



Biosorption of some heavy metals from Textile Wastewater by Green Seaweed Biomass

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Abstract:

The objective of this study was to evaluate the potential of green seaweed biomass to remove heavy metals such as iron (Fe), calcium (Ca), magnesium (Mg), potassium (K), silver (Ag) and chromium (Cr) present in textile wastewater. The wastewater sample was treated with the biomass at different contact time ranging from 10 to 90 minutes. The result showed that there was 87.5%, 99.9 %, 59.7 %, 57.2 %, 100% and 86.8% corresponding maximum reduction in the concentration of Fe, Ca, Mg, K, Ag and Cr at 60 min contact time, respectively. The experimental biosorption data fitted very well to both pseudo first-order and pseudo second-order kinetic models, however, the biosorption kinetics of Fe, Ca, Mg, K, Ag and Cr followed a pseudo first-order kinetic model and the biosorption mechanisms were controlled by boundary layer surface diffusion. Thus green seaweed biomass has the potential to be used as a low cost biosorbent for the treatment of industrial wastewater that contains the presence of heavy metals.

Keywords:

Biosorption; Heavy metals; Seaweed Biomass; Textile wastewater; Kinetics

1.0 Introduction:

Textile industries are one of the biggest consumers of water and complex chemicals during textile processing at various stages (Bansal et al., 2009). The unused materials from processes are discharge as wastewater that is high in color, biochemical oxygen demand (BOD), chemical oxygen demand (COD), PH, temperature, turbidity and toxic chemicals (Davies, 2003). The direct discharge of this wastewater into water bodies like lakes and rivers pollutes the water and affects the flora and fauna. Effluents from textile industries contain different types of dyes, which because of high molecular weight and complex structures, shows very low biodegradability (Donghee et al., 2006). An industrial waste is generated directly by industries. Untreated waste usually contains metals and a large number of potentially harmful compounds. It can cause environmental pollution as well as affect the ecosystem (Hussein et al., 2004). The treatment systems of industrial waste are many; one of the systems is through biosorption process using seaweed. Various seaweeds are found throughout the world's oceans and they come in three basic colors such as brown and red seaweeds which are exclusively aquatic life and green-colored seaweed,

vast majority of which are freshwater while few are terrestrial (Muhammad and Nwaedozi, 2011).

The presence of heavy metals in the environment is a major concern because of their toxicity and threat to plant and animal life (Romera, 2007). Many industries such as pigment manufacturing, iron and steel production, mining and mineral processing, the nonferrous metals industry, battery manufacture, the printing and photographic industries and metal-working and finishing processes (electroplating) are responsible for the release of heavy metals into the environment through their discharge wastewaters. However, recovery of heavy metals from industrial waste streams is becoming increasingly important as to neutralize the hazards of industrial waste that would make it not to be harmful to plant and animal life. This has led to developing effective alternative technologies for the removal of these potential damaging substances from effluents and industrial wastewaters. Many of the studies on metal biosorption by seaweeds have largely been restricted to various species of brown seaweeds (Surjani, 2010). On the other hand, green and red seaweed species have not been evaluated to any

great extent. Therefore, the objective of this study is to evaluate the potential of green seaweed to remove heavy metals from textile wastewater.

2.0 Materials and Methods:

2.1 Sample Collection:

Textile wastewater used for this study was obtained from NICHEMTEX Textile Company, Lagos, Nigeria. It was stored at room temperature prior to use. Green seaweed biomass (chlorophyta) used as the biosorbent for this work was collected from the side of a sea located in Epe town of Lagos State, Nigeria.

2.2 Sample Preparation:

The roots of the green seaweed were removed so as not to change the content of the green seaweed leaves. It was then washed with tap water, followed

by distilled water to remove sand and stones entangled in them and were later dried in the oven at 100 °C for 25 min as to completely remove the water content. The dried sample was blended into powder using a commercial blender and further reduced to finer particles of 0.5 m particle size using Fritsch Rotor Speed Mill-Purverisette 14 and then stored in a transparent container prior to use.

2.3 Characterization of Textile Wastewater:

The textile wastewater was analysed in triplicates for pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS) and heavy metals using standard methods (APHA-AWWA, 1985). The values of the various parameters for the untreated textile waste water are presented in Table 1.

Table 1: Characterization of the untreated textile waste effluents

Parameter	Concentration (mg/L)
pH	10.8 (No unit)
Biological oxygen demand (BOD)	5200 ± 100
Chemical oxygen demand (COD)	6410 ± 230
Total dissolved solids (TDS)	4560 ± 160
Heavy metals:	
Magnesium (Mg)	0.8095
Potassium (K)	0.0872
Iron (Fe)	0.0283
Calcium (Ca)	0.0815
Silver (Ag)	0.0006
Chromium (Cr)	0.0017
Cadmium (Cd)	-

2.4 Batch Biosorption Studies:

The dynamic sorption of the heavy metals present in textile wastewater by the chlorophyta biomass was investigated in batch mode. The batch biosorption study was carried out by contacting 2 g of the seaweed biomass with 200 ml of the waste water in a 500 ml flask. The flask was then agitated at 200 rpm on a water bath shaker for 60 min at room temperature (28 °C). At intervals of 10 min, sample solution was taken and immediately filtered using filter paper to remove the residue while the filtrate was analyzed for residual heavy metals using atomic absorption spectrophotometer. The amount of heavy metal sorbed at time *t*, *q_t* was calculated according to Eq. (1) (Xun et al., 2007):

$$q_t = \frac{(C_o - C_t)V}{W} \tag{1}$$

Where *C_t* is the concentration of heavy metal in waste water at time *t*. The percentage of heavy

metal removal was calculated using Eq. (2) (Hamad et al., 2011):

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100 \tag{2}$$

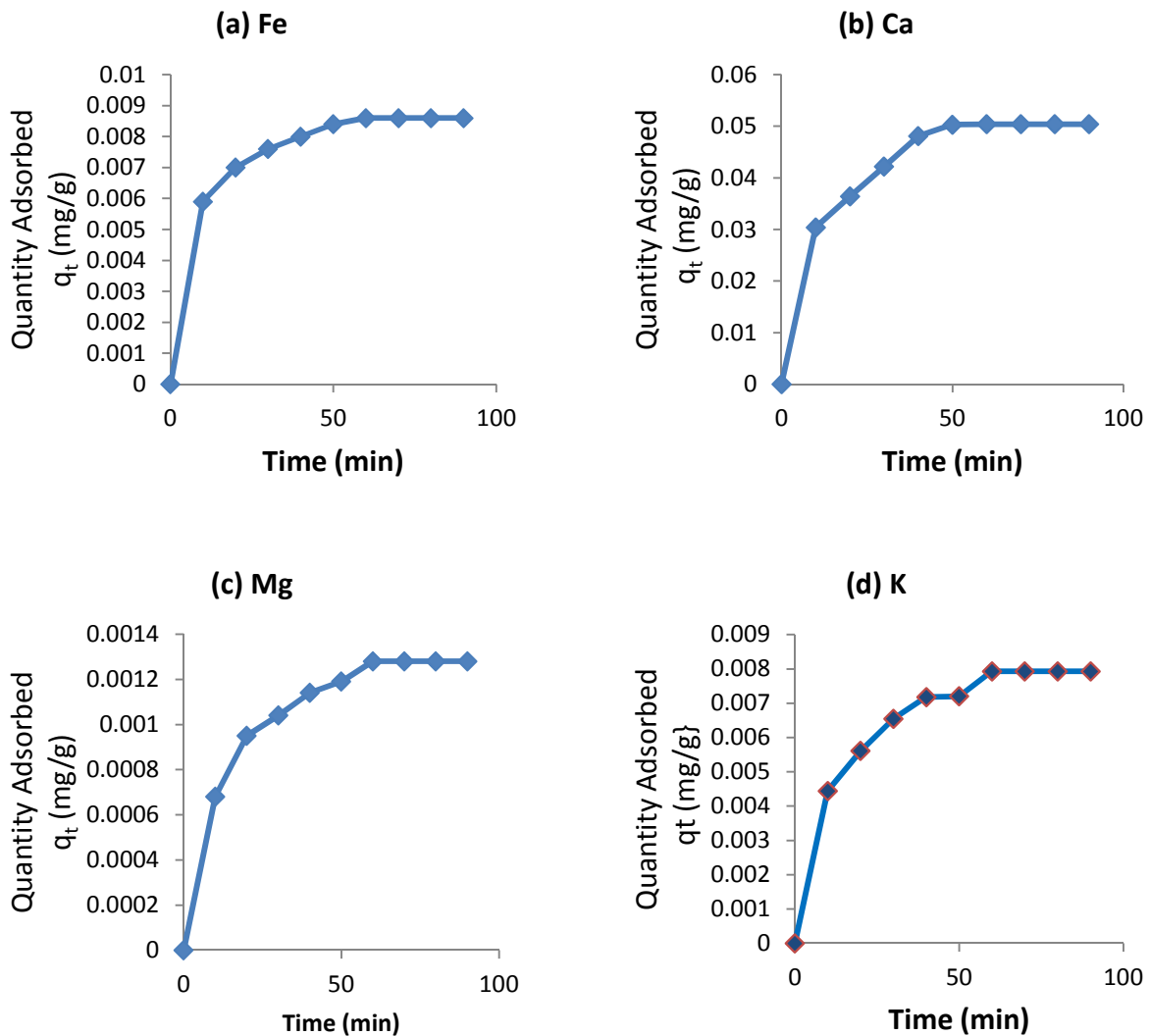
2.5 Heavy Metal Analysis:

The wastewater sample (200 ml) was taken into a 250 ml conical flask and sterilized glass pebbles were added into the sample to reduce the boiling point. Nitric acid (5 ml) was then added to the sample to obtain a clearer color. The sample was then put into the digestion machine. The sample collected from the digester was a clear light brown solution. The clear light brown solution from the digester was analysed for six different heavy metals using Atomic Absorption Spectrophotometer (AAS). The six different heavy metals analysed for are Iron (Fe), Calcium (Ca), Magnesium (Mg), Silver (Ag), and Chromium (Cr). The AAS machine was connected to a desktop computer where the results were directly assessed and printed.

3.0 Results and Discussion:

The biosorption of the heavy metals from textile wastewater by green seaweed biomass were studied at various time intervals (10 – 90 min). Fig. 1 shows that each of the heavy metal, Fe, Ca, Mg, K, Ag and Cr respective uptake was initially rapid for the first 10 min and gradually proceeded at a slower rate until saturation or equilibrium was attained and beyond which there was no significant increase in the rate of removal. The equilibrium was reached after 60 min for each of the heavy metal (Fig. 1). Thus, equilibrium time was taken as 60 min. The initial fast biosorption rate may be due to the increased number of vacant sites available for biosorption at the initial stage; as a result there exists increased concentration gradient between adsorbate in solution and adsorbate in the

biosorbent. Biosorption occurs rapidly and is normally controlled by diffusion process from the bulk to the surface while the slower biosorption rate at the later stage may be due to the remaining available biosorption site (or vacant sites) which has gradually decreased and becomes difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases (Agarry and Ogunleye, 2014). Thus, biosorption at the later stage may likely be an attachment-controlled process due to less available adsorption sites. Similar findings for biosorption of heavy metals such as chromium, nickel and lead by other biosorbents have been reported by other investigators (Badmus et al., 2007; Kannan and Veemaraj, 2009; Das and Mondal, 2011; Singh and Singh, 2012).



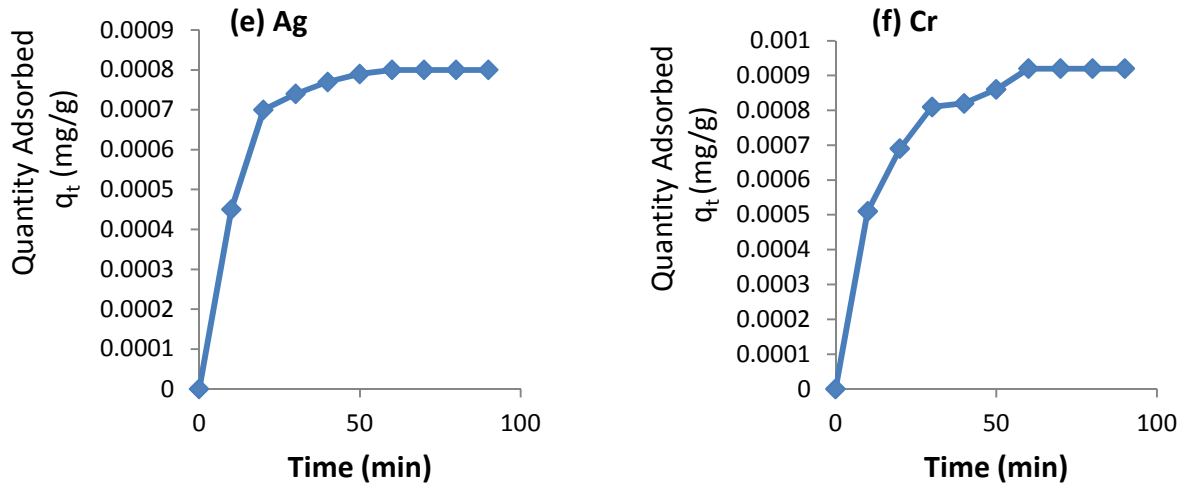


Fig. 1: Biosorption capacity of green seaweed biomass as a function of contact time

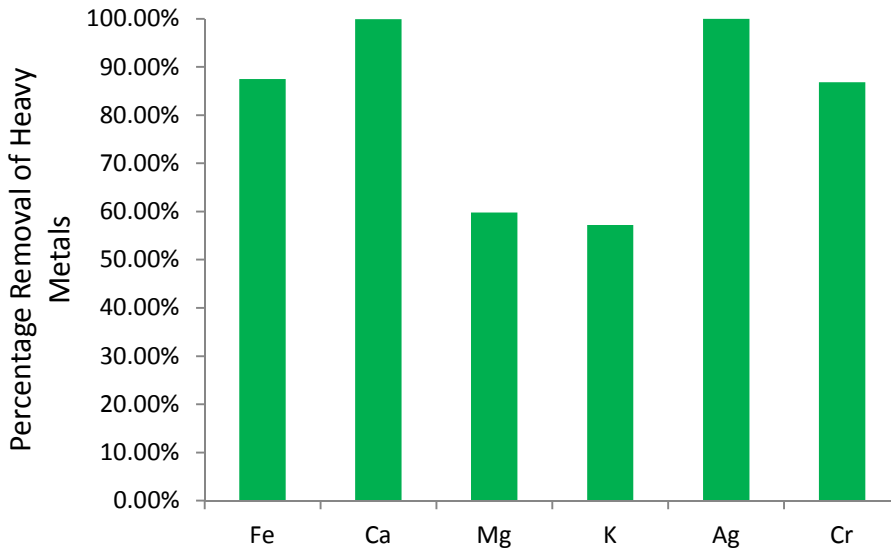


Fig. 2: Bio sorption efficiency of green seaweed biomass

Fig. 2 shows the observed biosorption percentages for the assayed heavy metal ion present in the textile wastewater (Fe, Ca, Mg, K, Ag and Cr) by GSW biosorbent. The percentage removal (adsorption efficiency) of Fe, Ca, Mg, K, Ag and Cr from the textile wastewater by the green seaweed biomass was found to be 87.5%, 99.9%, 59.8%, 57.2%, 100% and 86.8%, respectively, as shown in Fig. 2. Both Ag and Ca were completely removed from the wastewater at 60 min contact time and this is contrary to the 180 min reported in literature by earlier researchers for red and brown seaweeds (Davies et al., 2003). Thus, the results indicate that, among the heavy metal ions assayed, GSW biosorbent has the highest affinity (selectivity) for adsorbing Ag as well as Ca, followed by Fe, Cr, Mg

and K (i.e., $Ag/Ca > Fe > Cr > Mg > K$). This phenomenon depends on the metal hydrolysis constants of the six metal ions (Pagnanelli et al., 2003; Agarry et al., 2015) as well as on the ion size (ionic radius) and charge (electronegativity) (Palma et al., 2003; Agarry et al., 2015).

3.1 Biosorption Kinetics Modelling:

In order to analyze the rate of biosorption and possible biosorption mechanism of heavy metals by green seaweed biomass, the Lagergren pseudo first-order (Lagergren, 1898), pseudo second-order (Ho and Mckay, 2000) and intraparticle diffusion (Weber and Morris, 1963) were applied to the biosorption data.

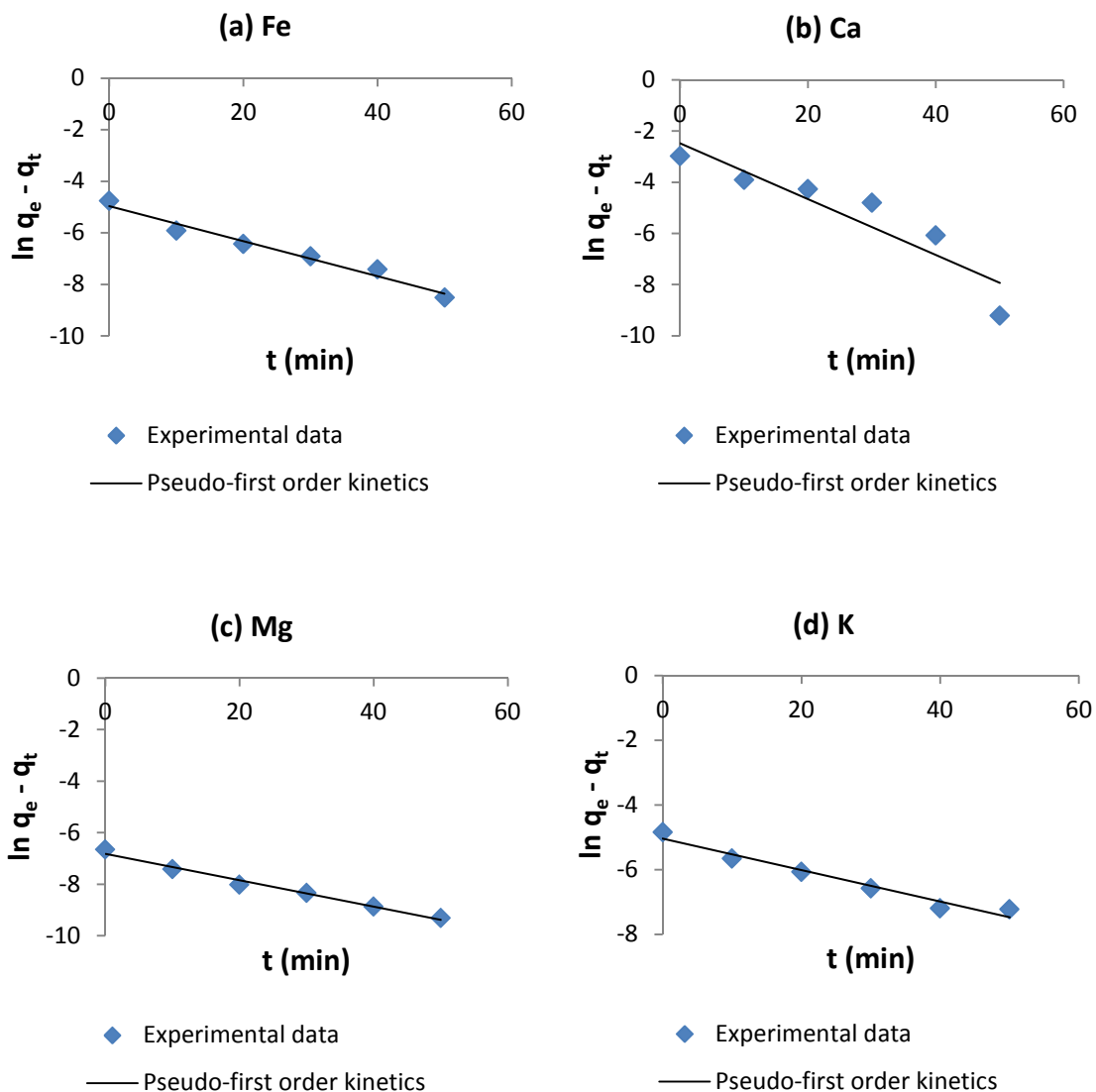
3.1.1 Pseudo First-Order Kinetic Model:

The Lagergren pseudo first-order kinetic model equation (Lagergren, 1898) is represented in an integral form as given in Eq. (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where, q_e is the calculated maximum equilibrium biosorption capacity (mg/g) and k_1 is the biosorption rate constant (min^{-1}). The values of q_e and k_1 for each heavy metal were calculated from the slope and intercept of the linear plots of $\ln(q_e - q_t)$ vs t (Fig. 3) and are listed in Table 1.

It is required that the theoretically calculated equilibrium biosorption capacity, q_e (theoretical), should be in accordance with the experimental biosorption capacity, q_e (experimental) values (Štrkalj and Malina, 2011). From Table 1, it was found that the coefficient of determination (R^2) is relatively high for each of the heavy metal (Fe, Ca, Mg, K, Ag and Cr) and a very good agreement was found between q_e (theoretical) and q_e (experimental) for Fe, Ca, Mg, K and Ag, respectively. This suggests that the biosorption of Fe, Ca, Mg, K and Ag follows pseudo first-order kinetics.



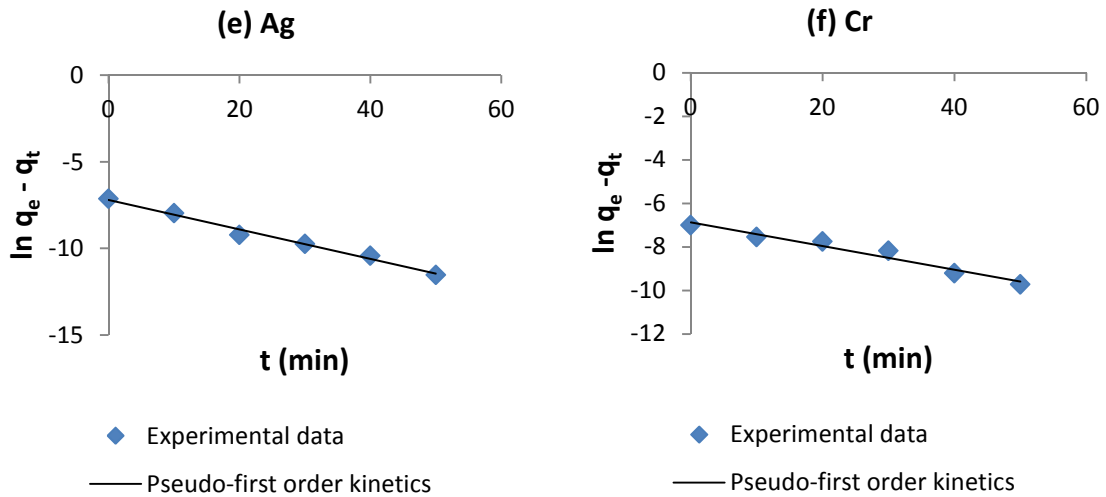


Fig. 3: Pseudo first-order kinetic model fitted to the experimental biosorption data of green seaweed biomass

3.1.2 Pseudo Second-Order Kinetic Model:

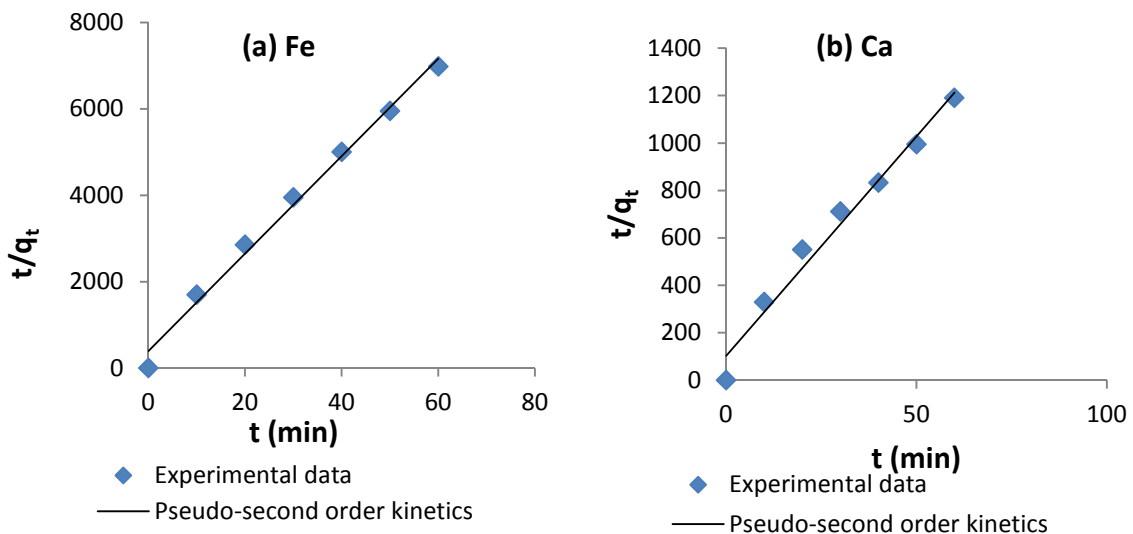
The pseudo-second-order kinetic model which is based on the assumption that chemisorption is the rate-determining step and can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where k_2 is the rate constant of second order biosorption (g/mg/min).

Values of k_2 and q_e were calculated from the plots of t/q_t vs. t (Fig. 4) for different heavy metals and are presented in Table 1. The high coefficient of determination (R^2) values of pseudo second-order (Table 1) suggests the applicability of

the pseudo second-order kinetic model to fit the experimental data. Also, it is expected that the theoretically calculated equilibrium biosorption capacity, q_e (theoretical) should be in accordance with the experimental biosorption capacity, q_e (experimental) values. It may be seen from Table 1 that the R^2 are relatively higher than the results obtained from pseudo first-order kinetics for Fe, Ca, Mg and Cr, respectively; however, there is no good agreement between q_e (theoretical) and q_e (experimental). This suggests that the biosorption of Fe, Ca, Mg and Cr from textile wastewater by GSWB does not follow a pseudo second-order type of reaction kinetics.



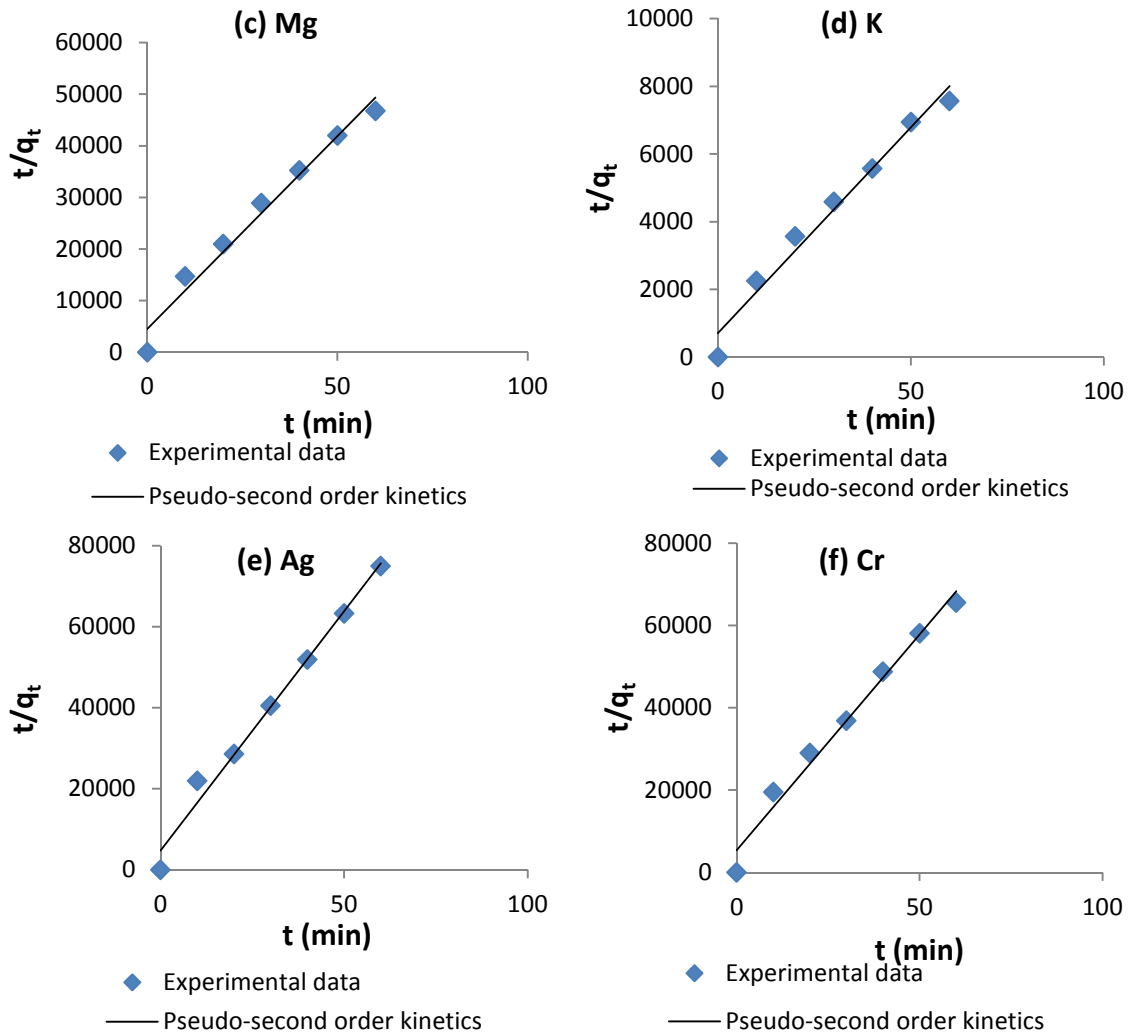


Fig. 4: Pseudo second-order kinetic model fitted to the experimental biosorption data of green seaweed biomass

3.1.3 Intra Particle Diffusion Kinetic Model:

The intra particle diffusion kinetic model (Weber and Morris, 1963) can be written as presented in Eq. (6):

$$q_t = K_p t^{1/2} + C \tag{6}$$

Where K_p is the intra particle diffusion rate constant ($\text{mg/g min}^{-1/2}$) and C is the intercept.

The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. Intra particle diffusion is the sole rate-limiting step if the regression of q_t vs. $t^{1/2}$ is linear and passes through the origin (Weber and Morris, 1963). In fact, the linear plots for each of the heavy metal (Fe, Ca, Mg, K, Ag and Cr) (Fig. 5) did not pass through the origin. This deviation from

the origin is due to difference in the rate of mass transfer in the initial and final stages of biosorption. This indicated the existence of some boundary layer effect and further showed that intra particle diffusion was not the only rate limiting step. The calculated diffusion coefficient K_p values for each heavy metal are listed in Table 1.

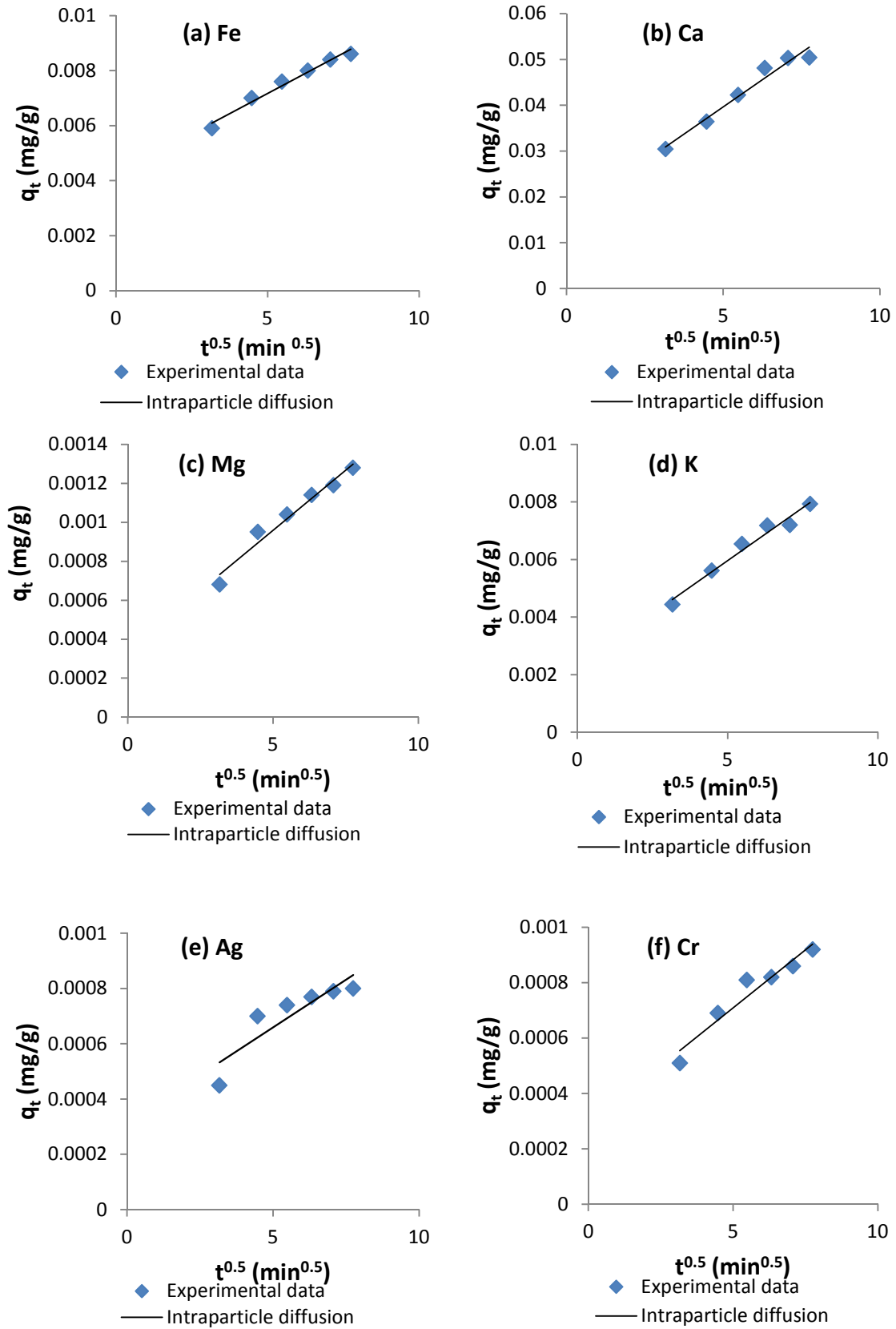


Fig. 5: Intra particle diffusion kinetic model fitted to the experimental biosorption data of green seaweed biomass

Table 1: Kinetic constants values of kinetic models fitted to the experimental biosorption data

Heavy Metals	Pseudo first-order			Pseudo second-order				Intra-particle diffusion	
	k_1^a	q_e (theor) ^b	R^2	k_2^c	q_e (theor)	q_e (exp) ^b	R^2	$K_p^{(d)}$	R^2
Fe	0.068	0.0070	0.9721	1316	0.0026	0.0086	0.9915	0.0006	0.9773
Ca	0.109	0.0833	0.8508	555.6	0.0097	0.0504	0.9767	0.0047	0.9660
Mg	0.051	0.0011	0.9857	27027	0.0002	0.0013	0.9744	0.0001	0.9666
K	0.049	0.0065	0.9598	4000	0.0014	0.0083	0.9750	0.0007	0.9720
Ag	0.085	0.0008	0.9884	18868	0.0002	0.0008	0.9866	0.00007	0.7931
Cr	0.055	0.0010	0.9593	27778	0.0002	0.0001	0.9811	0.00008	0.9332

Note: a= (min⁻¹), b= (mg/g), c= (g/mg/min), d= (mg/g/min^{-1/2})

4.0 Conclusion:

The biosorption of some heavy metals by green seaweed biomass from textile wastewater was studied in batch mode. It can be concluded from the results obtained that the green seaweed biomass has high biosorptive selectivity for some metals such as Fe, Ca, Ag and Cr in which there was corresponding 87.5%, 99.9 %, 100% and 86.8% maximum reduction in their concentration at 60 min contact time than Mg and K heavy metals where there was corresponding 59.7 % and 57.2 % reduction in concentration, respectively. The experimental biosorption data fitted very well to both pseudo first-order and pseudo second-order kinetic models, however, the biosorption kinetics of Fe, Ca, Mg, K, Ag and Cr followed a pseudo first-order kinetic model and the biosorption mechanisms were controlled by boundary layer surface diffusion. Thus green seaweed biomass has the potential to be used a low cost biosorbent for the treatment of industrial wastewater that contains the presence of heavy metals.

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