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Adsorption of Congo Red Dye from Aqueous Solutions Using Roots of *Eichhornia crassipes*: Kinetic and Equilibrium Studies

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Abstract

Adsorption of Congo red (CR) from aqueous solution using dried roots of *Eichhornia crassipes* was studied. Batch experiments were carried out for sorption kinetics and isotherms. Experimental results obtained showed that adsorption process was highly dependent on contact time, adsorbent dosage, initial dye concentration and particle size. The sorption equilibrium for Congo red dye by *E. crassipes* (roots) was reached within 90 minutes and adsorption efficiency of up to 96% achieved. The sorption kinetics followed a pseudo-second-order kinetic model while Freundlich isotherm model was best applicable for obtaining the equilibrium parameters. These results demonstrate that roots of *E. crassipes* are effective, environmentally friendly and low-cost biomaterial for dye removal from aqueous dye solutions and industrial effluents.

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1. Introduction

Synthetic dyestuffs are widely used in textile, paper, printing, plastic, leather and cosmetic industries. Dyeing effluent has a serious environmental impact because disposal of such effluent into the receiving water body causes damage to aquatic biota or humans by mutagenic and carcinogenic effects [1]. Furthermore, colored effluent can affect photosynthetic processes of aquatic plants, reducing oxygen levels in water and in severe cases, resulting in

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the suffocation of aquatic flora and fauna [2, 3]. Various pollutants such as dyes, degradable organics, surfactants, heavy metals, pH adjusting chemicals, etc., can be found in textile wastewater [4]. Conventional treatment methods for removal of pollutants from aqueous solution, like photochemical degradation, biological degradation, coagulation, chemical oxidation and adsorption have been investigated with varying degree of success [5, 6]. Among available wastewaters treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. The most widely used adsorbent is activated carbon, but its initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. This has led many researchers to search for cost effective and efficient alternative materials such as polylactide/spent brewery grains [7], activated carbons prepared from seawater algae [8], periodic mesoporous titanium phosphonate [9], graphene oxide [10] and carra sawdust [11].

Eichhornia crassipes (Water hyacinth) has attracted significant attention as amongst the world's worst invasive aquatic plant due to its extremely rapid proliferation and congest growth, causing serious challenges in transportation, fisheries, irrigation, hydroelectric power generation and environmental health. Efforts to develop an alternative technology of utilizing *E. crassipes* in solving environmental problems are worthwhile given its abundance in Lake Victoria [12]. In this research, the efficiency of *E. crassipes* roots in adsorption of CR dye from aqueous solution has been investigated. Batch experiments were carried out for sorption kinetics and isotherms. Langmuir and Freundlich isotherm model were used to analyze the experimental data. The sorption kinetics was analyzed by pseudo-second-order kinetic model. Effluent containing Congo red is largely produced from textiles, printing, dyeing, paper, and plastic industries etc. [13, 14]. CR is toxic to many organisms and is a suspected carcinogen and mutagen. This study explores the possibility of utilizing *E. crassipes* roots as low cost biomaterials for the adsorptive removal of CR dye from polluted wastewater.

2. Materials and Methods

2.1. Material

Fresh *E. crassipes* roots were collected from Winam Gulf and Kisumu Bay areas of Lake Victoria and extensively washed with tap water to remove water soluble impurities and other foreign particles. The biomass were dried in the sun for two weeks, ground into fine material and then washed several times with distilled water before drying in an oven at 60°C for 48 hours. The dried pulverized biomass adsorbent material were sieved through standard sieves to obtain particle sizes between 75 µm – 300 µm; 300 µm – 425 µm; and 425 µm – 950 µm. The sieved samples were subsequently used for adsorption studies. Congo red (CR) dye, analytical grade (C₃₂H₂₂N₆O₆S₂Na₂; molecular weight 696.68; λ_{max}= 500 nm) was obtained from RANBAXY Fine Chemicals Limited, Nairobi, Kenya and used without further purification. All solutions were prepared in double distilled water, and the initial pH was adjusted to 8.0±0.3 using either 0.1M HCl or NaOH.

2.2. Batch adsorption experiment

Batch adsorption experiments were conducted in 250 mL conical flask on a Thermolyne Orbital shaker at 200 rpm at different time intervals at 25°C. All experiments were conducted in duplicate and the average values reported. The effect of initial dye concentration was performed by varying the initial CR concentrations from 10.45 to 104.45 mg L⁻¹. *E. crassipes* roots (1.0 g) were added to 50 mL volume of CR solution. After different interval times, aliquots from the reaction mixture were analyzed for residual CR concentration using a UV-VIS spectrophotometer (SP8-15 Turner) by monitoring changes in absorbance. The effect of contact time was investigated using 1.0 g of *E. crassipes* roots, and 50 mL CR solution mixed in 250 mL flask placed on an orbital shaker. Samples were collected from the flask at various intervals and analyzed for residual CR concentration. The effect of particle size on equilibrium dye uptake was investigated by employing CR concentration of 104.45 mg L⁻¹ and *E. crassipes* roots of particle sizes 75 – 300 µm; 300 – 425 µm; and 425 - 950 µm. The adsorbent dose was investigated using 104.45 mg L⁻¹ initial CR concentration with sorbent masses of 0.25, 0.50, 1.00, and 1.50 g. The amount of dye adsorbed at equilibrium onto *E. crassipes*, q_e (mg g⁻¹), was calculated by the following mass balance relationship:

$$q_e = V \frac{(C_0 - C_e)}{M} \quad (1)$$

Where C_o and C_e are the initial and the equilibrium dye concentrations (mg L^{-1}), V is the volume of solution (L) and M is the amount of biomass used (g). Percent dye removal (%) was calculated using the following equation;

$$\text{Dye removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

The kinetics of the adsorption was examined for different concentrations of CR dye at 25°C by varying the contact time intervals. 1.0 g of *E. crassipes* roots of particle size $75 - 300 \mu\text{m}$ was added to 50 mL CR dye solution in 250 mL conical flasks at a constant agitation speed of 200 rpm. After different interval times, 3 mL of the solution was taken from the conical flask, analyzed for residual CR concentration and then quickly returned to conical flask to prevent changes in the volume of solution.

3. Results and Discussion

3.1. Effect of contact time

The effect of contact time on adsorption of CR onto *E. crassipes* roots is shown in Fig. 1. The results show that adsorption process reached equilibrium within 90 minutes and percentage dye removal increased with increase in contact time. *E. crassipes* roots biomass rapidly adsorbed over 64 % of the dye within the first 5 minutes of contact time. The changes in percentage adsorption after the 5th minute became relatively gradual with the equilibrium being reached within 90 minutes with 96% dye removal achieved. The high removal rate at the start of the contact time was due to the large amount of surface area available for adsorption of the dye during the initial stage and the capacity of the adsorbent became gradually exhausted with time since the few remaining vacant surface sites became difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar results have been previously reported in the literature for dye removal [7].

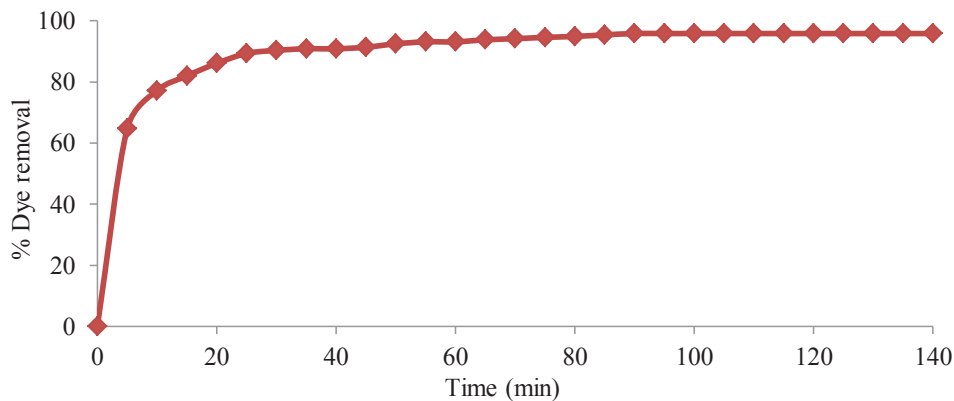


Fig. 1. Effect of contact time on Congo red dye sorption. Conditions: (Congo red: 104.45 mg L^{-1} , *E. crassipes* roots: 1.0 g/ 50 mL, particle size: $75 - 300 \mu\text{m}$, at 25°C).

3.2. Effect of adsorbent dosage

The amount of adsorbent used in adsorption is particularly important because it determines the sorbent–sorbate equilibrium in the system and can also be used to predict the treatment cost of adsorbent per unit of dye solution. The effect of adsorbent dosage on percentage CR dye removal was studied and the results presented in Fig. 2. The percent dye removal increased with an increase in adsorbent dosage. For instance, the percent removal of CR at equilibrium increased from 72.9 to 96.2% when the adsorbent weight increased from 0.25 to 1.5 g. The increased percentage of CR dye removal by *E. crassipes* roots was as a result of increased surface area and increased adsorption site occasioned by increased adsorbent dose. Similar results have been previously reported [15].

3.3. Effect of dye initial concentration

The effect of different initial dye concentrations on adsorption of CR is shown in Fig. 3. The amount of CR adsorption increases with increasing initial CR concentration. For instance the amount of CR adsorbed at equilibrium increased from 0.65 to 4.81 mg g⁻¹ when CR concentration increased from 10.45 to 104.50 mg L⁻¹. This may be attributed to an increasing concentration gradient acting as an increasing driving force to overcome all mass transfer resistances of the dye molecules between the aqueous and solid phase, leading to an increasing equilibrium sorption until saturation is achieved. A similar trend was observed for the biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge [16].

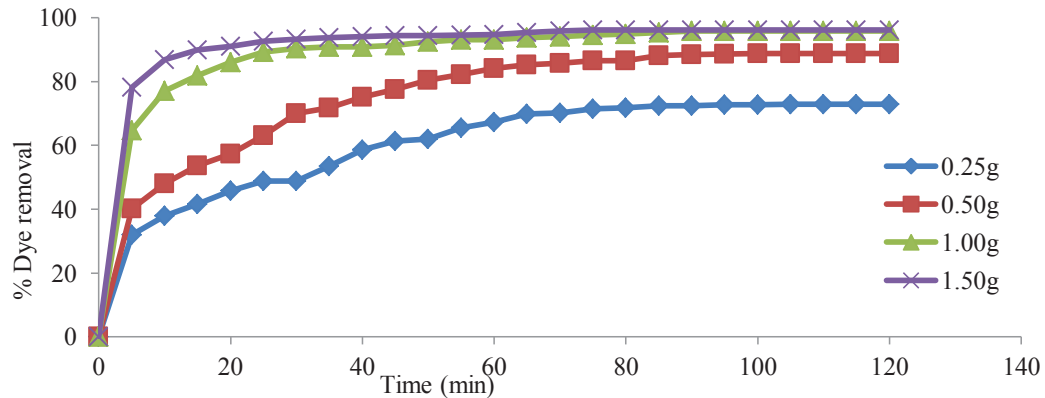


Fig. 2. Effect of adsorbent dose on % Congo red dye removal. Conditions: (Congo red: 104.45 mg L⁻¹, particle size: 75–300 μm, at 25°C).

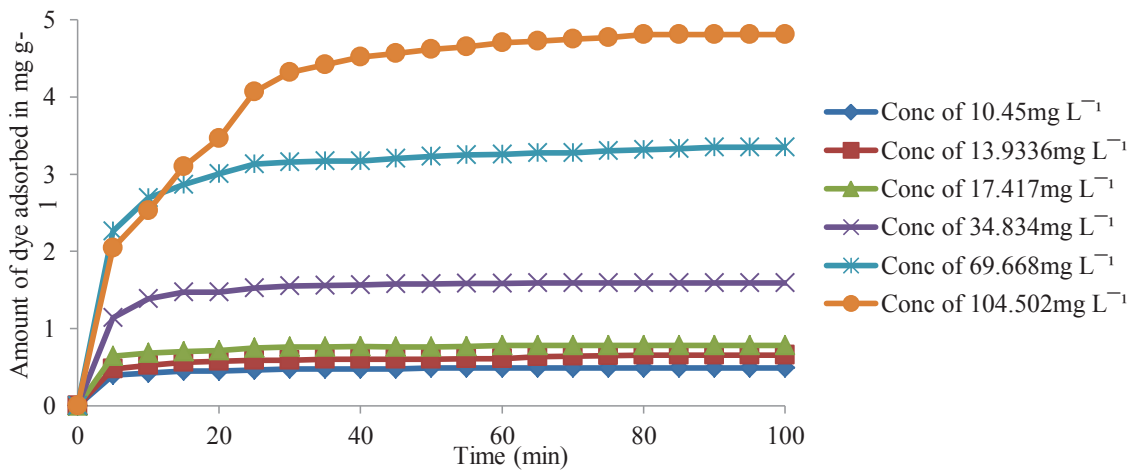


Fig. 3. Effect of initial dye concentration on sorption of Congo red. Conditions: (*E. crassipes*: 1.0 g/50 mL roots, particle size: 75–300 μm, at 25°C).

3.4. Effect of particle size

The surface area available for adsorption is greatly determined by particle size of the adsorbent and is an important controlling parameter in the adsorption process. The effect of particle size on CR adsorption was studied and results presented in Fig 4. It was established that adsorption of CR decreased with increase in particle size of *E. crassipes* roots. This can be attributed to larger total surface area of smaller particles for the same amount of sorbent. These findings are consistent with related studies done on adsorption of Malachite Green dye by cyclodextrin-based

adsorbent [17]. This relationship indicates that powdered fine adsorbent would be advantageous over granular particles in adsorption of CR.

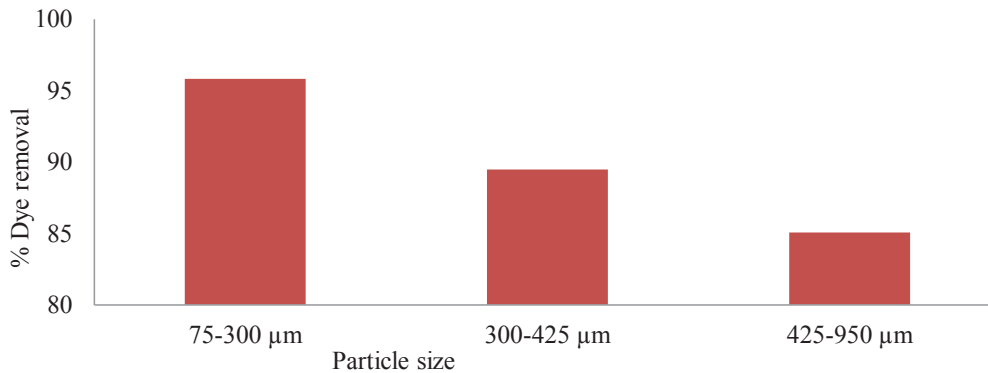


Fig. 4. Effect of particle size on Congo red sorption. Conditions: (Congo red: 104.45 mg L⁻¹, *E. crassipes* roots: 1.0 g L⁻¹, at 25°C).

3.5. Adsorption Isotherms

An adsorption isotherm is a curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [18]. In order to determine the applicability of adsorption as a means of removing CR dye from aqueous solutions using *E. crassipes* roots, Langmuir and Freundlich isotherms models were used.

Langmuir isotherm model [19] assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The nonlinear and linearized forms of Langmuir isotherm equation is as follows:

$$q_e = \frac{(Q_0 b C_e)}{1 + b C_e} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left(\frac{1}{Q_0 b}\right) \frac{1}{C_e} \quad (4)$$

Where q_e (mg g⁻¹) is the amount of dye adsorbed at equilibrium, C_e (mg L⁻¹) is the equilibrium dye concentrations (mg L⁻¹), Q_0 is the maximum monolayer coverage capacities (mg g⁻¹), and b (L mg⁻¹) is Langmuir isotherm constant related to the affinity of the binding sites. When $(1/q_e)$ is plotted against $(1/C_e)$, a straight line with slope $1/(bQ_0)$ and intercept $1/Q_0$ are obtained. The Langmuir parameters, Q_0 and b can be calculated from the slope and intercept of the plot. A further analysis of the Langmuir equation was made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor, given by:

$$R_L = \frac{1}{1 + b(C_0)} \quad (5)$$

Values of R_L indicate the shapes of isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$). Fig. 5 shows a plot of $1/q_e$ versus $1/C_e$ for the adsorption of CR onto *E. crassipes* roots and the corresponding Langmuir isotherm constants are presented in Table 1. The experimental data shows a good fit to Langmuir adsorption isotherm model and the dimensionless parameter R_L ranges between zero and one ($0 < R_L < 1$) consistent with the requirement for a favorable adsorption process.

Freundlich isotherm model [20] is applicable for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The nonlinear and linearized forms of the equation are as follows:

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (7)$$

Where K_F (mg g^{-1}) ($\text{L mg}^{-1/n}$) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption conditions. Values of K_F and n are calculated from the intercept and slope of the plot of $\ln q_e$ against $\ln C_e$. Fig. 6 shows a plot of $\ln q_e$ versus $\ln C_e$ for the adsorption of CR onto *E. crassipes* roots and corresponding Freundlich isotherm constants summarized in Table 1. The high correlation coefficients ($R^2 = 0.923$) indicate that Freundlich isotherm model was best applicable for describing the adsorption of CR onto *E. crassipes* roots. This is also an indication of surface heterogeneity of the *E. crassipes* roots responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites.

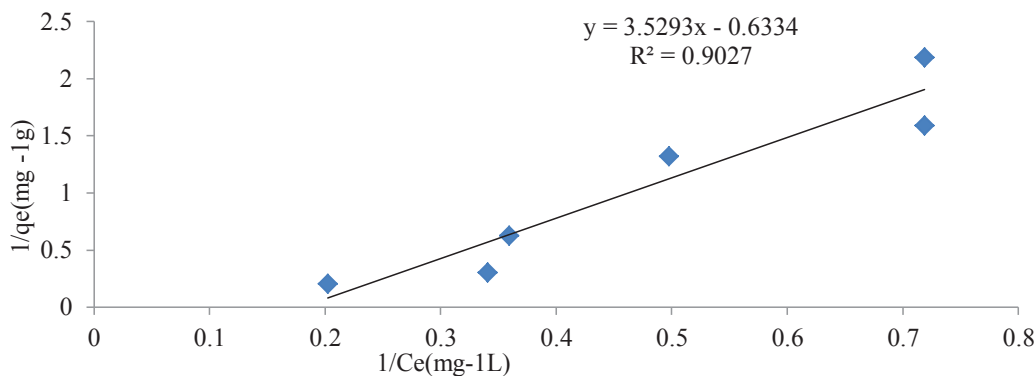


Fig. 5. Langmuir adsorption isotherm for CR dye on 1.0 g *E. crassipes* roots

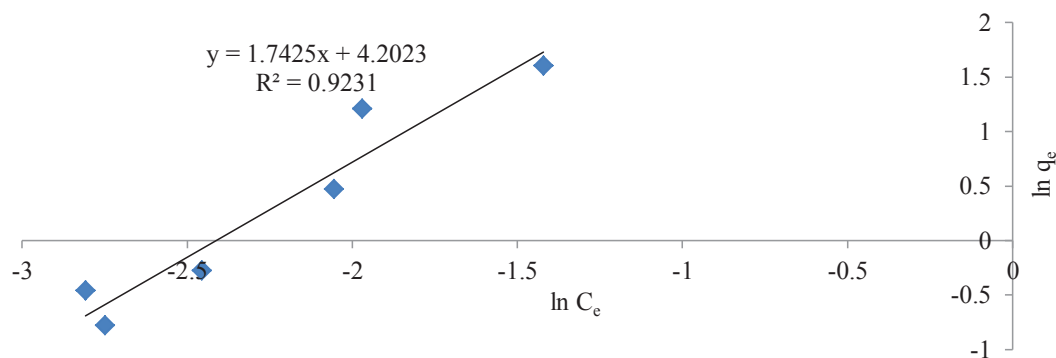


Fig. 6. Freundlich adsorption isotherm for CR on 1.0 g *E. crassipes* roots

Table 1. Langmuir and Freundlich isotherm constants for adsorption of CR dye on 1.0 g *E. crassipes* roots

Langmuir adsorption isotherm				Freundlich adsorption isotherm		
Q_0	b	R^2	R_L	K_F	n	R^2
1.580	0.179	0.903	0.411	1.436	0.574	0.923

3.6. Adsorption kinetics

In order to analyze the sorption kinetics of CR on *E. crassipes* roots, the pseudo-second-order kinetic model was applied to the experimental data. The pseudo second-order model is expressed as:

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

When the initial condition is $q_t = 0$ at $t = 0$, integration leads to equation (9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

Where k_2 is the rate constant of the pseudo second order adsorption ($\text{gmg}^{-1}\text{min}^{-1}$), q_e and q_t are the amounts of CR adsorbed (mg g^{-1}) at equilibrium and at time t (min) respectively. The plot of t/q_t vs t of eqn 9 gives a linear relationship, from which, q_e and k_2 can be determined from the slope and intercept of the plot. Fig. 7 shows pseudo-second - order kinetics plot for the adsorption of CR dye by *E. crassipes* roots at different concentrations. The rate constants, predicted equilibrium uptakes and the corresponding correlation coefficients for all concentrations tested have been calculated and summarized in Table 2. It can be seen that the correlation coefficients for the pseudo-first-order kinetic model was very high ($R^2 > 0.99$) and the theoretical $q_{e,cal}$ values were closer to the experimental $q_{e,exp}$ values at all studied initial CR concentrations indicating that the adsorption of CR onto *E. crassipes* roots perfectly follow pseudo second order kinetic model. These suggested that the pseudo-second-order adsorption mechanism was predominant and that the overall rate of the CR sorption process appeared to be controlled by chemical process involving valence forces through sharing or exchange of electrons between CR dye and *E. crassipes* roots. It was also observed that the pseudo-second-order rate constant (k_2) decreased with increased initial concentration. Similar kinetics was also observed in adsorption methylene blue on papaya seeds [21], biosorption of malachite green onto poly lactide/spent brewery grains films [7] and adsorption of Congo red dye on cattail root [15].

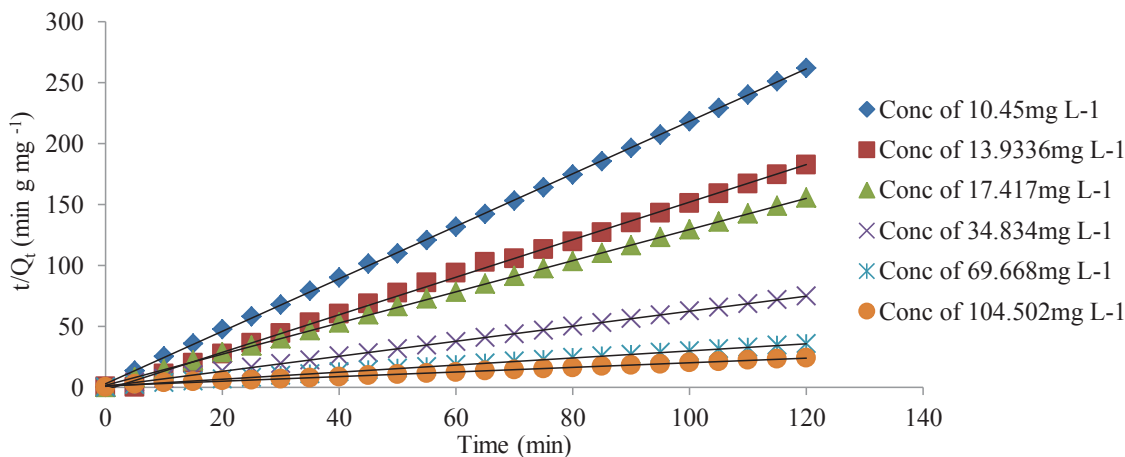


Fig. 7 Pseudo-second-order kinetics plot for the adsorption of CR dye by *E. crassipes* roots

Table 2. Pseudo-second-order models parameters for the adsorption of Congo red dye by *E. crassipes* roots

Concentration of Congo red dye (mg L^{-1})	Pseudo-second-order kinetic parameters			
	$q_{e,cal}$ (mg g^{-1})	$q_{e,exp}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	R^2
10.450	0.464	0.458	1.596	0.999
13.934	0.649	0.630	1.103	0.999
17.417	0.783	0.772	0.893	0.999
34.834	1.622	1.603	0.502	0.999
69.668	3.408	3.338	0.119	0.999
104.502	5.285	4.971	0.030	0.997

4. Conclusions

The study demonstrates that *E. crassipes* roots is indeed viable, cost effective adsorbent materials for the adsorptive removal of CR dye from polluted wastewater with over 96% dye removal. The adsorption of CR dye onto *E. crassipes* roots was found to be highly dependent on contact time, initial dye concentration, adsorbent dosage and particle size. The amount of dye uptake (mg g^{-1}) was found to increase with increase in initial dye concentration. Percent CR dye removal was found to increase with increase in contact time, adsorbent dosage and decreased with increase in particles size. The results indicated that the Freundlich isotherm model gave a better fit to the experimental data than the Langmuir isotherm model with high correlation coefficients ($R^2 = 0.923$). This suggests that multi-layer adsorption occurs which is in agreement with the better applicability of the Freundlich isotherm model. R_L value showed that adsorption was favorable. The rate of adsorption was found to conform to pseudo-second-order kinetics with high correlation coefficient ($R^2 = 0.99$) for all studied concentrations. Consequently, it can be concluded that *E. crassipes* roots can be used as a cost effective alternative material for CR dye removal in wastewater treatment processes without any laborious pre-treatment.

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References

- [1] Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol* 2006; 97: 1061- 1085.
- [2] Cheung WH, Szeto YS, McKay G. Enhancing the adsorption capacities of acid dyes by chitosan nanoparticles. *Bioresour. Technol* 2009; 100: 1143 - 1148.
- [3] Hu TL, Wu SC. Assessment of the effect of azo dye RP2B on the growth of a nitrogen fixing cyanobacterium – *Anabaena* sp. *Bioresour. Technol* 2001; 77: 93 - 95.
- [4] Wijetunga S, Xiufen L, Wenquan R, Chen J. Evaluation of the efficacy of up flow anaerobic sludge blanket reactor in removal of color and reduction of COD in real textile wastewater. *Bioresour. Technol* 2008; 99: 3692 - 3699.
- [5] Dizge N, Ayiner C, Demirbas E, Kobyra M, Kara S. Adsorption of reactive dyes from aqueous solutions by fly ash: kinetic and equilibrium studies. *J. Hazard. Mater* 2008; 150:737-746.
- [6] Dos Santos AB, Cerantes FJ, Van lier JB (2007). Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. *Bioresour. Technol.* 98: 2369 - 2385.
- [7] Chanzu HA, Onyari JM, Shiundu PM. Biosorption of malachite green from aqueous solutions onto polylactide/spent brewery grains films: kinetic and equilibrium studies. *J Polym Environ* (2012); 20(3): 665 – 672
- [8] Nemchi F, Bestani B, Benderdouche N, Belhakem M, de Minorva LC. Adsorption of Supranol Yellow 4GL from Aqueous Solution onto Activated Carbons Prepared from Seawater Algae. *Adsorpt. Sci. Technol* 2012; 30 (1): 81- 96.
- [9] Ren TZ, Zhu XH, Ma TY, Yuan ZY. Adsorption of Methylene Blue from Aqueous Solution by Periodic Mesoporous Titanium Phosphonate Materials. *Adsorpt. Sci. Technol.* 2013; 31(6): 535 -548.
- [10] Zhang W, Zhou C, Zhou W, Lei A, Zhang Q, Wan Q, Zou B. Fast and considerable adsorption of methylene blue dye onto graphene oxide. *Bull Environl Contam Toxicol* 2011; 87: 86 - 90.
- [11] Sanchez N, Benedetti TM, Vazquez M, de Torresi SIC, Torresi RM. Kinetic and Thermodynamic Studies on the Adsorption of Reactive Red 239 by Carra Sawdust Treated with Formaldehyde. *Adsorpt. Sci. Technol.* 2012; 30(10): 881- 900.
- [12] Wanyonyi WC, Onyari JM, Shiundu PM. Adsorption of methylene blue dye from aqueous solutions using *Eichhornia crassipes*. *Bull Environl Contam Toxicol* 2013; 91(3): 362 - 366.
- [13] Purkait MK, Maiti A, DasGupta S, De S. Removal of Congo red using activated carbon and its regeneration. *J. Hazard. Mater* 2007; 145: 287 - 295.
- [14] Pavan FA, Dias SLP, Lima EC, Benvenuto EV. Removal of Congo red from aqueous solution by anilinepropylsilica xerogel. *Dyes Pigments* 2008; 76: 64 - 69.
- [15] Hu Z, Chen H, Ji F, Yuan S. Removal of Congo red from aqueous solution by cattail root. *J. Hazard. Mater* 2010; 173: 292 – 297.
- [16] Gao J, Zhang Q, Su K, Chen R, Peng Y. Biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge. *J. Hazard. Mater* 2010; 174: 215 - 225.
- [17] Crini G. Kinetic and Equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dyes Pigments* 2008; 77: 415 - 426.
- [18] Limousin G, Gaudet JP, Charlet L, Szenknect S, Barthes V, Krimissa M. Sorption isotherms: a review on physical bases, modeling and measurement. *Applied Geochemistry* 2007; 22: 249 - 275.
- [19] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc* 1918; 40: 1361-1403.
- [20] Freundlich H. Over the adsorption in solution. *J. Phys Chem.* 1906; 57: 385 - 470.
- [21] Hameed BH. Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue. *J. Hazard. Mater* 2009; 162: 939 - 944.