batch mode in which 2 g of seaweed biomass was inoculated in 200 ml of dye effluent in 500 ml conical flask. the constant agitation speed of 80 rpm was maintained throughout the experiment in flask shaker for better contact of biomass surface area at ambient condition. The samples were taken at every 10 minutes interval and immediately filtered the effluent with Whattman paper no. 40 to prepare the effluent adsorbent free. The filtered effluent samples were analyzed using atomic adsorption spectrophotometer (Make-Shimadzu, Model-AA 7000). The biosorption equilibrium was calculated by

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Co and Ce is the initial and equilibrium dye effluent respectively, W and V are the weight of the biomass (g) and V is the volume (ml). The concentration of adsorbed heavy metal at time t mentioned as qt was calculated according to equation (2) [37]

$$q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

Where Co is the initial concentration (ppm) and Ct is concentration of metal in filtrate effluent at time t; W is the weight of biomass (g) and V is the volume (ml). The percentage heavy metal removal was determined by equation as below:

$$\text{Biosorption yield (\%)} = \frac{C_o - C_t}{C_o} \times 100 \tag{3}$$

Scanning electron microscopy (SEM)

The morphological study of *Kappaphycus alvarezii* for before and after treatment of effluent E1, E4 and E6 was induced by Field emission gun- scanning electron microscopy (Make: FEI Ltd., Model: Nova NanoSEM 450)

Fourier Transform Infrared Analysis (FTIR)

The FTIR spectra was studied by FTIR spectrophotometer (Make: Perkin Elmer, U.S.A., Model: Spectrum GX) by analyzing treated and untreated seaweed biomass which is achieved by K-Br disk method. The 2 mg of biomass samples were crushed with 200 mg of K-Br (spectroscopic grade). It was analyzed and scanned under 4000 to 400 cm^{-1} range.

RESULT AND DISCUSSION

The heavy metal quantity absorbed by the *Kappaphycus alvarezii* as a function of contact time with the heavy metal Cr, Ni and Cu is shown in Fig-1. Biomass indicates slow adsorption initially and reaches equilibrium at 70 to 80 minutes and then it becomes steady and slowly lowered. It was occurred due to the *Kappaphycus alvarezii* has strong adsorption capacity because of the presence of porous surface and vacant space available, it get swollen slowly after accumulation of water inside the cells and after equilibrium the adsorption rate was found decreased due to repulsive forces in molecules and lowered vacant space availability therefore initially the adsorption rate was found initially slow [38]. Similar work was found by various scientists for biosorption of heavy metal such as Cd, Hg, Pb, As, Co, Cu, Mo (VI) [39][40][41][42][43][44][45]
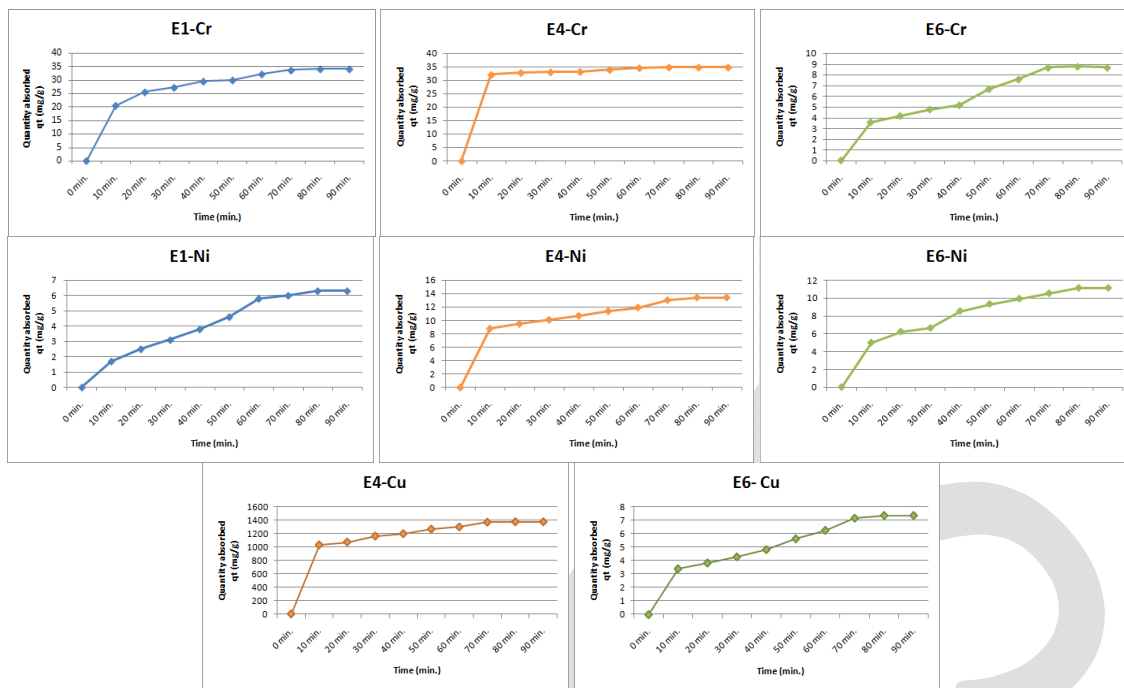
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Fig-1 Biosorption capacity of red seaweed *Kappaphycus alvarezii* as function of contact time

The heavy metal such as Cr and Ni removal was observed maximum as 68.78 % and 90.22 % respectively in E1 effluent and Cu removal was observed maximum as 81.53 % in E4 effluent indicated in Figure-2. There are so many literatures available on biosorption treatment of effluent in 250 to 180 minutes by seaweed biomass [46][47][48]. Higher metal affinity is depending on hydrolysis constant, ionic charge and ionic size of individual metals [49][50][51]. In the present study highest metal affinity was found as Ni > Cr > Cu in *Kappaphycus alvarezii*
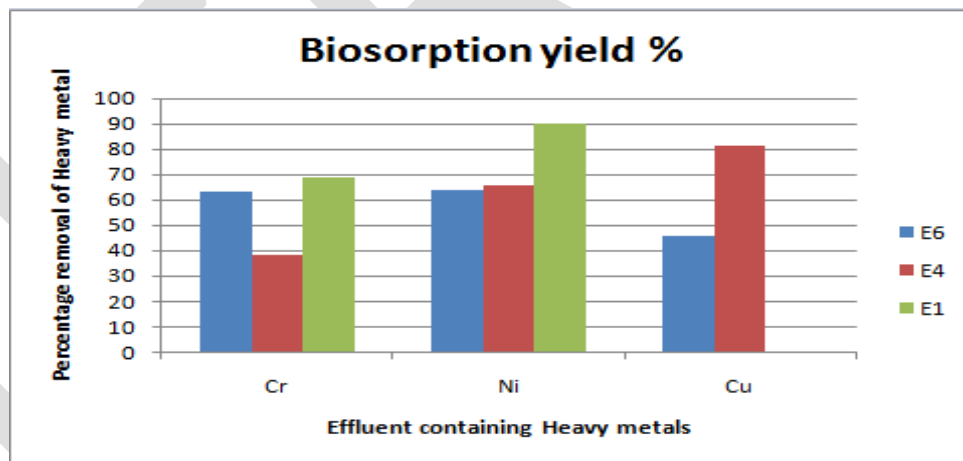
Fig-2 Percentage heavy metal removal

Biosorption isotherms

The equilibrium isotherms such as Langmuir and Freundlich were applied to derive adsorption characteristics such as gain of adsorbate and adsorbate in bulk on surface of adsorbent at equilibrium concentration. The effluent samples E1, E4 and E6 were taken for the removal of heavy metals such as metals Cr, Ni & Cu to evaluate biosorption capability of *Kappaphycus alvarezii*. As mentioned the Langmuir and Freundlich isotherms were successfully applied in the sorption study [52][53]. The Langmuir equation [54] in linerized form is as below.

$$\frac{Ce}{Qe} = \frac{b}{Qo} + \frac{Ce}{Qo} \tag{4}$$

The plot of adsorption ($Ce/q e$) verses equilibrium concentration (Ce) is shown in Fig-3 to Fig-10 represents the Langmuir model. Table-2 indicates the values of Q_m and b. The vital characteristics of Langmuir model can be stated by constant separation factor R_L shown in equation below:

$R_L = \dfrac{1}{1+bC0}$ (5)

The RL value shows the adsorption character to be unfavorable (RL > 1), favorable (0 < RL < 1), linear (RL = 1) or irreversible (RL = 0).

The Freundlich isotherm equation [55] is indicated as below:

$\ln Qe = \ln Kf + \dfrac{1}{n}\ln Ce$ (6)

Where n and K_f are Freundlich constants; which is determined by slope of the plot and intercept shown in Fig-11 to Fig-18 indicates the intensity and adsorption capability respectively.

Equillibrium studies

The values of Freundlich and Langmuir are represented in Table-2. The plots of Langmuir isotherms shown in Fig-3 to Fig-10 indicate adsorption of metals onto the biomass. The straight lines explains Langmuir model for equilibrium adsorption. The Langmuir and Freundlich model were observed favorable in all metals as shown in Table-2. The Freundlich model was found favorable in all samples except Cr in E4 and E6 & Cu in E4 effluent. The Freundlich isotherm indicates high adsorption capacity of biomass *Kappaphycus alvarezii* with quite rapid progression for metal adsorption.
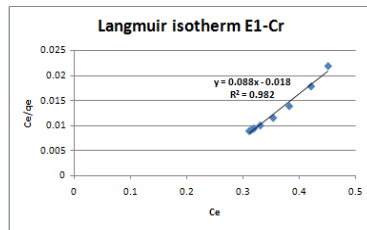
Figure-3
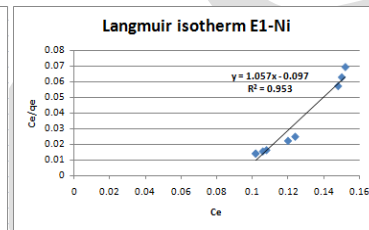
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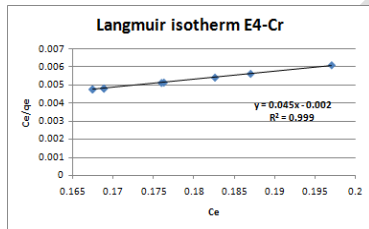
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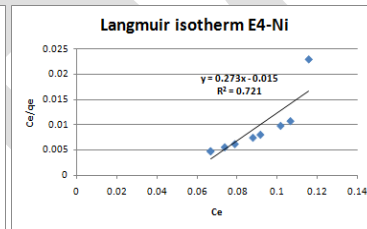
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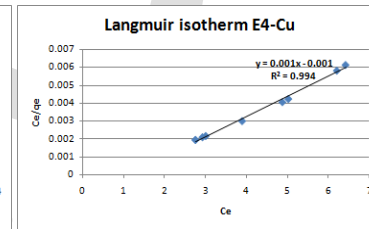
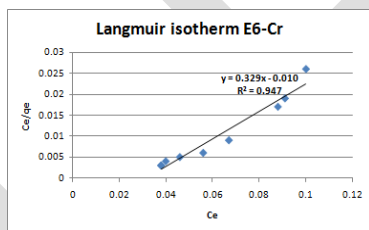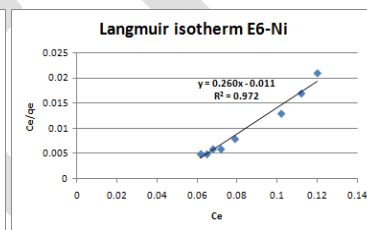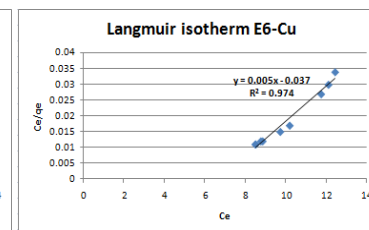

Figure-7

Figure-8

Figure-9

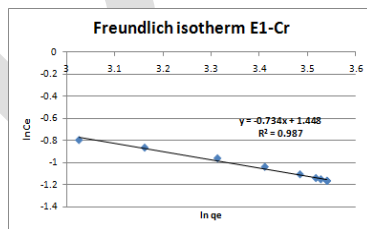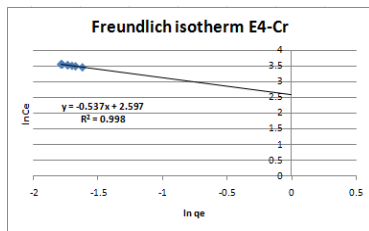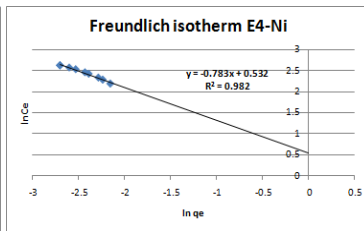(Fig-3 to Fig-10 shows Langmuir isotherm plot for chromium, nickel and copper)
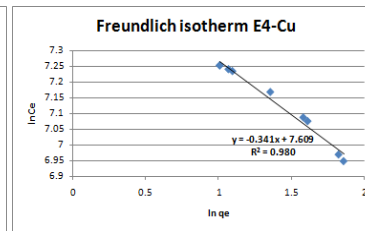

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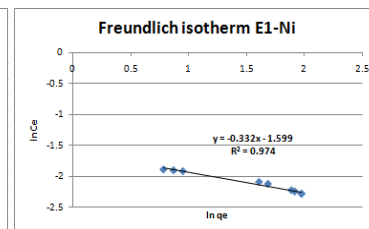
Figure: 11

Figure: 12

Figure:13

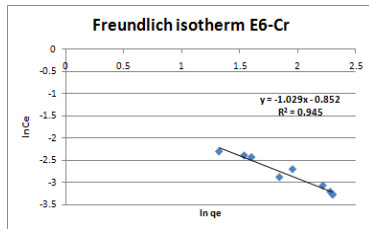
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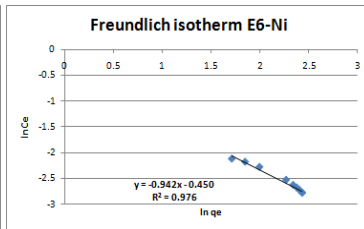

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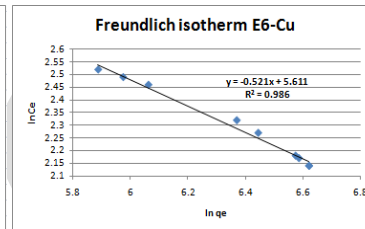

Figure:16

Figure:17

Figure:18

(Fig-11 to Fig-18 shows Freundlich isotherm plot for chromium, nickel and copper)

Table-2: Biosorption isotherm parameter for heavy metal sorption onto *Kappaphycus alvarezii*

Isotherm	Metal	Parameter	Value		
			E1	E4	E6
Langmuir Isotherm	Chromium	R^2	0.982	0.999	0.947
		q_{max}(mg/g)	55.55	500	100
		B	0.204	0.044	0.030
	Nickel	R^2	0.953	0.721	0.972
		q_{max}(mg/g)	10.30	66.66	90.9
		B	0.091	0.054	0.042
	Copper	R^2	-	0.994	0.974
		q_{max}(mg/g)	-	1000	27.02
		B	-	10	7.40
Freundlich isotherm	Chromium	R^2	0.987	0.998	0.945
		K_F	1.362	1.862	0.97
		N	0.69	0.38	1.173
	Nickel	R^2	0.974	0.982	0.976
		K_F	3.012	1.355	1.061
		N	0.62	1.879	2.22
	Copper	R^2	-	0.980	0.986
		K_F	-	2.932	1.919
		N	-	0.131	0.178

Sorption kinetics

The binding of metals was monitored with time. The rapid binding of metals to the biomass was found initially slow and then it become rapid followed by reaching the equilibrium time at 70 to 80 minutes, after 80 minutes no change was observed in equilibrium time. This process occurred because of availability of vacant space inside the biomass cells. The kinetics was studied by the pseudo first and second order rate equation models.

The Lagergren's first order equation describes adsorption rate depended on adsorption capacity of the biomass. It is given as below in linear form (Lagergren, 1898) [56]:

ln (qe - qt) = ln (qe - K₁ t)   (7)

The pseudo second order model in linerized form is given by the Ho [57] (Ho, 1995) is:

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe} t$$ (8)

Where, q_e & q_t were the content metals (mg/g) adsorbed at equilibrium & time t and the K is pseudo-second order rate constant of adsorption (g/mg/time). The linear plot of t vs t/qt was obtained which shows the kinetic data best fitted in pseudo-second order model.

The linear plot of ln (qe-qt) vs t for pseudo-first order reaction and t/qt vs t for pseudo-second order reaction of the metal adsorption onto *Kappaphycus alvarezii* was shown in Fig-19 to Fig-34. The correlation coefficients are closer to the correlation coefficient of second-order kinetics indicates that the reaction follows pseudo second order model
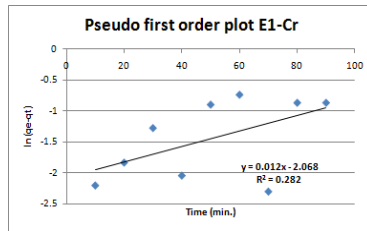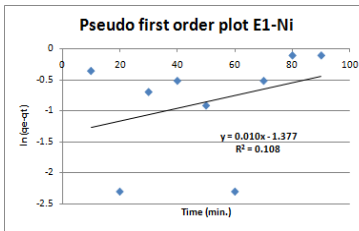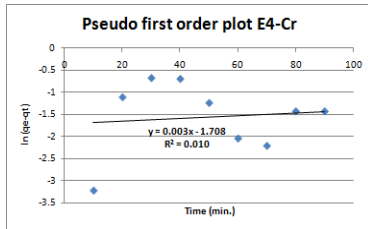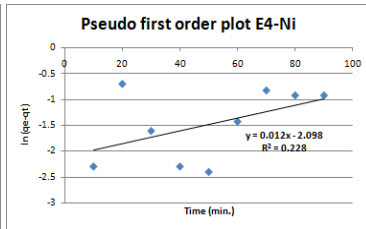

Figure-19   **Figure-20**

Figure-21   **Figure-22**   **Figure-23**

(Fig-19 to Fig-26 shows pseudo first order kinetic plot for chromium, nickel and copper)
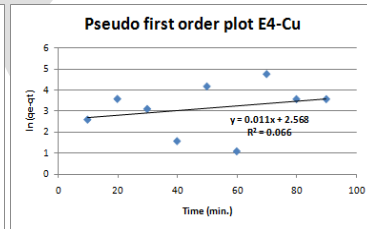
Figure-24   **Figure-25**   **Figure-26**
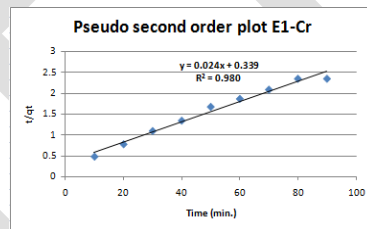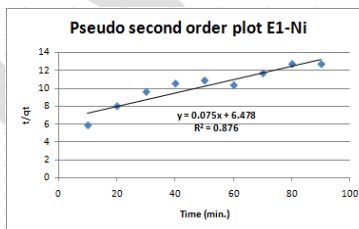
Figure-27   **Figure-28**

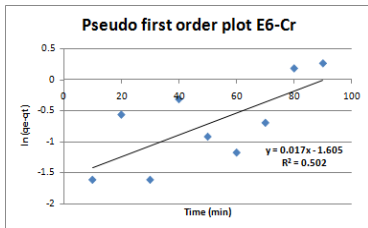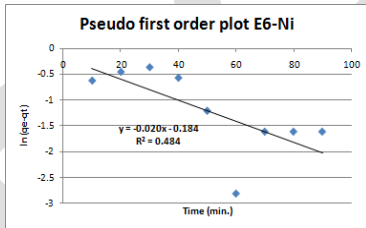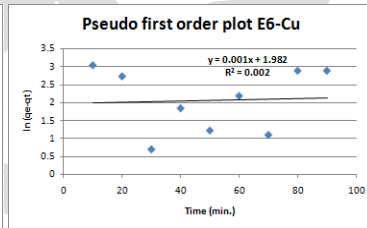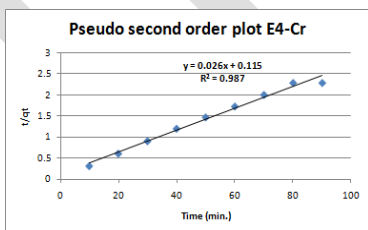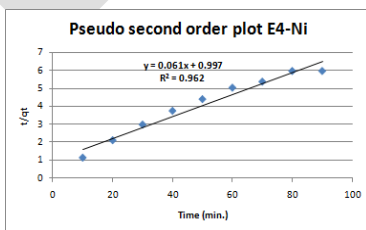**Figure-29**   **Figure-30**   **Figure-31**

(Fig-27 to Fig-34 shows pseudo first order kinetic plot for chromium, nickel and copper)
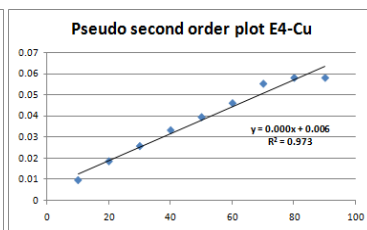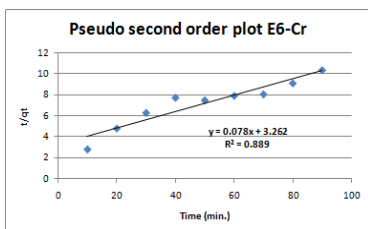
Figure-32   **Figure-33**   **Figure-34**

Fourier Transform Infrared Interpretation (FTIR)

The spectra analysis shows the functional group variation in the seaweed biomass of *Kappaphycus alvarezii* for before and after treatment of metal containing dye effluents shown in Fig-35 to Fig-38. The recorded spectra gives different adsorption peaks which represents the presence of various functional groups in *Kappaphycus alvarezii* such as O-H alcohol, N-H amino salt, C=N oxime/imine, S=O sulfate, S=O sulfonic acid, C-O aliphatic ether, C-O primary alcohol, C-O vinyl ether, O-H carboxylic acid, P-C organo-phosphorus compound, C-O alkyl aryl ether, C-H alkane, C=C alkane disubstituted (cis), C-F fluro compound, C-O primary alcohol, C-O secondary alcohol, C-O tertiary alcohol, N-O nitro compound, C-O aromatic ester, S=O sulfonamide, S=O sulfoxide. Adsorption of metals inside the biomass of *Kappaphycus alvarezii* indicates alternation of the functional groups of the biomass and by comparison of after treatment spectra show decrease in intensity of peaks and band shifts described in Table-3. The IR spectrum of the biomass shows significant variation in peak frequencies due to binding of metals with active sites of the biomass indicates the presence of ionizabal functional groups inside *Kappaphycus alvarezii* which has potential to interact with other cations [58][59][60]. Thus it play important role in removal of metals from the effluents.

The Image-1 represents Scanning electron microscopy (SEM) of untreated & treated biomass of *Kappaphycus alvarezii* with effluent E1, E4 and E6. The biomass surface was smooth and even but after exposure it resulted to swollen cells and uneven surface. This is due to the damaged cells because of the accumulation of metals. It occupies the free binding sites inside the cells of the biomass represents strong cross linkage of the heavy metals due to ion exchange mechanism [37](M. M. Ghoneim, 2014).

Table-3: Fourier transform infrared analysis (FTIR) Interpretation of *Kappaphycus alvarezii*

Kappaphycus alvarezii	Adsorption bands (cm⁻¹)			Assignment
	Initial	Final	Difference	
E₁-effluent	3428.06	3426.27	1.79	O-H stretching alcohol bonded
	2925.56	2925.12	0.44	C-H stretching alkane
	1651.87	1640.08	11.79	C-H aromatic compound bending, C=N stretching imine/oxime, C=C alkane disubstituted (cis)
	1545.93	1543.97	1.96	N-O stretching nitro compound
	1417.43	1412.33	5.1	O-H bending carboxylic acid, O-H alcohol bending, S=O stretching sulfate, C-F fluro compound
	1258.05	1234.64	23.41	C-O stretching aromatic ester, C-O stretching alkyl aryl ether, C-N stretching amine
	1157.83	1127.07	30.76	S=O stretching sulfonamide, S=O stretching sulfone, C-O stretching tertiary alcohol
	1071.23	1069.80	1.43	C-O stretching primary alcohol, S=O stretching sulfoxide, C-O stretching secondary alcohol
E4-effluent	3428.06	3433.50	5.44	O-H stretching alcohol bonded
	2925.56	2925.43	0.13	C-H stretching alkane
	1651.87	1638.31	13.56	C-H aromatic compound bending, C=N stretching imine/oxime, C=C alkane disubstituted (cis)
	1545.93	-	-	N-O stretching nitro compound
	1417.43	1404.24	13.19	O-H bending carboxylic acid, O-H alcohol bending, S=O stretching sulfate, C-F fluro compound
	1258.05	1255.91	2.14	C-O stretching aromatic ester, C-O stretching alkyl aryl ether, C-N stretching amine
	1157.83	1126.90	30.93	S=O stretching sulfonamide, S=O stretching sulfone, C-O stretching tertiary alcohol
	1071.23	1089.98	(-18.75)	C-O stretching primary alcohol, S=O stretching sulfoxide, C-O stretching secondary alcohol
E6-effluent	3428.06	3428.31	(-0.25)	O-H stretching alcohol bonded
	2925.56	2925.32	0.24	C-H stretching alkane
	1651.87	1640.57	11.3	C-H aromatic compound bending, C=N stretching imine/oxime, C=C alkane disubstituted (cis)
	1545.93	-	-	N-O stretching nitro compound
	1417.43	1405.39	12.04	O-H bending carboxylic acid, O-H alcohol bending, S=O stretching sulfate, C-F fluro compound
	1258.05	1253.15	4.9	C-O stretching aromatic ester, C-O stretching alkyl aryl ether, C-N stretching amine
	1157.83	1126.95	30.88	S=O stretching sulfonamide, S=O stretching

			sulfone, C-O stretching tertiary alcohol
1071.23	1070.86	0.37	C-O stretching primary alcohol, S=O stretching sulfoxide, C-O stretching secondary alcohol
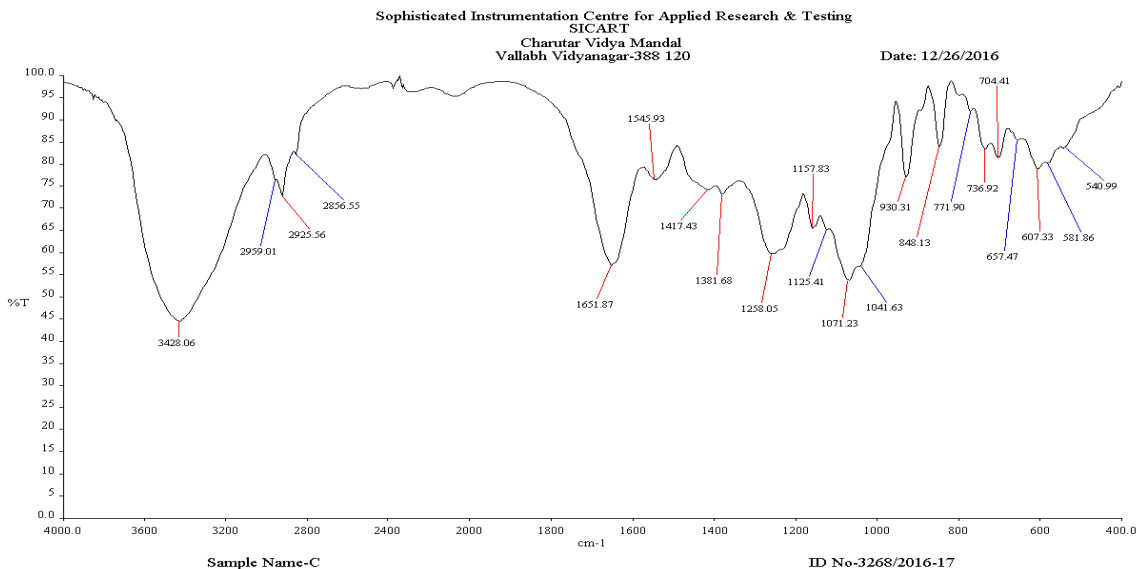
Figure-35

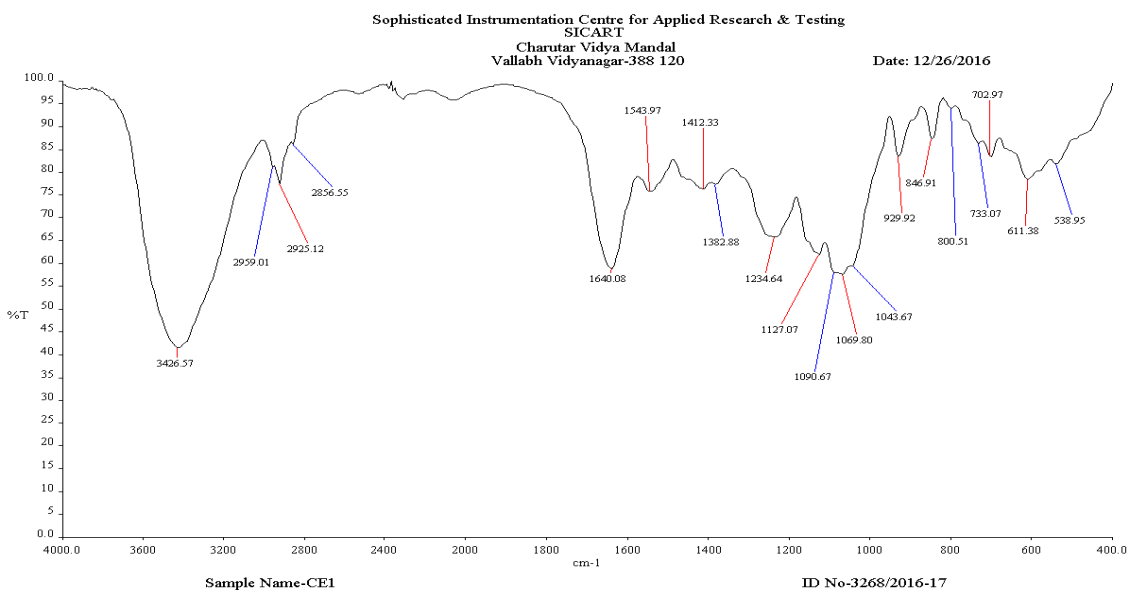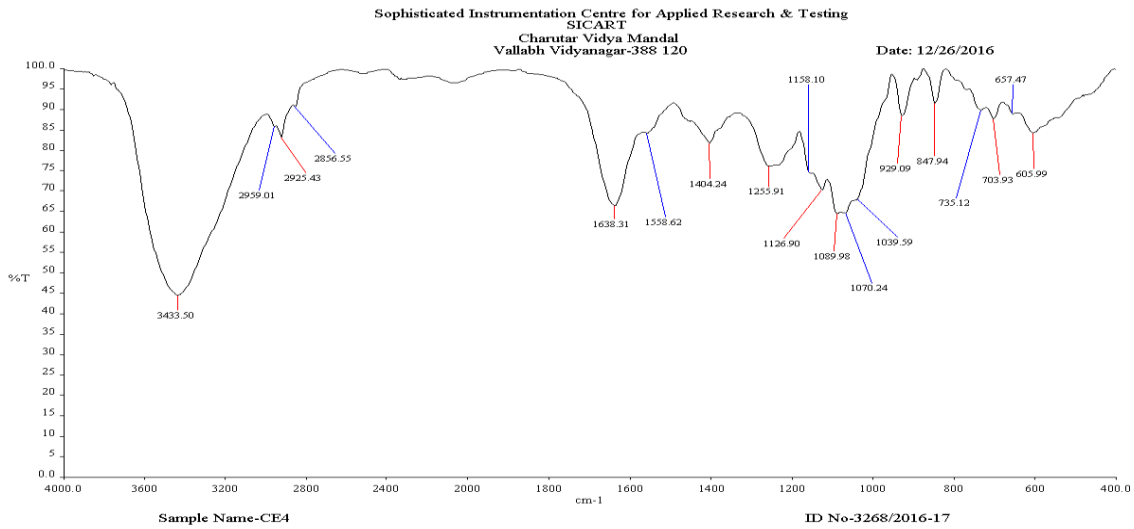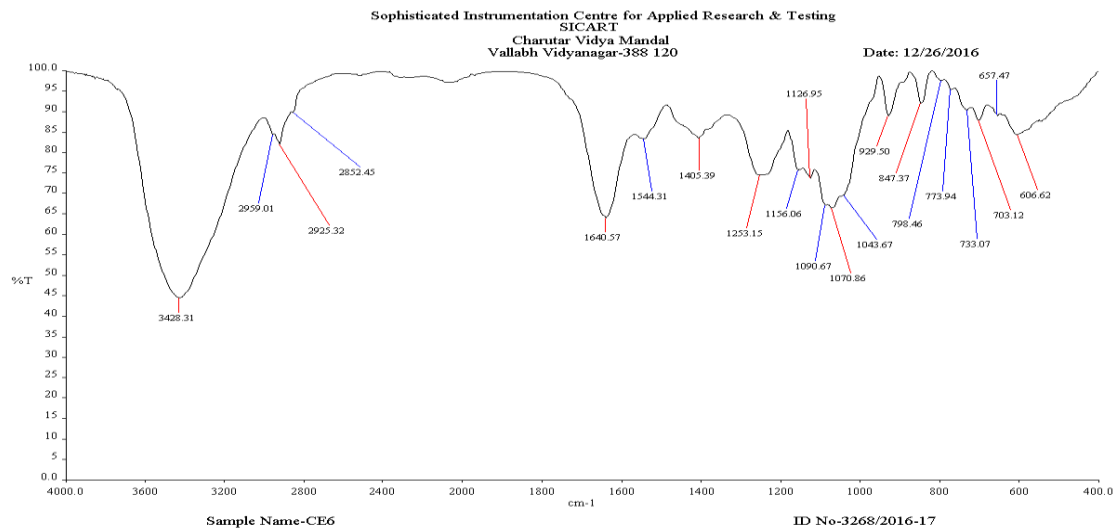**Figure-36**

Figure-37

Figure-38

Image-1: Scanning electron microscopy (SEM) of Untreated & Treated *Kappaphycus alvarezii*
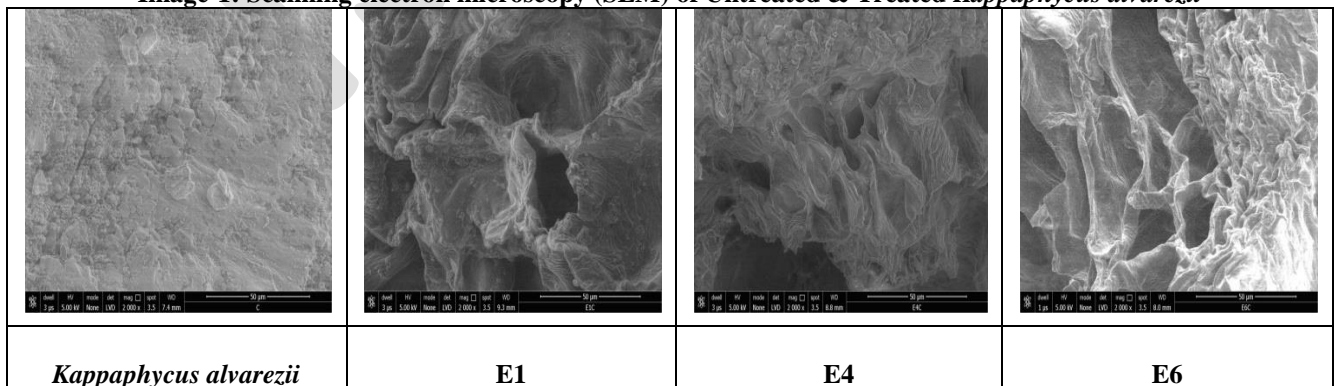
| *Kappaphycus alvarezii* | E1 | E4 | E6 |

ACKNOWLEDGMENT

CONCLUSION

The present study shows that red seaweed biomass of *Kappaphycus alvarezii* has high biosorption capacity for Cr, Ni and Cu. In the present study the highest biosorption was observed as Ni > Cu > Cr as 90.22 % > 81.53 % > 62.93 % respectively in each effluent in 70 to 80 minutes of contact time respectively. The data are well fitted by the Freundlich isotherm and the Langmuir isotherm shows the favorable biosorption of heavy metal and the data on the kinetic studies fitted well which shows the adsorption kinetics of metals by red seaweed biomass of *Kappaphycus alvarezii* followed the pseudo-second order model for biosorption of Cr, Ni and Cu in each effluent shown as E1, E4 & E6. The SEM and FTIR analysis represents strong cross linkage of the metals and functional groups variation which resulted the potential biosorption capability of the biomass. Thus the red biomass *Kappaphycus alvarezii* has considerable potential as biosorbent for the removal of heavy metal from effluent.

REFERENCES:

[1] V. Sivasubramanian "Environmental sustainability using green technologies" Boca Raton, FL: CRC Press, 2016

[2] H. D. Bhimani "Bacterial degradation of Azo Dyes and its derivatives" Thesis PhD, Saurashtra University, Gujarat, India., 2005.

[3] B. H. Hameed, U. G. Akpan, K. P. Wee "Photocatalytic degradation of Acid Red 1 dye using ZnO catalyst in the presence and absence of silver" Desalin. Water Treat 27: 204-209, 2011.

[4] R. H. Souther, T. A. Alspaugh "Textile waste treatment studies" J Water Pollut. Control Fed 29: 918–934, 1957.

[5] N. K. Daud, U. G. Akpan, B. H. Hameed "Decolorization of sunzol black DN conc. in aqueous solution by Fenton oxidation process effect of system parameters and kinetic study" Desalin. Water Treat 37:1–7, 2012.

[6] C. V. Nachiyar, S. Sunkar, G. N. Kumar, A. Karunya, P. B. Ananth "Biodegradation of Acid Blue 113 Containing Textile Effluent by Constructed Aerobic Bacterial Consortia: Optimization and Mechanism" J Bioremed Biodeg 3:162, 2012.

[7] W. Delee, C. O'Neill, F. R. Hawkes, H. M. Pinheiro "Anaerobic treatment of textile effluents: a review" J Chem Technol. Biotechnol 73:323–335, 1998.

[8] S. Mondal "Methods of dye removal from dye house effluent – an overview" Environ Eng Sci 25: 383–396, 2008.

[9] H. S. Rai, M. S. Bhattacharyya, J. Singh, T. K. Bansal, P. Vats, U. C. Banerjee "Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment" Crit. Rev. Environmen. Sci. Technol 35: 219–238, 2005.

[10] T. Robinson, G. McMullan, R. Marchant, P. Nigam "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative" Bioresour Technol 77: 247–255, 2001.

[11] F. P. van der Zee, S. Villaverde "Combined anaerobic–aerobic treatment of azo dyes – a short review of bioreactor studies" Water Res 39: 1425–1440, 2005.

[12] M. T. Sulak, H. C. Yatmaz "Removal of textile dyes from aqueous solutions with eco-friendly biosorbent" Desalin. Water Treat 37: 169–177, 2012.

[13] A. Reife, D. Betowski, H. S. Freeman "Dyes and Pigments" Environmental Chemistry, in The Encyclopedia of Environmental Analysis and Remediation, John Wiley & Sons, New York 3: 1442-1465, 1998.

[14] T. Robinson, G. McMullan, R. Marchant, P. Nigam "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative" Bioresource Technol 77: 247–255, 2001.

[15] Y. Fu, T. Viraraghavan "Fungal decolorization of dyewastewaters: a review" Bioresource Technol 79: 251–262, 2001.

[16] K. Y. Pandya, R. V. Patel, R. T. Jasrai, N. Brahmbhatt "Biodecolorization and Biodegradation of reactive azo dyes by *Kappaphycus alvarezii* and optimization of biofertilizing potential" Res J of Recent Sci., 6 (6): 1-5, 2017.

[17] K. Y. Pandya, R. V. Patel, R. T. Jasrai, N. H. Brahmbhatt "Preliminary Study on Potential of Seaweeds in Decolorization Efficacy of Synthetic Dyes Effluent" Int. J. Plant, Animal and Environ Sci., 7: 59-69, 2017.

[18] Z. Aksu "Application of biosorption for the removal of organic pollutants: a review" Process Biochem 40: 997–1026, 2005.

[19] J. Y. Wu, S. C. J. Hwang, C. T. Chen, K. C. Chen "Decolorization of azo dye in a FBR reactor using immobilized bacteria" Enzyme Microb. Technol 37: 102–112, 2005.

[20] A. Ozer, G. Akkaya, M. Turabik "Biosorption of Acid Red 274 (AR274) on *Enteromorpha prolifera* in a batch system" J. Hazard. Mater 126: 119–127, 2005.

[21]   G. Akkaya, A. Ozer "Biosorption of Acid Red 274 (AR274) on *Dicranella varia*: determination of equilibrium and kinetic model parameters" Process Biochem 40: 3559–3568, 2005.

[22]   **N. Kuyucak "Feasibility of biosorbents application. In: Volesky B (ed) Biosorption of heavy metals" CRC Press, Boca Raton, FL, 371-378, 1990.**

[23]   A. G. El-Said, A. M. Gamal "Potential application of orange peel (OP) as an eco-friendly adsorbent for textile dyeing effluents" J of textile and apparel technol and managem 1(3): 1-13, 2012.

[24]   M. S. Chiou, H. Y. Li "Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads" Chemosphere 50: 1095–1105, 2003.

[25]   Y. C. Wong, Y. S. Szeto, W. H. Cheung, G. McKay "Adsorption of acid dyes on chitosan-equilibrium isotherm analyses" Process Biochem 39: 695–704, 2004.

[26]   C. Namasivayam, N. Kanchana, R. T. Yamuna "Waste banana pith as adsorbent for the removal of rhodamine-B from aqueous solutions" Waste Manage.13: 89–95, 1993.

[27]   Z. Aksu "Reactive dye bioaccumulation by *Saccharomyces cerevisiae*" Process Biochem 38: 1437–1444, 2003.

[28]   Z. Aksu, S. Tezer "Equilibrium and kinetic modelling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: effect of temperature" Process Biochem 36: 431–439, 2000.

[29]   J. Swamy, J. A. Ramsay "The evaluation of white rot fungi in the decoloration of textile dyes" Enzyme Microb Technol 24: 130–137, 1999.

[30]   B. Volesky in: B. Volesky (Ed.), Biosorption of Heavy Metals, C CRC Press, Boca Raton, FL, 3, 1990.

[31]   N. Kuyucak, B. Volesky "Biosorption by algal biomass. In biosorption of heavy metals; Volesky B", Ed.; CRC Press: Boca Raton, FL, 173-198

[32]   F. A. Bertoni, A. C. Medeot, J. C. Gonzalez, L. F. Sala, S. E. Bellu "Application of green seaweed biomass for MoVI sorption from contaminated waters. Kinetic, thermodynamic and continuous sorption studies" J of Colloid and Interface Sci 446: 122–132, 2015.

[33]   C. Das, K. Naseera, A. Ram, R. M. Meena, N. Ramaiah "Bioremediation of tannery waste water by a salt-tolerant strain of *Chlorella Vulgaris*" J of Appl Phycol 29: 235-243, 2016.

[34]   L. S. Badescu, D. Bulgariu, L. Bulgariu "Alternative utilization of algal biomass (*Ulva* sp.) loaded with Zn (II) ions for improving soil quality" J Appl Phycol 29: 1069-1079, 2016.

[35]   S. M. H. Nasab, A. Naji, M. Yousefzadi "Kinetic and equilibrium studies on biosorption of cadmium (II) from aqueous solution by Gracilaria corticata and agar extraction algal waste" J Appl Phycol 29: 1-10, 2017.

[36]   A. Siklina, G. D. Nelson, C. E. Bayliss, C. L. Pooley "Bioremediation efficacy – Comparison of nutrient removal from an anaerobic digest waste-based medium by an algal consortium before and after cryopresearvation" J Appl Phycol 29: 1331-1341, 2017.

[37]   Y. Xun, Z, Shu-Ping, Z. Wei, C. Hong-You, D. Xiao-Dong, L. Xin-Mei and Y. Zi-Feng "Aqueous dye adsorption on ordered malodorous carbons" Journal of Colloid Interface Science 310, 83–89, 2007.

[38]   G. K. Latinwo, L. A. Jimoda, S. E. Agarry, J. A. Adeniran "Biosorption of some heavy metals from Textile Wastewater by Green Seaweed Biomass" Univ J of Env Res and Technol 5 (4): 210-219, 2015.

[39]   M. M. Ghoneim, H. S. El-Desoky, K. M. El-Moselhy, Adel Amer, E. H. Abou el-Naga, L. I. Mohamedein, A. E. Al-Prol "Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*" Egyptian J of Aqatic Res 40: 235-242, 2014.

[40]   N. H. Brahmbhatt and R. V. Patel "Bioremediation potential of *Spirogyra,* toxicity and biosorption on lead (Pb). Indian Hydrobiology" 15 (1): 90-94, 2012.

[41]   N. Brahmbhatt, R. V. Patel, R. T. Jasrai "Accumulation of Chromium by Spirogyra Sp. And its Effect on Its Biochemical Constituents" Int J of Green and Herbal Chem 2 (1): 15-19, 2013.

[42]   J. I. Nirmal Kumar, C. Oommen and R. N. Kumar "Biosorption of heavy metals from aqueous solution by green marine macroalgae from Okha Port, Gulf of Kutch, India" Am-Euras. J. Agric. Environ. Sci., 6, 317-323, 2009.

[43]   G. G. Patel, H. V. Doshi, M. C. Thakur "Biosorption and equilibrium study of Copper by Marine seaweeds from North West Cost of India" J of Env Sci, Toxic and Food Technol 10 (7): 54-64, 2016.

[44]   E.A. Bursali, L. Cavas, Y. Seki, S.S. Bozkurt, M. Yurdakoc, Sorption of boron by invasive marine seaweed: *Caulerpa racemosa var. cylindracea*, Chem. Eng. J. 150: 385–390, 2009.

[45]   F. A. Bertoni, A. C. Medeot, J. C. Gonzalez, L. F. Sala, S. E. Bellu "Application of green seaweed biomass for MoVI sorption from contaminated waters" Kinetic, thermodynamic and continuous sorption studies. J of Colloid and Interface Sci 446: 122–132, 2015.

[46]   M. Rathod, K. Mody, Shaik B "Efficient removal of phosphate from aqueous solutions by red seaweed, *Kappaphycus alverezii*" J of Cleaner Prod 1-10, 2014.

[47]   R. Aravindhan, J. R. Rao, B. U. Nair "Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*" J of Haz Mat 142: 68–76, 2007.

[48]   T. A. Davis, B. Volesky, RHSF Vieira "Sargassum seaweed as biosorbent for heavy metals" Wat Res 34(17): 4270-4278, 2000.

[49]   M. Kousha, E. Daneshvar, M. S. Sohrabi, M. Jokar, A. Bhatnagar "Adsorption of acid orange II dye by raw and chemically modified brown macroalga *Stoechospermum marginatum*" Chem Eng J 192: 67–76, 2012.

[50]   R. Pandimurugan, S. Thambidurai "Synthesis of seaweed-ZnOPANI hybrid composite for adsorption of methylene blue dye" J of Env Chem Eng 4(1):1332-1347, 2016.

[51]   S. E. Agarry, O. O. Ogunleye, O. A. Ajani "Biosorptive removal of cadmium (II) ions from aqueous solution by chemically modified onion skin: batch equilibrium, kinetic and thermodynamic studies" Chem Eng Communications 202: 655-673, 2015.

[52]   I. A. W. Tan, B. H. Hameed, A. L. Ahmad "Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon" Chem Eng J 127: 111–119, 2007.

[53]   B. H. Hameed, A. T. M. Din, A. L. Ahmad "Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies" J Hazard Mater 141: 819–825, 2007.

[54]   B. H. Hameed, D. K. Mahmoud, A. L. Ahmad "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (*Cocos nucifera*) bunch waste" J of Haz Mat 158: 65–72, 2008.

[55]   I. D. Mall, V. C. Srivastava, N. K. Agarwal, I. M. Mishra "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses" Chemosphere 61: 492–501, 2005.

[56]   S. Lagergren "Zur theorie der sogenannten adsorption geloster stoffe" Kungliga Svenska Vetenskapsakademiens Handlingar 24 (4): 1–39, 1898.

[57]   Y. S. Ho "Adsorption of Heavy Metals from Waste Streams by Peat" PhD Thesis, University of Birmingham, Birmingham, UK, 1995.

[58]   N. Ertugay, Y. K. Bayhan "Biosorption of Cr from aqueous solutions by biomass of *Agricus bisporus*" J of Haz Mater., 154: 432-439, 2008.

[59]   O. D. Uluozlu, A. Sari, M. Tuzen "Biosorption of antimony from aqueous solution by lichen (*phusica tribacia*)" Chem Eng J., 163: 382-388, 2010.

[60]   X. F. Sun, S. G. Wang, X. W. Liu, W. X. Gong, N. Bao, B. Y. Gao, H. Y. Zhang "Biosorption of malachite green from aqueous solutions onto aerobic granules: kinetic and equilibrium studies" Biores Technol., 99: 3475-3483, 2008.