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Industrial Wastewater Treatment Using Squid Bones as a Carbonate Mineral

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ABSTRACT

The aim of this study is to treat industrial wastewater by squid bones (cuttlebone) as a carbonate mineral. The objective was achieved through adsorption isotherm study of some heavy metals on squid bones. Characterization of the squid bones was done by FTIR spectroscopy and Scan Electron Microscope (SEM). The effect of various parameters such as pH, contact time, and metal ion concentration on the adsorption of metal ions onto squid bones was investigated. The experimental data have been modeled by Langmuir and Freundlich Isotherms. The data indicating that the adsorption of the metal ions followed both the Langmuir and Freundlich isotherm models. The adsorption kinetic was studied and the pseudo-second-order reaction was better than pseudo-first-order reaction. The results indicated that the order of adsorption capacity of squid bones for metal ions was as follows: $Hg^{2+} > Pb^{2+} > Cd^{2+}$. The calculated dimensionless separation factor ($R_L < 1$) indicates favorable adsorption process. With applying the squid bones on real wastewater, the average removal percentages for COD, TSS, TKN and heavy metals were 94%, 95%, 85% and 95%, respectively.

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INTRODUCTION

Water pollution by heavy metals through the discharge of industrial effluents, is a worldwide environmental problem. Studies have proved that the metals such as lead, zinc, cobalt, chromium and mercury are considered to be toxic. At low concentration lead can adversely affect the brain, the central nervous system, blood cells, and kidneys (Inglezakis *et al*., 2007). Lead compound is widely used in painting, plastics and batteries. The treatment of paint wastewater for reuse thus requires treatment for the removal of suspended solids and metal ions (Dey *et al*., 2004). In general, paint effluents are alkaline and have high BOD, COD, heavy metals, suspended solids and colored materials (Dey, 1999).

Many researchers had investigated the removal methods of heavy metals from wastewater (Tennakoon *et al*., 1996; Gotsi *et al*., 2005; Szpyrkowiez *et al*., 2005 and Mahmoud *et al*., 2015). A number of physical and chemical processes exists which include precipitation, solvent extraction, membrane processes, filtration, ion-exchange and adsorption (Fenglian *et al*., 2011). Among them, adsorption is an efficient and economical process. The efficiency of technique depends on the nature of adsorbent. The adsorbent such as activated carbon (Zaini *et al*., 2010), clay (Abu-Eishah, 2008), activated alumina (Bishnoi *et al*., 2004), silica (Aguado *et al*., 2009) and zeolite (Motsi *et al*., 2009) were used for heavy metal removal.

In recent years, great attention has been paid to the bioactivity of natural products obtained from plant, animal and in addition of marine origin. Adsorption by low-cost adsorbents and biosorbents is recognized as an effective and economic method for low concentration heavy metal wastewater treatment (Fenglian *et al*., 2011). Cuttlebone (squid bones) also known as cuttlefish bone, is a hard, brittle internal structure (an internal shell) found in all members of the family Sepiidae, commonly known as cuttlefish, a family within the cephalopods. Cuttlebone is composed primarily of aragonite. Aragonite is a carbonate mineral, one of the two common, naturally occurring, crystal forms of calcium carbonate, $CaCO_3$ (the other form being the mineral calcite). It is formed by biological and physical processes, including precipitation from marine and freshwater environments. Aragonite's crystal lattice differs from that of calcite, resulting in a different crystal shape, an orthorhombic system with acicular crystals. The microscopic structure of cuttlebone consists of narrow layers connected by numerous upright pillars (Rexfort *et al*., 2006).

In the past, cuttlebones were ground up to make polishing powder. The powder was added

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to toothpaste, and was also used as an antacid or as an absorbent. Today, cuttlebones are commonly used as calcium-rich dietary supplements for caged birds, chinchillas, hermit crabs, reptiles, and snails (Norman *et al*., 2000).

In this study, Cuttlebone powder was characterized by FTIR and SEM then employed for uptake Cd^{2+}, Pb^{2+} and Hg^{2+} ions from the aqueous solution. Factors such as pH, time, and initial metal ions concentration that affecting the uptake were carried out. Optimal conditions have been applied to treat a real wastewater of paint industries.

MATERIALS AND METHODS

2.1. Materials:

Cuttlebone (squid bone), Figure 1, was collected from fish processing plant, Alexandria, Egypt. Ball mill was used to prepare cuttlebone powder of less than 74 μm. Cuttlebone was characterized by FTIR spectroscopy using (Nicolet Is-10 FT-IR, USA). The surface morphological structure was done by JEOLJSM-5400 scanning electron microscopy SEM, Japan. All other chemicals used such as metal salts, HCl and NaOH were reagent grade and purchased from El-Nasr Co. for Chemical Industries (Egypt) and used without further purification. The bi-distilled water was used in all experiments.

2.2. Adsorption Experiments:

A stock standard of Cd^{2+}, Pb^{2+} and Hg^{2+} ions solutions of 2000 mg/L was prepared by dissolving an appropriate amount of analytical grade salt in distilled water. Batch adsorption experiments were carried out at 25°C. Exactly 50 ml of metal ions solution of known initial concentration (50–1000 mg/L) was shaken at the agitation speed (300 rpm) with 1gm of the cuttlebone powder. The pH values were adjusted by the addition of 0.1 M NaOH or HCl solution.

The clear solution was separated from the cuttlebone powder at desired intervals by centrifuge and the residual concentrations of metal ions were determined by Perkin Elmer atomic absorption spectrophotometer (Perkin Elmer model 2380). The adsorption capacity q_e (mg/g) at any time was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)\,V}{W}$$

Where V is the volume of the solution (liter), W is the mass of the cuttlebone powder used (g); C_0 and C_e are the concentrations of the initial and equilibrium metal ions solution (mg/L), respectively.

Fig. 1: Raw Cuttlebone (squid bone),

RESULTS AND DISCUSSION

3.1. Characterization of The Cuttlebone:

FTIR spectra of cuttlebones (Figure 2) shows two peaks of the carbonate vibration at 700 and 713 cm^{-1} which are diagnostic of aragonite (Florek *et al*., 2009). The peaks at 1083 and 854 cm^{-1} are also characteristic of aragonite (Adler *et al*., 1962). Aragonite is a meta-stable form of calcium carbonate $CaCO_3$. Preservation of aragonite, a meta-stable form of calcium carbonate, rather than the more stable calcite form, indicate the cuttlebones have undergone minimal diagenesis and thus had a greater potential to preserve original organics. Aragonite's crystal lattice differs from that of calcite, resulting in a different crystal shape, an orthorhombic system with acicular crystals (Adler *et al*., 1962).

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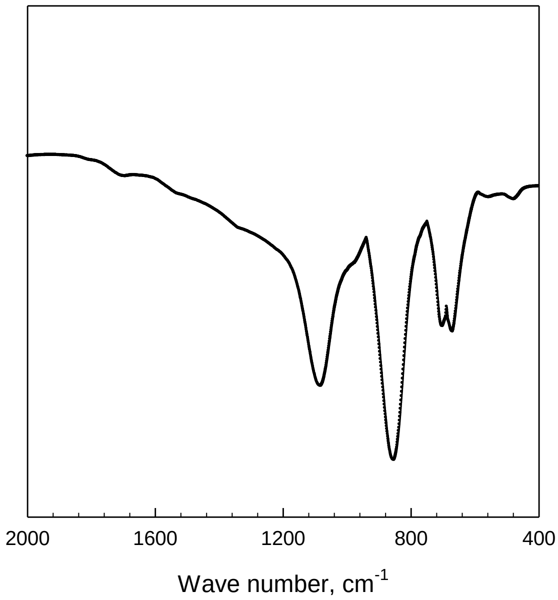
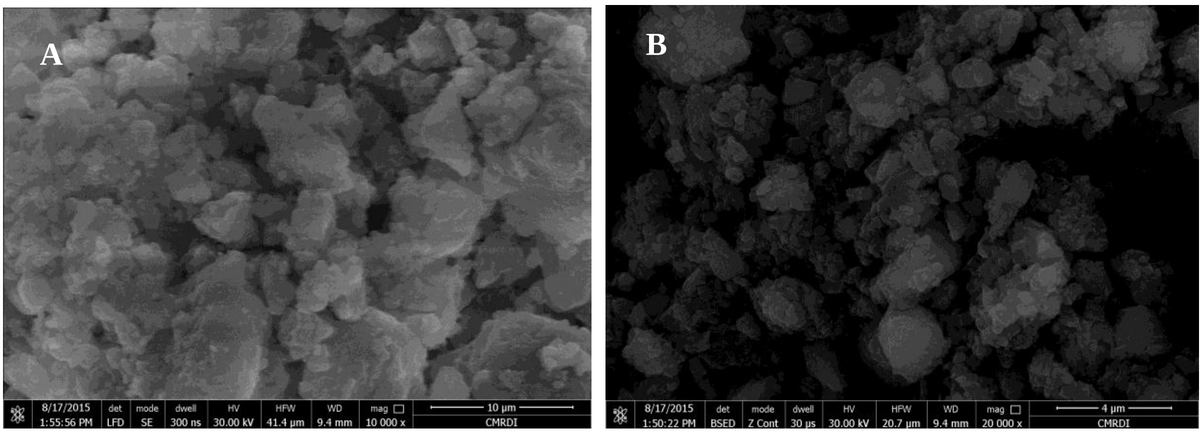


Fig. 2: FTIR spectra of cuttlebones.

SEM analysis of cuttlebones revealed ultra-structures (Figure 3), between carbonate layers. The "sheet-like" structures contain high amounts of phosphorous. Alternatively these originally organic structures could have served as a template for phosphatization (Martill *et al*., 1994) and some of the original organic material may have been preserved. The microscopic structure of cuttlebone consists of narrow layers connected by numerous upright pillars (Rexfort *et al*., 2006).

Organic layers within cuttlebones are protected by mineralized layers, similar to collagen in bones, and this mineral-organic interaction may also have played a role in their preservation. SEM shows preserved original aragonite as well as apparent original organics. These organics appear to be endogenous and not a function of exogenous fungal or microbial activity (Englington *et al*., 1991; Collins *et al*., 2002 and Schmidt *et al*., 2004). Also, SEM shows there is no evidence of tunneling, microbes, or wide-spread recrystallization of the aragonite.



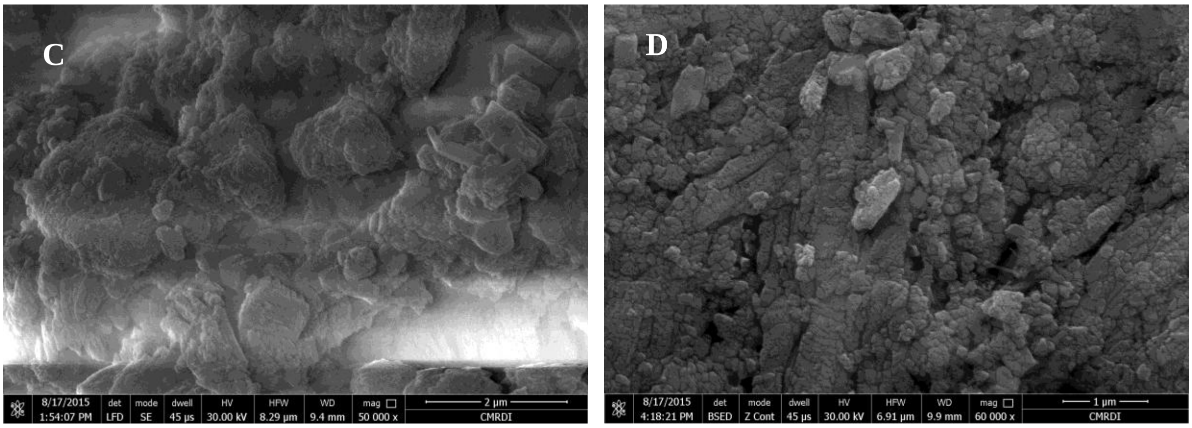


Fig. 3: SEM images of cuttlebones with different magnification, A (10K), B(20K), C(50K) and D(60K).

3.2. Adsorption Study:

3.2.1. Effect of Solution pH:

Figure 4 shows the effect of pH on the sorption of Cd^{2+}, Pb^{2+} and Hg^{2+} ions by cuttlebone by varying the solution pH from 4 to 7 at 25°C for 60 min. It can see that, the extraction efficiency of the ions increases significantly by increasing the pH of the solution up to pH of 6 which may be due to the increase of bonding between cuttlebone and ions. The decreasing in the metal ions uptake above this pH is observed which may be due to precipitation of ions as hydroxide (Bojdi *et al*., 2014). At lower pH, the cuttlebone reacts as carbonate mineral producing CO_2 gas and thus the pH increased.

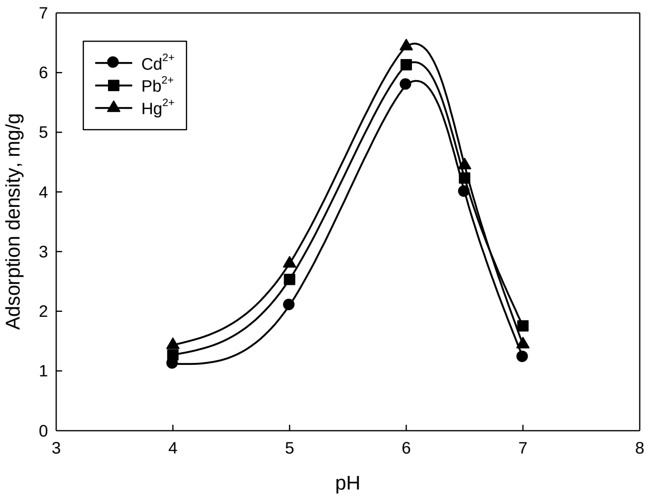


Fig. 4: Effect of pH on the Cd^{2+}, Pb^{2+} and Hg^{2+} uptake at 25°C and 200 mg/L for 60 min.

3.2.2. Effect of Metal ions Concentration:

To investigate the effect of the initial concentration, different initial concentrations (50 and 1000 mg/L) were used in batch experiments at 25°C and pH 6 for 60 min. Fig.5, shows that the adsorption capacity of the cuttlebone is increased with increasing the initial metal ions concentration. This indicates that at lower initial metal ions concentrations, the adsorption sites on the cuttlebone are sufficient. Increasing the initial concentration can accelerate the diffusion rate of ions into the cuttlebone matrix due to increasing the driving force of concentration (Mahmoud *et al*., 2013). The results indicated that the order of adsorption capacity of MACB nanocomposite for metal ions was as follows: $Hg^{2+} > Pb^{2+} > Cd^{2+}$. These results were due to that the fluctuation motion of $Hg^{2+} > Pb^{2+}$ and that which is greater than Cd^{2+} (Katima *et al*., 2001).

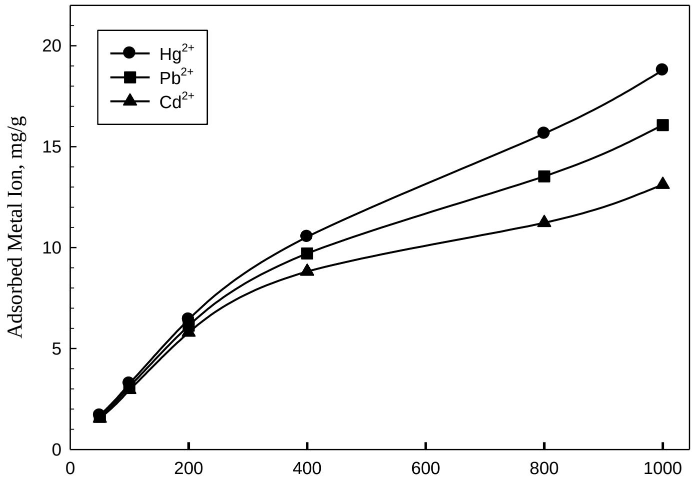


Fig. 5: Effect of initial concentration on Cd^{2+}, Pb^{2+} and Hg^{2+} uptake at 25°C and pH 6 for 60 min.

3.2.3. Adsorption Isotherms:

In this study, two typical isotherms are used for fitting the experimental data: The Langmuir adsorption model is applicable to homogeneous binding sites and assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule (chemical adsorption). The Langmuir equation could be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b.q_{max}}$$

Where q_{max} represents the maximum amount of adsorbed metal ions on the gel (mg/g), and b is the Langmuir model constant of (Wang *et al*., 2014).

The Freundlich model is employed to describe heterogeneous system (physical adsorption). The heterogeneity factor of 1/n is a measure of the deviation from linearity of the adsorption (Al-Duri, 1995). The Freundlich model is expressed as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

Where k_f is the Freundlich isotherm constant and 1/n (dimensionless) is the heterogeneity factor.

The Langmuir and the Freundlich model are applied for adsorption of Cd^{2+}, Pb^{2+} and Hg^{2+} ions onto cuttlebone (Fig. 6 and 7) and the obtained data are summarized in Table 1. The data indicating that the adsorption of the latter ions followed both the Langmuir (R^2 > 0.98) and Freundlich (R^2 > 0.95) isotherm models. Thus, the adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} ions onto cuttlebone are chemical and physical adsorption types.

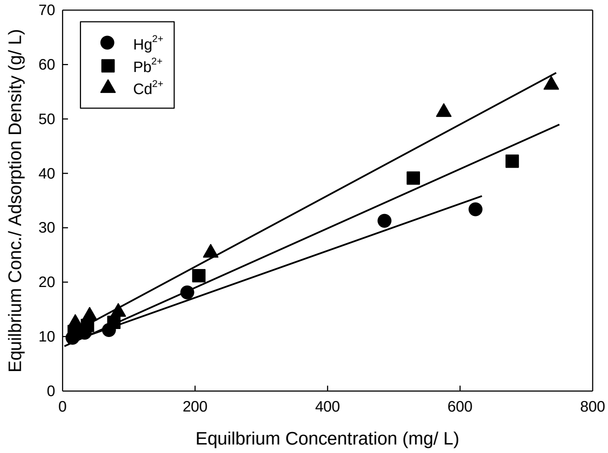


Fig. 6: Langmuir isotherm for adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} onto cuttlebone.

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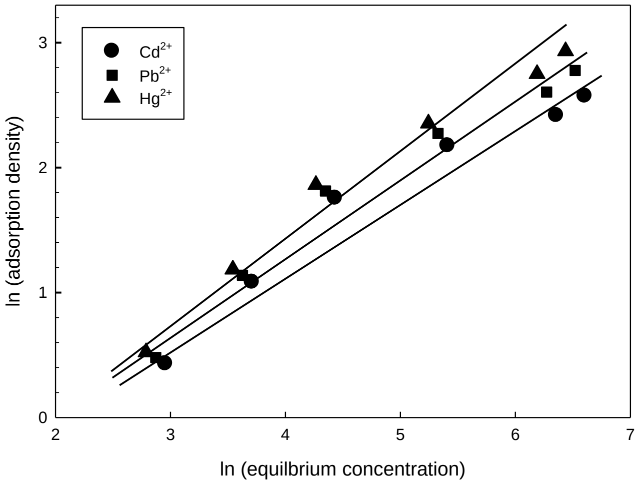

Fig. 7: Freundlich isotherm for adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} onto cuttlebone.

Table 1: Langmuir and Freundlich constants for Hg^{2+}, Pb^{2+} and Cd^{2+} adsorption onto cuttlebone.

Model	Parameters	Cd^{2+}	Pb^{2+}	Hg^{2+}
Langmuir	q_{max}	0.8133	0.7984	0.7716
	b	0.0060	0.0050	0.0045
	R^2	0.9904	0.9879	0.9853
	Calculated q_{max}	15.432	19.841	24.271
	Experimental q_{max}	13.116	16.066	18.781
Freundlich	K_f	0.3716	0.3498	0.3433
	1/n	0.5559	0.6003	0.6331
	n	1.7988	1.6658	1.5795
	R^2	0.9480	0.9657	0.9751

The effect of isotherm shape can also be used to predict whether an adsorption system is “favorable” or “unfavorable.” The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is defined by the following relationship (Alkan *et al*., 2008):

$$R_L = \frac{1}{(1 + bC_0)}$$

Where $\mathbf{C_0}$ (mg/L) is the initial concentration of dye and **b** is Langmuir constant. The value of R_L is indicator of the shape of adsorption isotherm to be favorable or unfavorable. The value of R_L between 0 and 1 indicates favorable adsorption, while R_L=1 suggests unfavorable adsorption and the adsorption process is linear adsorption, while R_L=0 represents irreversible adsorption.

Table 2: Langmuir dimensionless constant separation factor (R_L).

0.004500	0.005017	0.006003	b →
R_L			C_0 ↓ ppm
Hg^{2+}	Pb^{2+}	Cd^{2+}	
0.8163	0.7995	0.7691	50
0.6897	0.6659	0.6249	100
0.5263	0.4992	0.4544	200
0.3571	0.3326	0.2940	400
0.2174	0.1995	0.1723	800
0.1818	0.1662	0.1428	1000

The value of R_L between 0 and 1 indicates favorable adsorption for all metal ions.

3.2.4. Effect of Contact Time:

Fig.8 shows the metal ions uptake as a function of contact time. It can be noted that, the increase in contact time leads to an increase in the amount of metal ion adsorbed until the equilibrium is reached within 60 min.

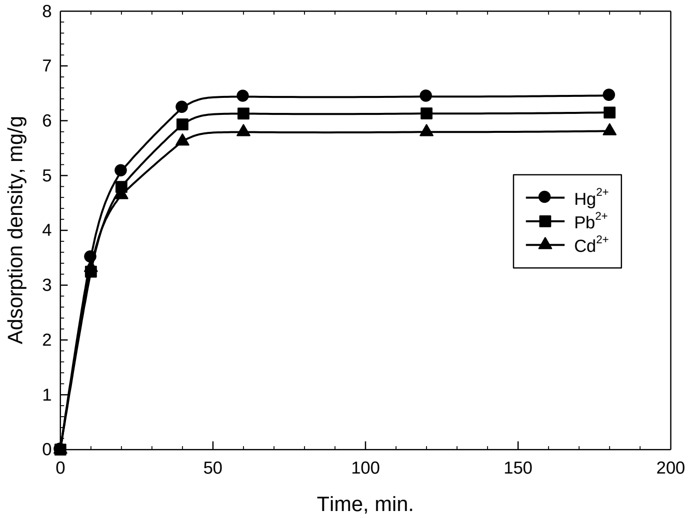

Fig. 8: Effect of contact time on Cd^{2+}, Pb^{2+} and Hg^{2+} uptake at 25°C, pH 6 and initial conc. 200 mg/L.

3.2.5. Adsorption Kinetics:

Lagergren's pseudo-first-order equation is describing the adsorption rate based on the adsorption capacity. The linear form of Lagergren's pseudo-first-order equation is generally expressed as (Xing *et al*., 2012):

$$\log\ (qe - qt) = \log qe - \frac{\mathrm{k1}}{2.303}\ \mathrm{t}$$

Where q_t (mg/g) is the adsorption capacity at any time t (min); k_1 is the pseudo-first-order rate constant of the equation (min^{-1}). q_e is the equilibrium adsorption capacity (mg/g). The adsorption rate constant k_1 can be determined by plotting of log ($q_e - q_t$) vs. time, Fig.9.

The pseudo-second-order model, which is fit for the chemisorptions of metal ions onto adsorbents from aqueous solutions with polar functional groups. Pseudo-second-order equation is expressed as (Mahmoud *et al*., 2014):

$$\frac{\mathrm{t}}{\mathrm{qt}} = \frac{1}{\mathrm{k_2 qe^2}} + \frac{1}{\mathrm{qe}}\ \mathrm{t}$$

Where k_2 (g/mg min) is the pseudo-second-order rate constant that is calculated by plotting t/qt vs. time, Fig.10.

The two modules are applied for the metal ions adsorption and their parameters are all listed in Table 3. It can be found that, the correlation coefficients R^2 for the pseudo-second-order kinetic plots for all investigated studied are about 0.99, indicating that the pseudo-second-order kinetic model can describe well the experimental data. Therefore, the adsorption on cuttlebone may be a chemical process through sharing electrons.

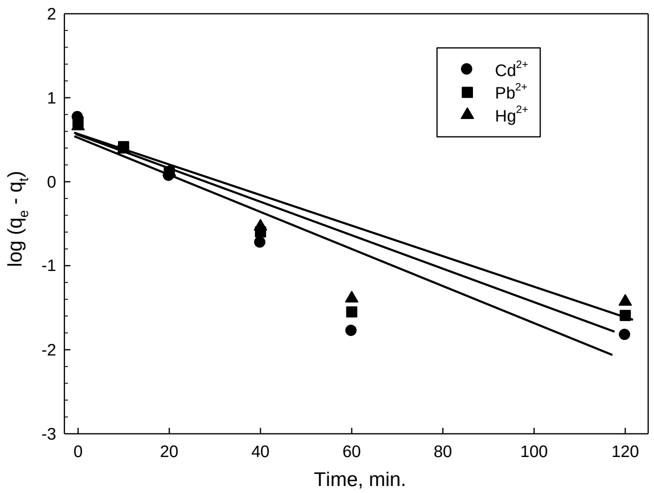

Fig. 9: Pseudo-first-order plot for the Cd^{2+}, Pb^{2+} and Hg^{2+} uptake at different initial concentrations.

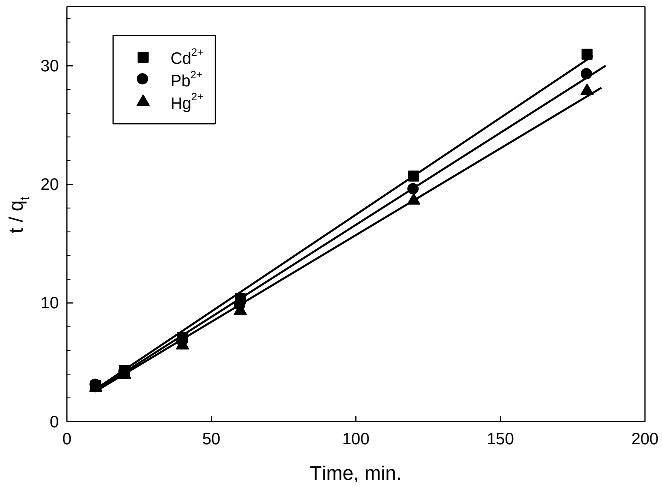

Fig. 10: Pseudo-second-order plot for the Cd^{2+}, Pb^{2+} and Hg^{2+} uptake at different initial concentrations.

Table 3: Coefficient of different kinetic models for Cd^{2+}, Pb^{2+} and Hg^{2+} ions adsorbed by cuttlebone

Model	Parameters	Cd^{2+}	Pb^{2+}	Hg^{2+}
Pseudo-first-order	K_1 (min^{-1})	-0.0522	-0.0490	-0.0474
	R^2	0.8133	0.7984	0.7716
	Calculated q_{max}	2.8067	2.6357	2.4774
	Experimental q_{max}	5.8109	6.1500	6.4599
Pseudo-second-order	K_2 (min^{-1})	0.0328	0.0264	0.0266
	R^2	0.9989	0.9983	0.9985
	Calculated q_{max}	6.0204	6.4102	6.7159
	Experimental q_{max}	5.8109	6.1500	6.4599

3.3. Industrial Wastewater:

The cuttlebone was employed for treatment of real wastewater at 25°C and pH 6 for 60 min. The average percentages of removals for Chemical oxygen demand (COD), Total suspended solids (TSS), Total Kjeldahl nitrogen (TKN) and heavy metals were 94%, 95%, 85% and 95%, respectively (Table 4).

Table 4: Chemical analysis of waste water before and after treatment with cuttlebone

Parameter	Concentration, mg/L		Removal %
	Before	After	
Conductivity (μs/cm)	315	51	84
Sulfide	243	12.1	95
COD	3524	211	94
TKN (mg/L)	219	32	85
TSS	2753	137	95
Cl_2	14	0.1	99
Heavy metals	213	10.6	95
Turbidity (NTU)	58	7.6	97
Color %	48	2.4	95

COD: Chemical oxygen demand
TSS: Total suspended solids
Conductivity (ms/cm) = 10^3 s/cm (siemens per meter (S/m))
TKN: Total Kjeldahl nitrogen (sum of organic nitrogen, ammonia (NH_3), and ammonium (NH_4^+))

Conclusions:

Cuttlebone (squid bones) is composed of aragonite which is a carbonate mineral. The microscopic structure of cuttlebone consists of narrow layers connected by numerous upright pillars. It has “sheet-like” structures contain high amounts of phosphorous and some organic materials.

The feasibility of using cuttlebone the removal of Cd^{2+}, Pb^{2+} and Hg^{2+} ions from an aqueous solution was investigated. The maximum adsorption of heavy metal ions was obtained at pH 6 and at contact time of 60 minutes. The experimental results indicated that the order of adsorption capacity of cuttlebone for metal ions was as follows: $Hg^{2+} > Pb^{2+} > Cd^{2+}$. The data indicating that the adsorption of the latter ions onto cuttlebone followed both the Langmuir and Freundlich isotherm models. Thus, the adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} onto cuttlebone is chemical and physical types. The value of dimensionless constant separation (R_L) between 0 and 1 indicates favorable adsorption for all metal ions.

The pseudo-first-order and pseudo-second-order equations are applied for the metal ions adsorption. The correlation coefficients for the pseudo-second-order kinetic plots for all investigated studied are about 0.99, indicating that the pseudo-second-order kinetic model can describe well the experimental data.

By applying the treatment process at optimum conditions on paint wastewater, the average percentages of removals for COD, TSS, TKN and heavy metals were 94%, 95%, 85% and 95%, respectively.

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