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Limestone residues of sculpting factories utilization as sorbent for removing Pb(II) ion from aqueous solution

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ABSTRACT

This study aims to use limestone wasted from the factory of stone carving for the adsorption of Pb(II) ion from aqueous solution. The process of adsorbing Pb(II) ion was achieved by using the patch method at conditions of (mass of adsorbent = 0.3, 0,6, 1.2 g, contact time = 15, 30, 45, 60, 120 min, particles size = 150, 250, 300 µm, pH media = 2, 3, 4, 5, 6, 7, 8, 9, temperature = 288, 298, 308, 318 K and initial concentration = 50, 70, 90, 100 mg/L) to obtain the best adsorption conditions. The atomic absorption spectroscopy was used to determine the concentration of the Pb(II) ion after the adsorption steps. Results show that the limestone was efficient for the removal of Pb(II) ion with efficiency reaching 99.5 % when 1.2 g of limestone was used. The study also revealed that the smaller particle size of limestone is, the higher percentage of removal will be. The adsorption increased almost rapidly with pH up to 5. The adsorbent uptake reaches the maximum after 15 min of contact. The Freundlich, Langmuir and Temkin isotherms plots show a good linearity, where R^2 was more than 0.99, suggesting a good agreement with the experimental data.

1. Introduction

Various industrial processes result in elevated concentrations of toxic ions, which are considered high-level environmental pollutants and pose a threat to human health and the eco-system [1–2]. The WHO limits permitted concentration of Pb(II) ions in drinking water at 0.05 mg/L and Pb(II) in wastewaters at a level of 0.05–0.10 mg/L before discharging [3–4]. There is a need to find a process that reduces this pollution. Many methods have been used for the removal of these toxic ions from aqueous solutions, including ion exchange, chemical precipitation, microfiltration, chemical reduction, reverse osmosis, and adsorption [2,5–9]. The adsorption method has proven to be an effective method for removing ions while using environmentally friendly materials and reducing costs as well [6,10–11].Table 1.

Because of the high toxicity of Pb(II) ion, extensive research have been focusing on the removal of this ion from aqueous solution using a variety of adsorbents. ZnO nano-powders functionalized by chelating reagent was used for the removal of Pb(II) and Cd(II) aqueous solution [12]. Graphene oxide functionalized with oxidethiol [13] and multi-walled carbon nanotubes grafted with acrylamide [14] was reported to have high adsorption capacities for Pb(II) ions. EDTA-Zr(IV)iodate showed a removal percentage that reaches 90 % where the initial concentration was 10 mg/L [15]. It has also been reported that activated carbon prepared from Rosa Canina-L seeds and composited with NiO has maximum monolayer adsorption capacity (qm) of up to 1428.57 mg/L [16].

The removal of Pb(II) ions using minerals relies on many factors including electrical properties, acidity and basicity of the minerals, ion charge, concentration and size, competition of other ions, and the pH and the temperature of the solution [22–23]. The minerals have many attractive properties that qualify them to be used as adsorbents. Of these is their high ability to adsorb resulting from the fact that minerals contain rough surface, pores and cavities [12]. Minerals may contain water that can be dried, and leave cavities behind it. They also have some cation in their structure, which acts like ion-exchanger that can replace their ions with toxic ions in the aqueous solutions [24–26]. The use of minerals' powder with fine particles gives them a high surface area that increases their ability for adsorption. Waste of limestone from the factory of stone carving is usually sent to landfilling [24–28]. Therefore, different strategies are proposed to use this type of waste as a low cost adsorbent material. This strategy is considered a promising application of green chemistry principles [29–33].

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Table 1
Adsorption capacities of Pb(II) ions onto various adsorbents reported in the literature.

Adsorbent	q_e (mg/g)	Ref.
Functionalized graphene oxide-thiol(prepared with 80 mg cysteamine (GO-SH2)	200	[13]
NH2-HMS (functionalized HMS type mesoporous silica with amine groups)	119	[16]
poly (acrylamide-*co*-itaconic acid)/multi walled carbon nanotubes	71	[14]
NiO/*Rosa Canina-L* seeds activated carbon nanocomposite	1428.57	[17]
magnetite nanoparticles	3.44	[18]
magnetic alginate beads based on maghemite nanoparticles	50	[19]
P(MMA-HEMA)	3.037	[20]
Phyllanthus emblica fruit stone (PEFS)	9.936	[21]
FMBM-functionalized ZnO nanopowders	61.2	[12]

This research aims to study the possibility of using limestone rocks for the removal of heavy metal ion from contaminated aqueous solutions produced from a variety of industries. The limestone is produced in large amounts as byproducts during the manufacturing of rocks; thus it is considered as a waste in rocks factories with very low cost. The limestone was used as an adsorbent of Pb(II) ion and the affection of ion concentrations, temperature and pH on its adsorption ability were investigated.

2. Methodology

2.1. Reagent

All the chemicals and reagents were obtained from Sigma Aldrich. The Pb(II) ion stock solution (1000 mg/L) was prepared by dissolving Pb$(NO_3)_2$ in deionized water. Experiments and analysis were conducted in the laboratories of the college of Science, University of Anbar.

2.2. Preparation of adsorbent

The limestone was collected from the waste of sculpting factories in the city of Hit, Anbar, Iraq. The limestone was firstly grinded by mill, dried at 105 °C and sieved to obtain three different particle sizes of 150, 250 and 300 mm [10].

2.3. Characterization of limestone

Field emission scanning electron emission (FE-SEM) was employed for the morphological characterization using HITACHI S-4500.

2.4. Adsorption procedure:

Adsorption procedure was carried out via batch method. A specified weight of limestone was mixed with 50 ml of Pb(II) ion solution in 100 ml of polyethylene container and shaken in a thermostatic water bath for a specific time = 5, 15, 30, 45, 60, 80, 120 min. The adsorption experiment was also carried out at pH = 2, 3, 4, 5, 6, 7, 8, 9, temperature = 288, 298, 308, 318 K and initial concentration = 50, 70, 90, 100 mg/L [10,22,34]. The mixtures were then filtered and residual Pb(II) ion in the solution was measured by flame atomic absorption spectroscopy (Phoenix 986 AAS, USA).

2.5. Theory basis of adsorption process

Experiments involving adsorption are normally described by the Freundlich, Langmuir and Temkin isotherms. In Freundlich isotherm:

$q_e = K_f C_e^{1/n}$ (1).where q_e is the amount of uptake in mg/kg of the adsorbent, C_e is the amount of adsorbate at the equilibrium, n is the Freundlich coefficient, and K_f the Freundlich adsorption capacity [22–23,34].

The isotherm of Langmuir is described by equation:

$Ce/qe = 1/(bq_m) + (1/q_m) C_e$ (2).where b is the Langmuir coefficients and qm is the monolayer capacity [22–23,34].

The Temkin isotherm is given by the equation:

$q_e = B \ln A_T + B \ln C_e$ (3).

$B = RT/b_T$ (4).where A_T = Temkin isotherm equilibrium binding constant (L/g), b_T = Temkin isotherm constant, R = universal gas constant (8.314 J/mol/K), T = Temperature at 298 K and B = Constant related to heat of sorption (J/mol) [35–37].

The linear Freundlich plots are obtained by drawing ln q_e vs ln C, where the adsorption coefficients are estimated. The linear Langmuir plots are obtained by drawing C_e/q_e against C_e. The linear Temkin plots are obtained by plotting C_e vs ln C_e.

3. Results and discussion:

3.1. Adsorbents

This study aimed to exploit limestone as an eco-friendly-adsorbent to eliminate heavy metals ions from wastewater. Although adsorption is a highly promising and efficient method, it suffers from the use of a relatively expensive materials as adsorbents [12,21,33,15–17,38–40]. With a view to find a simple and non-costly method in terms of materials, the effect of temperature, pH, contact time and particle size of limestone as adsorbent, on the removal of Pb(II) ion from aqueous solution were investigated. Fig. 1.

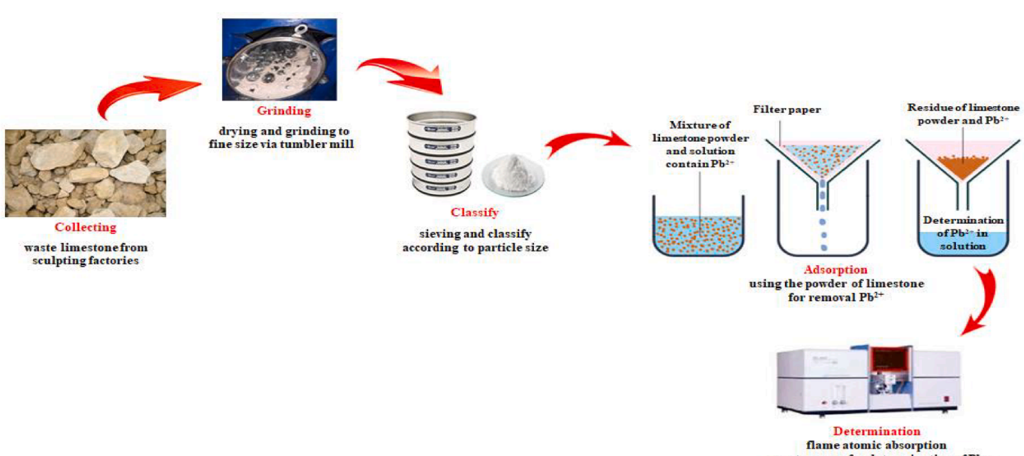

Fig. 1. Schematic representation of Pb(II) ion adsorption with limestone.

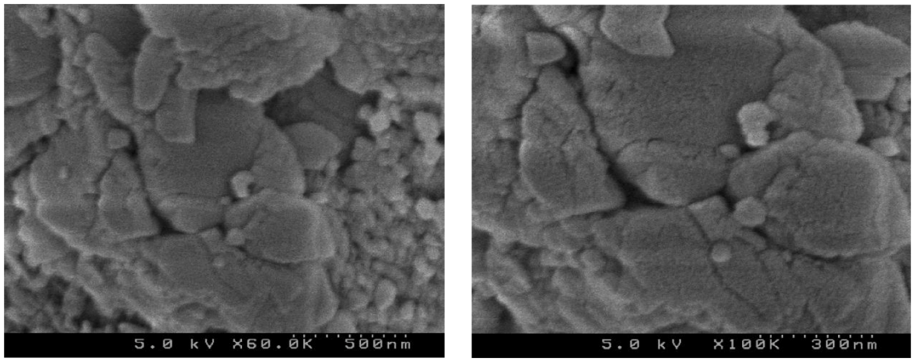

Fig. 2. SEM image of Limestone.

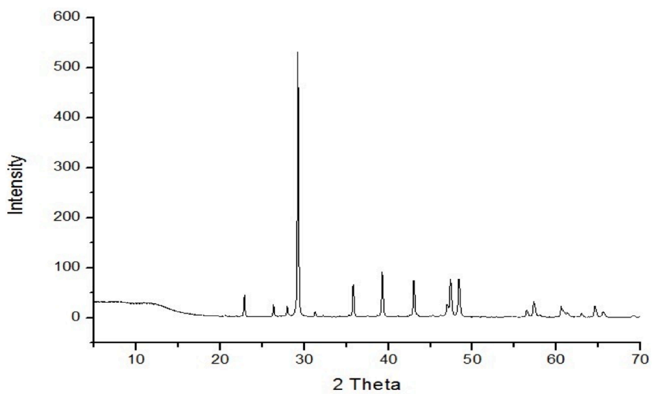

Fig. 3. XRD of limestone.

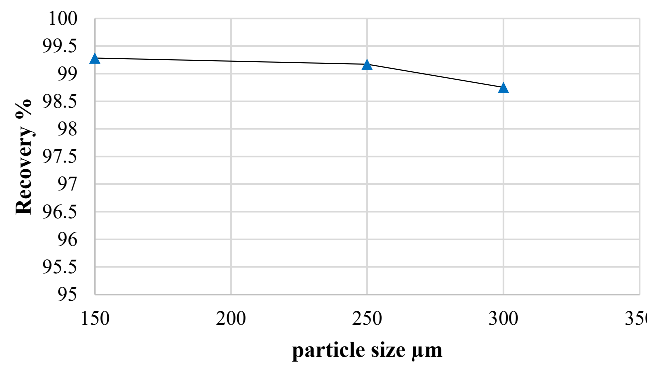

Fig. 5. Effect of particle size on adsorption of Pb(II) ion (q_e) (limestone 1.2 g/100 ml of aqueous solution, pH = 5 and initial Pb(II) ion concentration 50 mg/l).

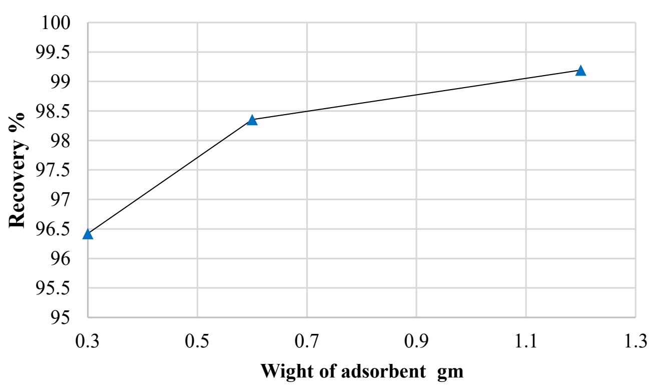

Fig. 4. Effect of weight of limestone on adsorption of Pb(II) ion (q_e) at 298 K (limestone 1.2 g/100 ml of aqueous solution, time 30 min and initial Pb(II) ion concentration 50 mg/l).

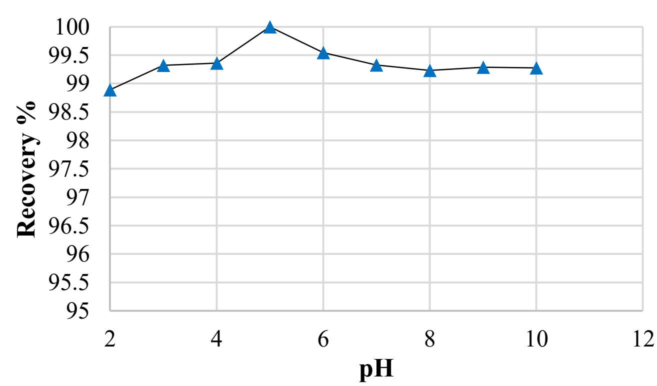

Fig. 6. Effect of pH on adsorption of Pb(II) ion (q_e) at 298 K (limestone 1.2 g/100 ml of aqueous solution, time 30 min and initial Pb(II) ion concentration 50 mg/l).

3.2. Characterization of limestone

The FE-SEM image of limestone shown in Fig. 2 clearly reveals a rough surface and high porosity which explain the excellent adsorption of Pb(II) ions from the aqueous solutions. The XRD pattern of the limestone (Fig. 3) shows that calcite is the dominant mineral in limestone [41–43]. The predominant calcite increases the surface polarity and surface hydrophilicity of the limestone, which increases the interaction with Pb(II) ions through electrostatic interaction. Therefore, the presence of calcite increases the removal of Pb(II) ions.

3.3. Effect of adsorbent dosage

The effect of limestone dosage was studied and 0.3, 0.6 and 1.2 g of limestone were used for the removal of Pb(II) ion from 50 ml aqueous solution at concentration of 50 mg/L. The percentage of adsorption shown in Fig. 4 significantly increased from 96 %, when 0.3 g of limestone was used, to up to 99.5 % when 1.2 g of limestone was used to remove the Pb(II) ion [44–46].

3.4. Effect of particle size:

The effect of particle size of limestone was studied, where three different particle sizes (150, 250 and 300 µm) were used. The percentage of adsorption was at the maximum when using limestone with particle size of 150 µm, and it slightly decreases when the particle size increases to 250 µm. The lowest percentage of adsorption was obtained when

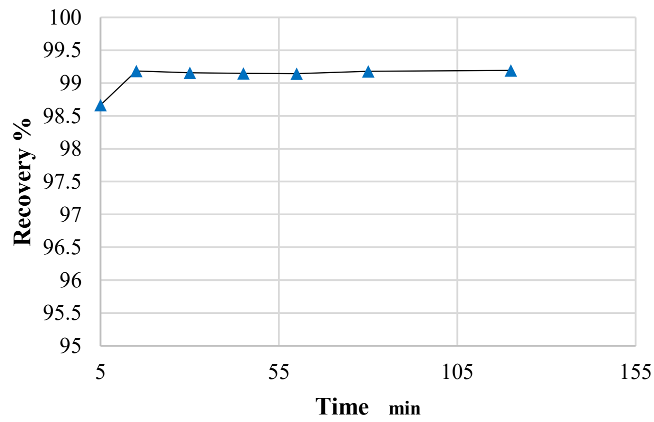

Fig. 7. Effect of contact time on adsorption of Pb(II) ion (q_e) at 298 K (limestone 1.2 g/100 ml of aqueous solution, pH = 5 and initial Pb(II) ion concentration 50 mg/l).

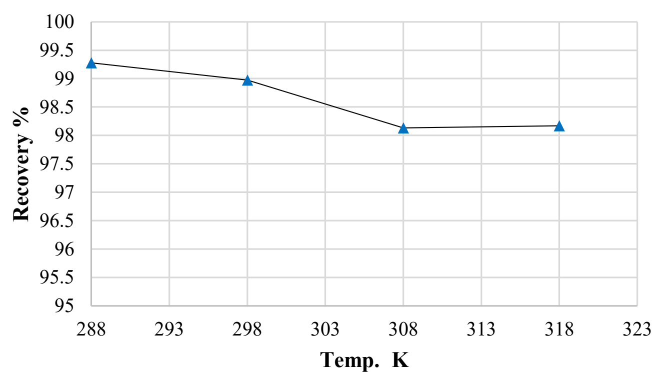

Fig. 8. Effect of temperature on adsorption of Pb(II) ion (q_e) (limestone 1.2 g/100 ml of aqueous solution, pH = 5 and initial Pb(II) ion concentration 50 mg/l).

using limestone with particle size of 300 µm as shown in Fig. 5. This finding clearly agreed with the fact that increasing the particle size decreases the surface area of contact between the adsorbent and the Pb (II) ion solution [47–49].

3.5. Effect of pH

The adsorption of Pb(II) ion was investigated at pH = 2 to 10 where all other conditions were constant and the limestone amount was 1.2 g/100 ml of Pb(II) ion solution at concentration of 50 mg/l (Fig. 6). The adsorption curve sharply increased up to pH 5. The adsorption was then gradually decreasing until pH 8. At pH > 8 there were no increase in the adsorption up to pH 10. The low pH leads to free the active sites of the limestone and be ready to adsorb more Pb(II) ions. The uptake of Pb(II) ion mostly reaches the equilibrium at pH = 5 [46,49–51].

3.6. Effect of contact time

The effect of contact time were experimentally investigated at pH = 5 using the limestone as adsorbent (1.2 g/100 ml of 50 mg/l Pb(II) ion solution). The samples were shaken for contact times of 5–120 min. It is fundamental to estimate the influence of contact time between the limestone and the Pb(II) ion solutions. As shown in Fig. 7, the adsorbent uptake reaches the maximum after 15 min of contact, where no additional uptake can be noticed when increasing the contact time up to 120 min [46,52–53].

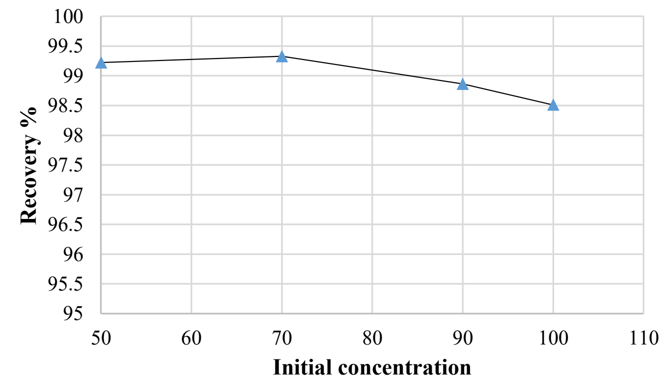

Fig. 9. Effect of initial concentration of Pb(II) ion (q_e) at 298 K (limestone 1.2 g/100 ml of aqueous solution, pH = 5).

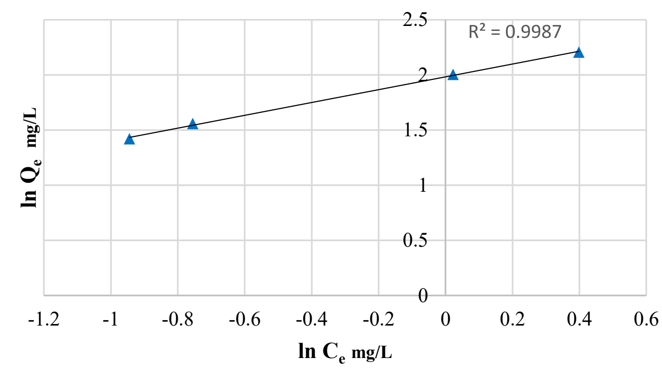

Fig. 10. Freundlich isotherm at 298 K (limestone amount 1.2 g, pH 5, initial Pb (II) ion concentration 50, 70, 90 and 100 mg/l, time 30 min).

3.7. Effect of temperature

The effect of increasing temperature (from 288 to 318 K) on the efficiency of limestone as adsorbent material was studied. The amount of adsorption decreases as the temperature increases as shown in Fig. 8, which confirms that the adsorption is exothermic [50,54].

3.8. Effect of initial Pb(II) ion concentration

The effect of initial Pb(II) ion concentration on adsorption is shown in Fig. 9. The initial concentration was in range of 50–100 mg/L. The results show that adsorption percentage reaches maximum (99.3 %), when the initial concentration of Pb(II) ion was at 50 and 70 mg/L. At higher initial concentrations of Pb(II) ion of 90 and 100 mg/L, the adsorption percentage slightly decreased to 98.5 %, which may be caused by the fact that all the limestone as adsorbent had a finite active sites number. These active sites probably become occupied when concentration of Pb(II) ion reaches above a certain value [39,50,55–56].

Table 2
Freundlich, Langmuir and Temkin adsorption coefficient at 298 K (limestone amount 1.2 g, pH 5, initial Pb(II) ion concentration 50, 70, 90 and 100 mg/l, time 30 min).

Freundlich coefficient		Langmuir coefficient		Temkin coefficient	
K_f	n	q_m	b	A_T	b_T
−0.6839	1.7217	10.1626	2.7563	4.0917	3022.904

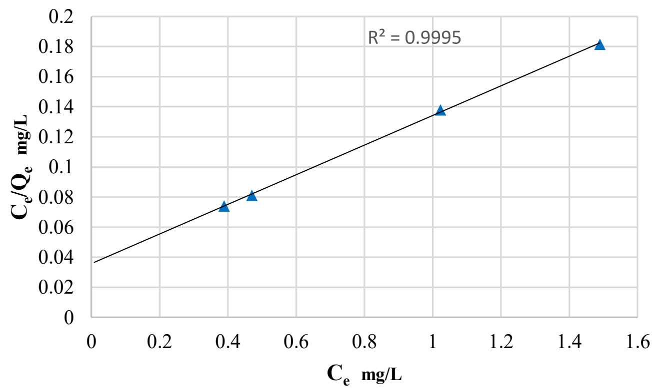

Fig. 11. Langmuir isotherm at 298 K (limestone amount 1.2 g, pH 5, initial Pb (II) ion concentration 50, 70, 90 and 100 mg/l, time 30 min).

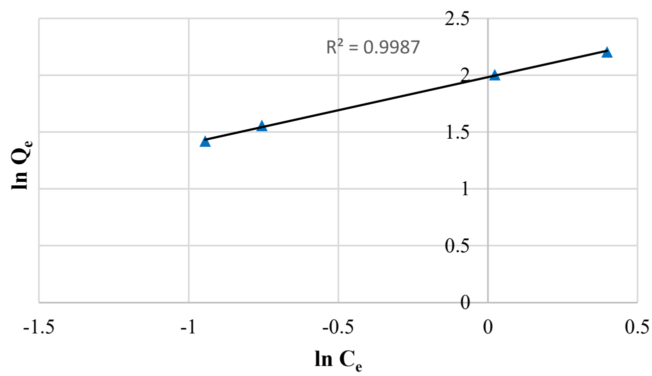

Fig. 12. Temkin isotherm at 298 K (limestone amount 1.2 g, pH 5, initial Pb(II) ion concentration 50, 70, 90 and 100 mg/l, time 30 min).

3.9. *Adsorption isotherm*

The adsorption isotherm experiments were conducted for Pb(II) ion by changing the initial concentration between 50 and 100 mg/L.

The results of adsorption match with the experimental isotherm of Freundlich (Fig. 10) i.e. it is usable to describe nonspecific adsorption of Pb(II) ion onto heterogeneous surfaces of limestone. The Freundlich isotherm plots show a good linearity, where $R^2 = 0.99$. The Freundlich coefficients calculated from the drawn chart are summarized in Table 2. The coefficients suggest that Pb(II) ion is preferable adsorption on the limestone [57,35–37]. The n value is 1.72 and K_f value is −0.68.

The experimental Langmuir isotherm were also tested. A plot of (C_e/q_m vs the remain concentrations of the Pb(II) ion (C_e) is shown in Fig. 11. The constants of Langmuir model and the correlation coefficient value (R^2) for adsorption of Pb(II) ions onto limestone are summarized in Table 2. The correlation coefficient value was up to 0.999 for Pb(II) ion, which indicates that the experimental results have an excellent agreement with the Langmuir model confirming that the Pb(II) ion adsorption is chemically in nature and bound by chemical forces to the active sites onto the limestone surface [22,58–61]. The highest adsorption capacities (q_m) obtained by this isotherm were10.16 mg/g.

The experimental Temkin isotherm was studied. A plot of C_e vs ln C_e is shown in Fig. 12. The Temkin constants for the Pb(II) ion are summarized in Table 2. The correlation coefficient value was $R^2 = 0.99$ for Pb(II) ion, which suggests that the experimental results have an excellent agreement with the Temkin model [59,61–62].

4. Conclusion

The results showed that the limestone is a superior adsorbents material in the removal of Pb(II) ion from aqueous solution. The optimum pH for the removal of Pb(II) ion by the limestone was at 5. The adsorption process of Pb(II) ion on the limestone is exothermic. The adsorption equilibrium was reached after 15 min of contact. The percentage of adsorption was around 96 %, which increased to 99.5 % when amount of limestone increased from 0.3 g to 1.2 g. The optimum temperature of adsorption was found to be 288 K and increasing the temperature negatively affects the removal of Pb(II) ion. The adsorption percentage was up to 99.3 % when the initial concentration of Pb(II) ion is 50 mg/L and slightly decreased to 98.5 % at higher initial concentrations of 100 mg/L. The experimental results clearly showed an excellent agreement with the isotherms model. In addition to the ability of limestone to adsorb heavy metal ions from aqueous solutions, the low cost and easy limestone obtaining make it a superior choice for application of wastewater treatment and consider a promising application of green chemistry principles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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