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INVESTIGATION OF THE USE OF WALNUT SHELLS AS A NATURAL BIOSORBENT FOR ZINC REMOVAL

CEVİZ KABUĞUNUN DOĞAL BİYOSORBENT OLARAK ÇİNKO GİDERİMİNDE KULLANILMASININ ARAŞTIRILMASI

Sevda Esma DARAMA [1] (ORCID: 0000-0002-6747-4679)
Başak MESCİ OKTAY [2*] (ORCID: 0000- 0002-1204-0195)
Semra ÇORUH[1] (ORCID: 0000-0002-8306-1890)

[1,3] Ondokuz Mayıs University, Engineering Faculty Department of Environmental Engineering, Samsun, Turkey
[2] Ondokuz Mayıs University, Engineering Faculty Department of Metallurgical and Materials Engineering, Samsun, Turkey

* Corresponding Author: Başak MESCİ OKTAY, basakm@omu.edu.tr

ABSTRACT

Heavy metal contamination is a primary concern worldwide, and it is discharged from industrial wastewater to a large amount of heavy metal receiving environments. In recent years, the effective use of agricultural by-products is a significant challenge in waste management. The fact that agricultural residues are more easily obtained and cheaper than commercial adsorbents makes it attractive. In this study, removal of zinc from industrial wastewater using natural and thermally modified (biochar) walnut shells as biosorbent was investigated. It tried to remove zinc in aqueous solutions with different concentrations using walnut shells at different rates. The effects of initial concentration, contact time, and adsorbent dosage were studied. In addition, adsorption isotherms and kinetics were also studied. With the modified form of the walnut shell, up to 97% zinc removal efficiency was obtained. Also, adsorption was consistent with pseudo-second kinetics and Freundlich isotherm. The results showed that the modified walnut shell in zinc removal was a potential adsorbent. The adsorption of zinc onto walnut shells was found to fit Freundlich isotherm. The results obtained in the tests with wastewater showed the possible use of walnut shells for the removal of zinc.

Keywords: Biochar, walnut shell, zinc removal, isotherm, kinetic.

ÖZET

Ağır metal kirliliği dünya çapında endişe kaynağıdır ve endüstriyel atık sulardan büyük miktarda ağır metal alıcı ortamlara deşarj edilmektedir. Son yıllarda, tarımsal yan ürünlerin etkin kullanımı, atık yönetiminde kesinlikle büyük bir zorluktur. Tarımsal kalıntıların ticari adsorbentlere göre daha kolay elde edilmesi ve daha ucuz olması onları cazip kılmaktadır. Bu çalışmada, biyosorbent olarak doğal ve biyokömür haline getirilmiş ceviz kabukları kullanılarak endüstriyel atık sudan çinkonun giderimi araştırılmıştır. Ceviz kabukları farklı oranlarda kullanılarak farklı konsantrasyonlardaki sulu çözeltilerdeki çinko giderilmeye çalışılmıştır. Başlangıç konsantrasyonunun etkileri, temas süresi, adsorbent dozu araştırılmıştır. Ayrıca adsorpsiyon izotermleri ve kinetiği de incelenmiştir. Ceviz kabuğunun modifiye edilmiş şekli ile %98'e varan çinko giderimi elde edilmiştir. Ayrıca yalancı ikinci derece kinetiği ve Freundlich izotermiyle uyumlu olduğu gözlemlenmiştir. Sonuçlar, çinko gideriminde modifiye edilen ceviz kabuğunun potansiyel bir adsorban olduğunu göstermiştir. Ceviz kabukları üzerine çinko adsorpsiyonunun Freundlich izotermine uyduğu bulunmuştur. Atık su ile yapılan testlerde elde edilen sonuçlar, çinkonun giderilmesi için ceviz kabuklarının potansiyel kullanımının uygun olduğunu göstermiştir.

Anahtar Kelimeler: Biyoçar, ceviz kabuğu, çinko giderimi, izoterm, kinetik

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INTRODUCTION

In recent years, heavy metal contamination, mainly discharged from industrial wastewater, has become a severe environmental problem (Zhang et al.., 2017). Due to toxicities, carcinogenicity and scarcity of natural resources, the removal and recovery of heavy metals from wastewater is of great importance (Fu & Wang, 2011). Heavy metals such as zinc are frequently encountered in industrial wastes and wastewater from agricultural irrigation. High zinc concentrations are widely present in wastewater from galvanizing plants, pigments, mine drainage, etc. (Qiang, 2011; Bhatti, 2007; Bhattacharya et al., 2006). The presence of heavy metals in water causes them to accumulate in plants through translocation and negatively affects the environment and human health (Demirtaş, 2008).

To solve this problem and control the biological activities of heavy metals in the environment, various methods such as sedimentation, electrokinetic recovery, membrane, adsorption, ion exchange and biological improvement are used (Pour & Ghaemy, 2015). However, these technologies have high operational, equipment and chemical costs. These processes are usually expensive and sometimes ineffective, especially when heavy metal concentrations are low (Hawari et al. 2009; Mohan and Pittman, 2006). Among these methods, adsorption is of increasing interest due to ease of use and the possibility of regeneration (Malik et al., 2007).

Conventional adsorbents used in water treatment are activated carbons, polymers, oxides, zeolites, etc. Still, engineered sorbents can be very expensive and in recent decades, the interest in using alternative low-cost sorbents can be observed. (Wanga, 2012). Recently, adsorption by using agricultural wastes has become an economical and applicable method for removing different pollutants from wastewaters (Kadirvelu et al., 2003). The use of agricultural wastes is preferred because it is abundant, cheap and easily accessible (Moreno-Barbosa et al., 2013). Biomass is defined as living or recently dead organisms and by-products, plants or animals (Agarwal et al., 2017). Walnut shell, an abundant agricultural residue has successfully been used in the removal of heavy metals in aqueous solutions such as Pb, Cr, and Zn, etc., by adsorption (Ding et al. 2013; Wolfova et al. 2013).

Biochar is a carbon-containing material produced by pyrolysis in a limited or completely oxygen-free environment, immobilizing heavy metals and reducing their toxicity (Wang et al., 2018; Liu et al., 2015). The potential utilization of biochar for various applications depends on its inherent property. Controlling the chemistry and morphology of the surface area is key to optimizing biochars for specific applications. Recent research on pyrolysis of the walnut shell to biochar has elaborated the process parameters effect on biochar physical–chemical characteristics (Bar et al., 2022). There are studies in the literature that high removal is obtained from the use of biochar as an adsorbent obtained from agricultural wastes.

In this study, the effect of natural and thermally modified (biochar) walnut shells on the removal of zinc ions from wastewaters was investigated. The effects of biosorbent dosage, contact time, and initial zinc concentration on sorption performance were analyzed in the study that adsorption method applied.

MATERIALS AND METHODS

Materials

Walnut shells collected by our own means were washed three times with pure water and dried in an oven at 105°C for 24 hours to remove moisture content. Then the walnut shells were crushed with the help of a mixer crusher. Sieved for a particle size of 2-4 mm. Zinc solution used in the experiment was prepared by using a 2000mg/l stock solution with $ZnSO_4$.

Characterization of Adsorbents

Characterization of the adsorbent before adsorption studies were analyzed for Brunaer-Emmett-Teller (BET) surface area. BET surface area of the modified walnut shell is 3.696 m^2/g. This value was lower than most commercial adsorbents. Nonetheless, a natural walnut shell showed an excellent zinc removal adsorption capacity. The element C, H, N, O and S composition in the walnut shell sample was determined using an elemental analyzer. The elemental analysis revealed the walnut shell mainly consists of oxygen (11.61%) and carbon (65.65%) (Table 1). A scanning electron microscope (SEM) was employed to determine the surface physical morphology (Figure 1). Fragmented appearance and shape of the walnut shell after pyrolysis in Fig. 1 b.

Table 1. Elemental Composition of the Modified Walnut Shell

Adsorbent	**% C**	**%O**	**%N**	**%H**	**%S**
Modified walnut shell	65.65	11.61	0.93	3.79	0.01

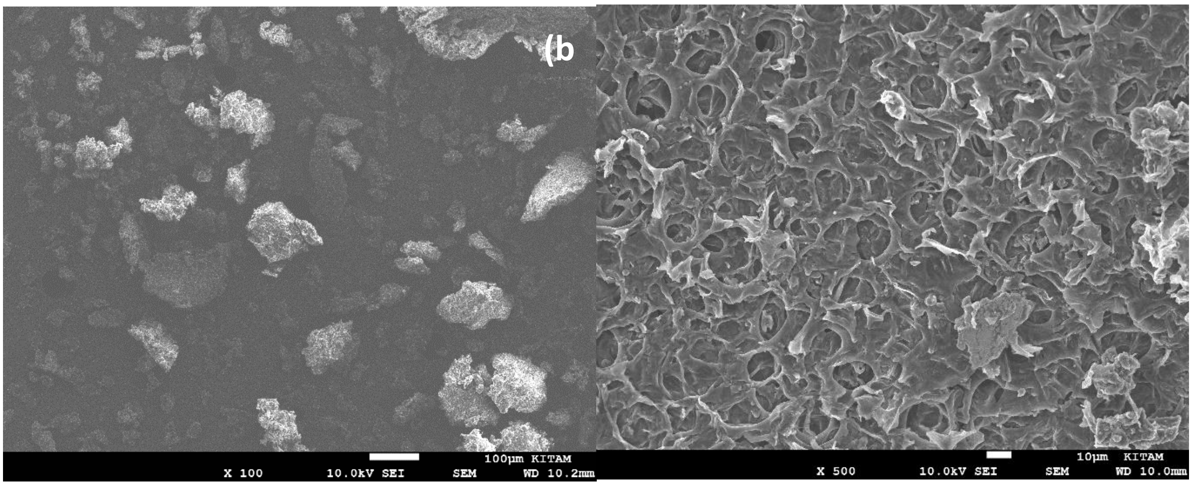

Figure 1. SEM Micrographs of the Natural and Modified Walnut Shell

Method

Pyrolysis was applied to walnut shells which will be converted to biochar form by thermal treatment. The pyrolysis step was carried out by placing 30g sample into the reactor; 600 °C pyrolysis temperature, 1 hour standby time, 100ml/min under nitrogen gas flow, 5°C/min slow pyrolysis rate. Pyrolysis resulted in 8g biochar walnut shells. Adsorption was carried out at different initial zinc concentrations, walnut shell dosages, and contact times. General adsorption conditions;

30ml zinc solution volume,
100mg/L initial zinc concentration,
0.15g (5g/L) natural and biochar walnut shell
1.5 hour at 150rpm agitation.

Adsorption samples were filtered with 0.45 syringe filters. The obtained filtrates were read after adsorption using a zinc lamp with atomic absorption spectrophotometer (AAS) of the UNICAM 929 model. The removal efficiency values according to concentration, dosage and contact time after adsorption were calculated with the following formula (E).

$$E(\%) = (C_o - C_e)/C_o \times 100 \quad (1)$$

In formula; E: Removal efficiency Co: Initial zinc concentration, Ce: Zinc concentration after adsorption.

RESULT AND DISCUSSION

The Effect of Initial Concentration on Removal Efficiency

Initial concentrations of 100-200-400-800-1000-1500 mg/L were selected to examine the effect of concentration. Experiments were carried out at 50mL solution volume, 2.5g/L adsorbent dosage, and 165rpm under 1 hour shaking conditions. As shown in Figure 2, both the natural and biochar walnut shell forms exhibited similar behaviors in removal efficiency. Up to 400mg/L concentration increases with concentration, the efficiency reaches 97%. At the concentration of 1500mg/L, the efficiency decreases to 76%.

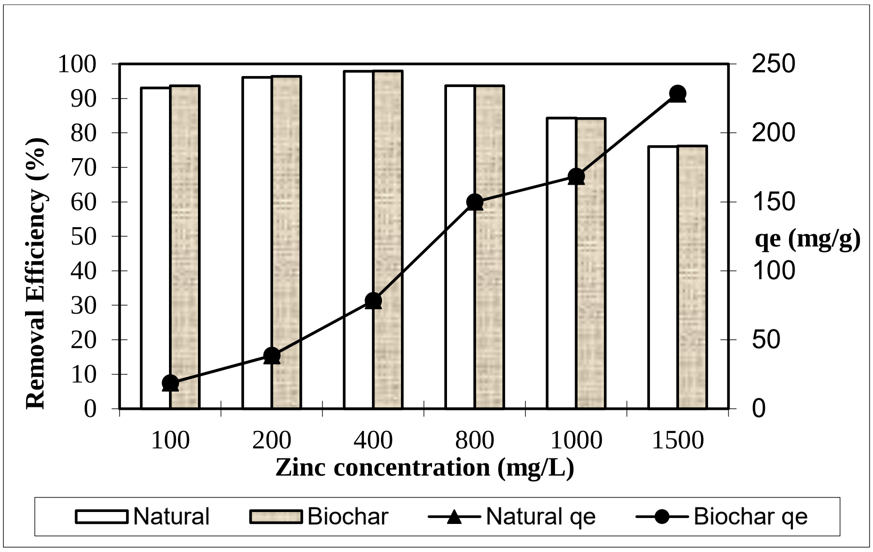

Figure 2. Effect of Initial Concentration on Zinc Adsorption

The Effect of Dosage on Removal Efficiency

To investigate the effect of walnut shell dosage on adsorption, 2.5-5-10-20g/L adsorbent dosages were selected. In the dosage study, 100mg/L initial zinc concentration, 50mL sample volume, 1 hour shaking conditions at 165rpm were selected. Figure 3 shows the removal yields and qe values of natural and biochar walnut shells. In general, the dosage does not significantly affect the adsorption efficiency. 90% removal efficiencies were obtained in all walnut shell dosages for natural and biochar forms.

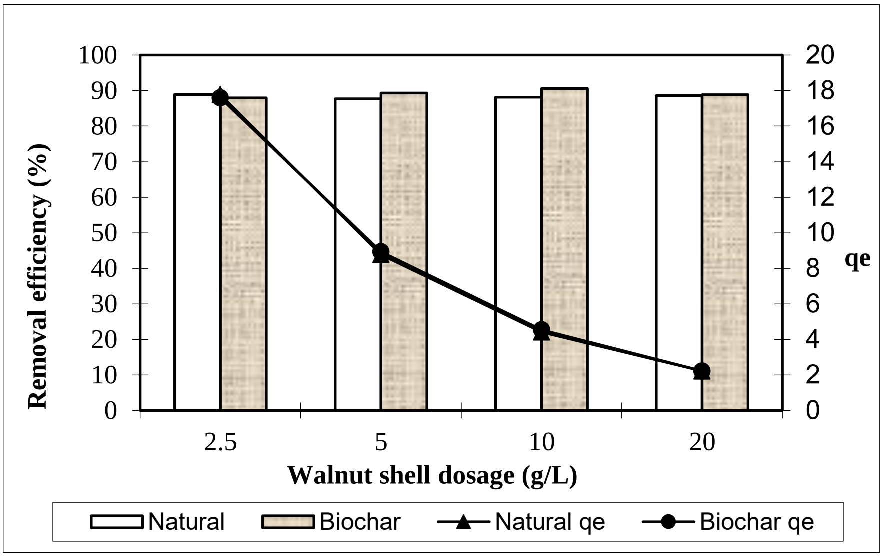

Figure 3. Effect of Adsorbent Dosage on Zinc Adsorption

The Effect of Contact Time on Removal Efficiency

Adsorption experiments to investigate the effect of contact time were studied 1-15-30-60-90-120min. Contact time on zinc removal experiments were carried out at 100mg/L initial zinc concentration, 2.5g/L adsorbent dosage, 50mL sample volume at a shaking rate of 165rpm. Figure 4 shows the removal efficiency of the contact time and adsorption qe values. Biochar forms have been found to have 2% higher yield than natural forms. Approximately 90% removal efficiency was achieved from the first minute of contact time. The high removal efficiency was achieved even with long adsorption contact times.

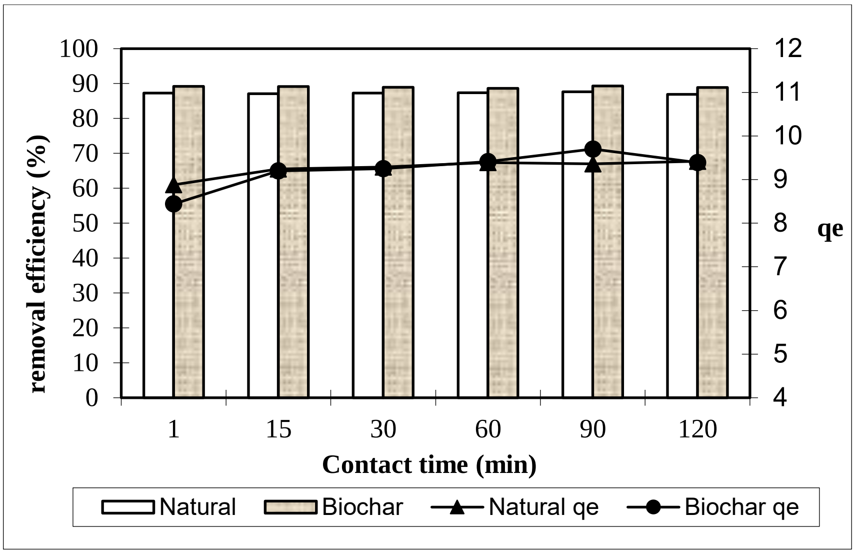

Figure 4. Effect of contact time on zinc adsorption

Adsorption Isotherms

Adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption and ion-exchange systems since they indicate how the metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of increasing metal concentrations.

Langmuir and Freundlich isotherms for removal of zinc ions using natural and biochar walnut shells are presented in Figure 5. The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 2. The data obtained were well fitted with the Langmuir equation compared to the Freundlich equation under the different concentrations.

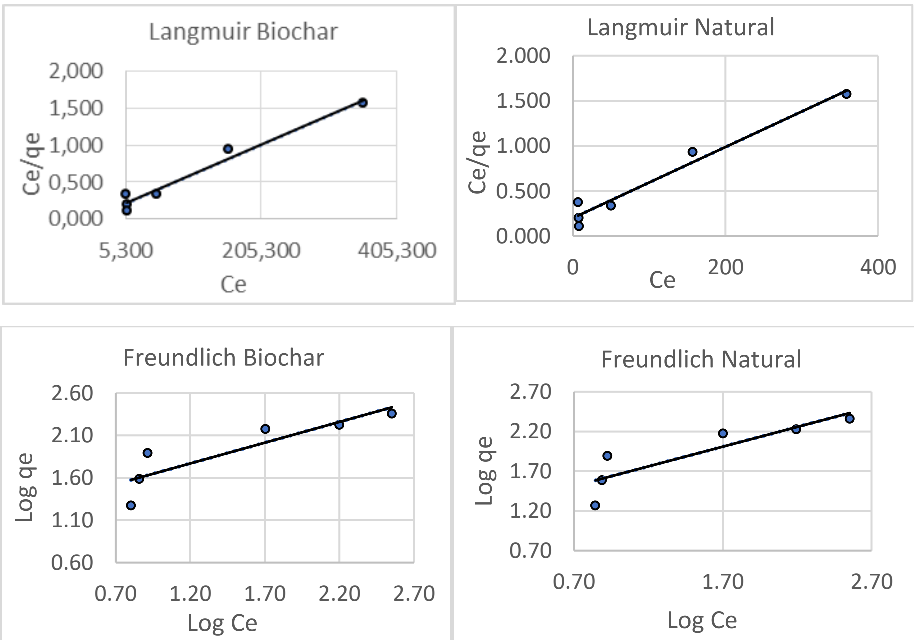

Figure 5. Langmuir and Freundlich Adsorption İsotherm Graphs

The values R^2 for Langmuir are calculated as 0.96 for both natural and biochar walnut shells. The values of qm, defined as the maximum capacity of sorbent, have been calculated from the Langmuir plots. The greatest equilibrium sorption capacity q_m for natural and biochar adsorbents were obtained for 256,4mg/g and 250mg/g, respectively.

Table 2 Langmuir and Freundlich Models Correlation Coefficients

Isotherm Model	Formula	Linear formula	Parameter	Natural	Biochar
Langmuir	$qe = \frac{qmax.b.Ce}{1+b.Ce}$	$\frac{Ce}{qe} = \frac{1}{qmax.b} + \frac{Ce}{qmax}$	q_m (mg/g)	256.4	250
			b (L/mg)	0.019	0.021
			R^2	0.9637	0.9686
Freundlich	$qe = kF.Ce\,x\,\frac{1}{n}$	$lnqe = lnkF + \frac{1}{n}lnCe$	n	2.01	0.0002
			K_F (L/g)	14.59	15.2
			R^2	0.7679	0.7813

Adsorption Kinetics

Different kinetics models study adsorption properties depending on adsorption time. This study applied pseudo-first order, pseudo second order and intra particle diffusion kinetics models to adsorption times ranging from 1-120 min. It was clear that the adsorption process for walnut shells achieves balance quickly. As shown in Figure 5, the adsorption corresponds to the pseudo-second order kinetic model.

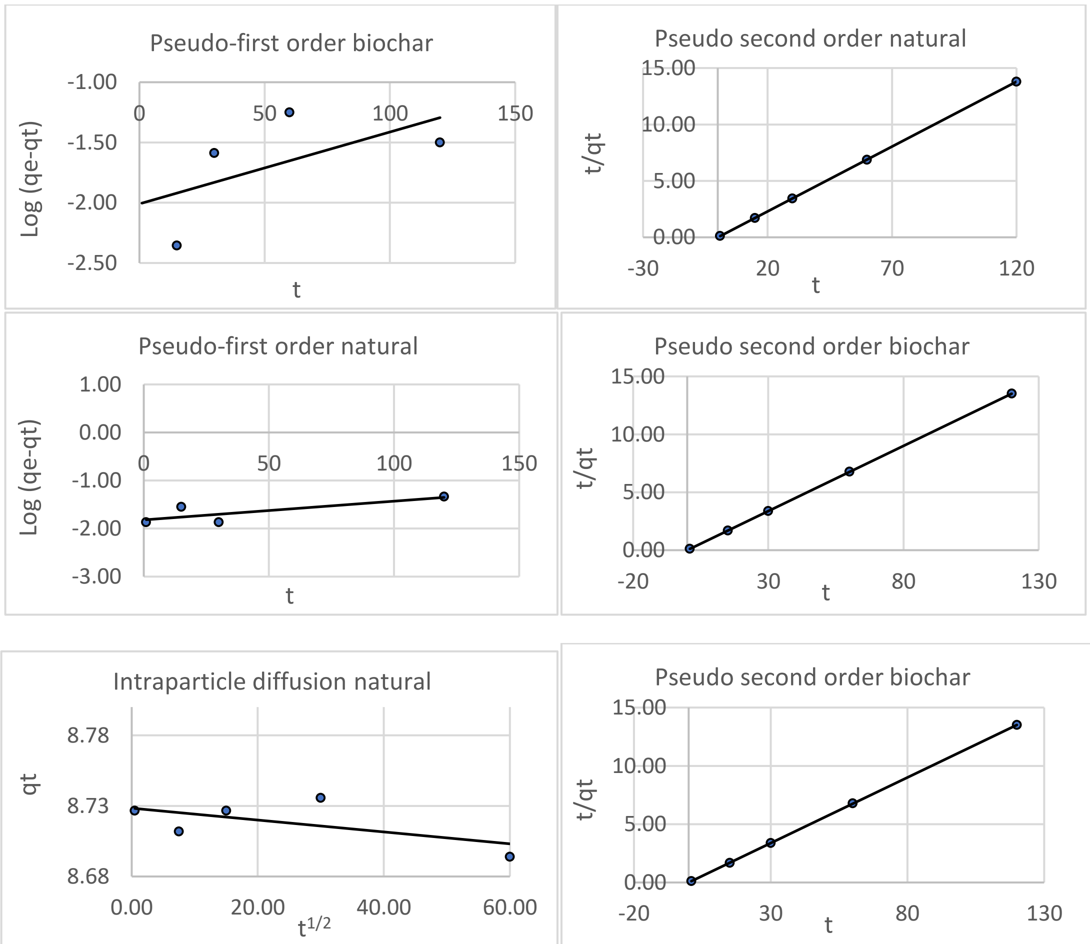

Figure 5 Pseudo-First Order, Pseudo Second Order and Intra Particle Diffusion Kinetics Graphs

The linear forms, the way of plots and the correlative parameters of these kinetic models with the correlation coefficients (R^2) were represented in Table 3. It could be seen that the experimental data were fitted best for the pseudo-second order kinetic model with 0,9999 correlation coefficient for both of natural and biochar walnut shells.

Table 3 Formulas and Calculated Parameters of Kinetic Models

Adsorbent Type	Kinetic Models								
	Pseudo-first order			Pseudo second order			Intra particle diffusion		
	$\log(qe - qt) = logqe - \left(\frac{k1}{2,303}\right).t$			$\frac{t}{qt} = \frac{1}{k2.qe2} + \left(\frac{1}{qe}\right)t$			$qt = ki.t^{1/2} + C$		
	k1 (dk^{-1})	qe (mg/g)	R^2	k2 (g/mg.dk)	qe (mg/g)	R^2	Ki (mg/g.dk^2)	C	R^2
Natural	0.0089	65.96	0.6291	1.43	8.69	0.9999	0.0004	8.284	0.3654
Biochar	0.0138	102.16	0.3367	42.27	8.88	0.9999	0.0006	8.9102	0.3913

A comparison of the maximum adsorption capacity of the walnut shell sample with that of some other studies reported in literature is given in Table 4.. The obtained results are in the range of cited values in the literature (Segovia-Sandovala, et al 2018; Kazemipour et al., 2008). A comparison of the maximum adsorption capacities of some low-cost adsorbents for the Zn^{2+} removal is given in Table 4. The sorption affinity of the clinoptilolite is comparable to or more to the other available adsorbents.

Table 4. Adsorption Capacities of Zinc on Various Adsorbents

Low-cost adsorbents	Adsorption capacity (mg/g)	Reference
Fallen leaves (Platanus)	86.2	(Park et al., 2022)
Chitosan	74.6	(Xu et al., 2022)
Seaweed	27.11	(Basha et al., 2008)
Banana	45	(Oyewo et al., 2017)
Sugar beet bagasse	52.8	(Ghorbani et al., 2020)
Walnut Shell	27.86	(Segovia-Sandoval et al., 2018)
Present study	**25.64**	-

CONCLUSION

This study aimed to investigate the potential use of natural walnut shells and biochar as a biosorbent for removing zinc ions. The adsorption process functions contact time, biosorbent dosage, and zinc ion concentration. The results show that biochar effectively removed zinc ions from an aqueous solution. The maximum adsorption capacities (qm) of natural and biochar walnut shell were found to be 256,4, and 250 mg/g, respectively, and the highest removal efficiency was found to be 97% at 400mg/L zinc concentration. The experimental data was applied to various isotherm and kinetic models. The data were well fitted to the Langmuir isotherm model and pseudo-second-order kinetic model equation, with good correlation coefficients. The results show that natural walnut shells and biochar could be used as low-cost adsorbents to remove zinc ions from an aqueous solution. In addition, natural walnut shell values show removal efficiencies close to the biochar form, so walnut shell alone can be used as the adsorbent for zinc removal.

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