BATCH ADSORPTION OF Pb(II) BATCH USING HUMIC ACID FROM GOAT DUNG

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Abstract

This research focuses on the batch adsorption process, then looks for kinetic models and Freundlich model adsorption isotherms. In the process of adsorbing the heavy metal Pb, humic acid from goat dung has the potential to be employed as a promising adsorbent since it offers benefits, including being economical, being able to work accurately, quickly, sensitively, selectively, and helping to maintain public health. Parameters for testing humic acid from goat dung as an adsorbent for heavy metal Pb were determined by optimizing pH test variations, contact time, and concentration of Pb solution. Humic acid from goat manure could work optimally to absorb heavy metal Pb at pH 5, contact time 30 minutes, and metal concentration Pb 20 ppm with an adsorption capacity of 19.784 mg/g. Data modeling revealed that the adsorption process followed a pseudo-second-order kinetics model with the acquisition value of $R^2 = 0.9595$ and the Freundlich isotherm with the acquisition value of $R^2 = 0.9166$.

INTRODUCTION

Industrialization is a critical process to foster advanced economic growth for the population [1]. The industrial revolution, which is advancing quickly, might, nevertheless, pollute the environment. Heavy metal ions are one of the most common environmental pollutants that are dumped as trash from many businesses. Waste containing poisonous heavy metal ions builds up in rivers and soil, harming the environment and life [2] because poisonous heavy metal ions cannot be broken down, they are heavily present in freshwater reservoirs. This has led to a global worry over its prevalence in water bodies. The food chain causes heavy metal ions to bioaccumulate in living things.

The type of heavy metal with the highest rate of accumulation is lead (Pb), which is one of the numerous heavy metal ions that also includes arsenic, cadmium, cobalt, manganese, and mercury. Waste containing Pb ions can come from the metal coating industry, fertilizers, leather tanning, and paper [3]. Pb is harmful even at low concentrations and is known to have some chronic and acute health impacts, including mucosal damage, growth and development issues, and damage to the central nervous system, which can cause memory loss, particularly in children [4]. It can be lethal in the development of cancer in adults and result in hypertension and renal damage [5]. To protect consumer health, it is essential to adhere to the World Health Organization's (WHO) established quality guidelines for lead in drinking water [6]. So we need a breakthrough to control Pb waste contamination accurately, quickly, sensitively, selectively, and economically to help maintain public health.

Recently, technology using the adsorption method has been widely studied to overcome the dangers of waste contamination because the technology has economic, practical, and environmentally friendly value. In addition, this technology has a superior value compared to other waste separator technologies because adsorption can take place continuously, the process can be combined with other separation processes, does not require a lot of additives does not require a lot of additional materials during the synthesis and application, is suitable for compounds that are not heat resistant, and does not generate waste. This is because the adsorbent that has been used for waste treatment applications can be used as fertilizer [7]. Adsorption is a series of processes consisting of surface reactions of solids (adsorbents) with pollutants (adsorbates) in the liquid and gas phases. Different organic and inorganic waste pollution can be removed using the adsorption technique. An adsorption procedure in batches will be used in this investigation, whereas in a batch/static system it is an adsorption process in which the adsorbent is mixed with a fixed amount of solution and the quality changes are observed at certain time intervals [8].

Humic compounds are organic compounds that occur naturally in aquatic and terrestrial environments. Humic substances are operationally categorized as humic, fulvic, and human based on their solubility in acids and bases [9]. Humic acid can be formed from the decomposition of plant and animal tissues and can be found in aquatic, soil, and sedimentary environments [10]. Humic acid is a polyelectrolyte macromolecule organic substance that can interact with various heavy metals; this can affect metals' adsorption and desorption properties. Humic acid's ability to act as an adsorbent depends heavily on its ability to form bonds with metal ions [11]. Khan and Bagla (2022) proved the removal of Cs(I) and Sr(II) pollutants using humic acid as an adsorbent was demonstrated to be effective. At a pH range of 7.0 to 8.5 and a contact period of 10 minutes, humic acid can be employed as an effective Cs(I) and Sr(II) adsorbent.

Humic acid can be used as an adsorbent because humic acid meets the general requirements of adsorbents, namely having functional groups that act as ligands, including –COOH, –OH phenolic, and –OH alcohol which can be seen from the molecular structure of humic acid [12]. The effectiveness of humic acid as a metal adsorbent is based on the high acid content of humic acid. The carboxylic group, the phenolic hydroxyl group, and the alcoholic hydroxyl group connected to the aromatic and aliphatic rings can all contain protons, which contribute to the acidity of humic acids [13].

Nowadays, it takes innovation in the processing of goat manure to become something that has efficiency. If not used properly, goat dung can cause odors and the growth of fungi and microorganisms that arise from the dung. This makes the presence of untreated goat dung can interfere with daily activities. Several bacterial compounds found in goat dung, including Anseongella, Gillisia, and Actinomadura, influence the transformation of organic matter and humic acids [14]. This can be used as a potential for utilizing goat manure as the main ingredient for producing humic acid. In addition, goat manure is often used for plants with high potassium (K) content which can facilitate rapid plant growth. Apart from being a fertilizer, goat manure can also be used as a humus because it contains high potassium (K). With the presence of humus, it can bind to toxic chemicals in soil and water, such as permanganate, perchlorate, dichromate, peroxide, and persulfate [15]. Based on this background, it is necessary to research the isolation of humic acid from goat manure to adsorb Lead (Pb) by using several evaluations of variations in pH, contact time, and concentration to determine optimal results.

EXPERIMENT

Materials

As an adsorbent, humic acid is derived from goat manure. Pb(II) solution with a 20 mg/L concentration. For pH correction, use a NaOH, and 65% HNO_3 solution from Merck, USA. Deionized water is used to dissolve samples, and universal pH is used to verify pH tests.

Instrumentations

The tools used in this study were an oven (Memmert), centrifuge (Biocen22), analytical balance (Mettler Toledo AL-204), sieve, stirring rod, measuring cup, magnetic stirrer (Thermo SH4), dropper, laboratory glassware (Pyrex), Whatman filter paper no. 42 and AAS (Atomic Adsorption Spectrophotometer) Ice 3000.

Procedures

Determination of pH, time, and optimum concentration of Pb metal adsorption. A 20 mL solution of Pb(II) with an initial concentration of 20 mg/L was added along with up to 20 mg of humic acid (AH) as an adsorbent. With adjustments of pH 1, 3, 5, 7, and 9, the ideal pH was identified. HNO_3 and NaOH solutions of 0.1 M each were employed in the pH set, which was then agitated for 30 minutes using a magnetic stirrer. To calculate the best contact duration, which is set at 10, 20, 30, 40, 50, and 60 minutes, the optimal pH was then employed. By adjusting the starting concentrations of 5, 10, 20, 30, 40, and 50 mg/L while utilizing the ideal pH and contact duration, the adsorption capacity was discovered. A magnetic stirrer with a fast speed was used to conduct the test. The adsorbate and adsorbent were separated using Whatman paper filter no. 42. The filtrate obtained was then analyzed using AAS. The adsorbed Pb(II) was calculated using the formula in the equation:

$$\%\ \text{Adsorption Efficiency} = \left(\frac{[C_o - C_e]}{C_o}\right) \times 100\%$$

$$\text{Adsorption Capacity} = \left(\frac{[C_o - C_e]}{W}\right) \times V$$

Adsorption kinetics, which describes how a chemical is absorbed by the adsorbent as a function of time, is required to explain the adsorption process. The adsorption rate may be used to determine the features of the adsorbent's capacity to bind to the adsorbate. By using an adsorption kinetics model to predict the sequence of the reaction and the adsorption rate constant (k), it is possible to determine the adsorption rate. Following is an expression for the equation corresponding to the first-order and second-order kinetic models:

$$\ln C_e = -k.t + C_0 \qquad \text{(First-order)}$$

$$\frac{1}{C_e} = k.t + \frac{1}{C_0} \qquad \text{(Second-order)}$$

The graphs (ln Ce) to (t) and (1/Ce) to (t) are used to develop the kinetic model for order 1 and order 2 reactions for each parameter (t). The kinetic model with the highest R2 value is the model that the study's findings support. The adsorption process that occurs at a constant temperature may be determined using both adsorption kinetics and an adsorption isotherm. The Langmuir and Freundlich isotherm models are the most typical and often employed adsorption isotherm models.

$$qe = K_f \cdot Ce^{1/n} \qquad \text{(Freundlich isotherm model)}$$

$$\frac{Ce}{Qe} = \frac{1}{qm \cdot KL} + \frac{Ce}{qm} \qquad \text{(Langmuir isotherm model)}$$

RESULTS AND DISCUSSION

Adsorption Process on pH Variation

This study used an adsorbent of humic acid to examine the impact of pH on the adsorption of the heavy metal Pb. This experiment uses variations of pH 1, 3, 5, 7, and 9. The pH value significantly influences the physical and chemical form of metals because pH controls the solubility and concentration of metals. This can occur due to oxygen-containing humic acid functional groups, namely –COOH groups, –OH phenolics, –OH alcoholates, –OH phenols, and –C=O groups [16].

Serves to separate the solution from the filtrate [7]. **Figure 1** displays the graph of the pH fluctuation test and the Pb adsorption capacity. **Figure 1** demonstrates that from pH 1 to pH 5, the amount of Pb metal adsorption increased. Because H ions surround the surface of the adsorbent at low pH, there is a barrier between the adsorbent and metal ions, which reduces the adsorption of the adsorbent to metal ions [17]. Adsorption reached its peak at pH 5 with an adsorption capacity of 18.279 mg/g. The H+ ion concentration starts to decline around pH 5, which allows the adsorbent to absorb metal ions more effectively [18]. The adsorption capability decreases at pH 7. This occurs as a result of the hydrolysis reaction that metal ions go through at neutral pH, which is unstable for metal ion adsorption and reduces humic acid's capacity as an adsorbent [17].

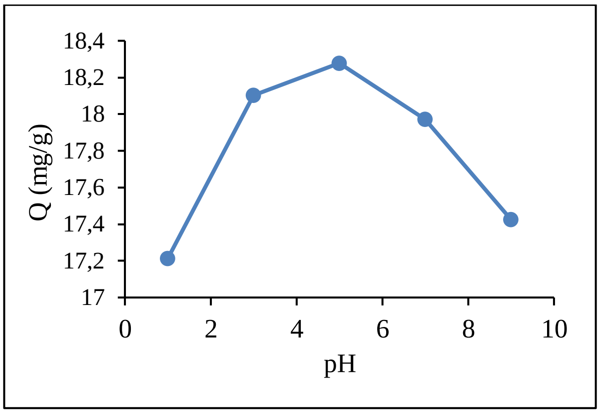

Figure 1. Graph of pH variation and adsorption capacity.

Figure 2 displays the outcomes of a test to determine how pH affects the adsorption of the heavy metal Pb.

Figure 2. Different color changes are caused by the heavy metal Pb's adsorption in different pH conditions.

Adsorption Process on Contact Time Variation

Contact time is the amount of time needed for the adsorbent to absorb effectively. The study's contact time ranges were 5, 10, 20, 30, 40, 50, and 60 minutes. Humic acid will adsorb more heavily on Pb heavy metal ions with longer contact times. However, during specific contact durations, the Pb heavy metal ions can be absorbed ideally and there may also be a reduction in adsorption [19].

The pH of 5 is considered to be ideal for this range of contact duration. **Figure 3** illustrates the outcomes of the contact time variation test on adsorption capacity. According to the graph of time variation on the heavy metal Pb's capacity for adsorption in Figure 3, the amount of heavy metal Pb that was adsorbed increased with longer contact times. Because the amount of Pb absorbed by the humic acid adsorbent and the amount of Pb still present in the solution had not achieved equilibrium at the contact times of 5 minutes, 10 minutes, and 20 minutes, there was a rise in progressively at each of these times. Adsorption is not ideal because the adsorbent still has an active side that does not bind Pb since it has not achieved equilibrium [20].

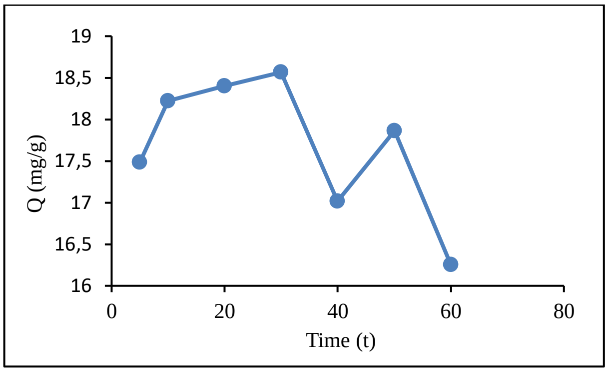

Figure 3. Graph showing the impact of contact duration on adsorption capacity.

This experiment's ideal contact time with an adsorption capacity of 18.566 mg/g was at a contact period of 30 minutes. For humic acid to best bind heavy metal Pb, there was a balance between the quantity of heavy metal Pb that had been absorbed by it and the amount that was still present in the solution. At the contact time of 40 minutes to 50 minutes, there was a decrease in the adsorption of heavy metal Pb because the adsorbent conditions had reached the saturation point. In addition, there is a bond between the humic acid adsorbent group and the heavy metal Pb which weakens and finally releases into the solution. So that only a strong Pb heavy metal group can bind to the humic acid adsorbent. The amount of collision between the adsorbate particles and the adsorbent increases with adsorption contact time [20]. **Figure 4** displays the outcomes of the heavy metal Pb adsorption as a function of time.

Figure 4. The Pb heavy metal adsorption with a time variation.

Heavy Metal Adsorption Kinetics of Pb

Studying adsorption kinetics requires knowledge of the reaction rate constant. This work employed pseudo-first order and pseudo-second order reaction kinetics to determine the rate of humic acid adsorption on the heavy metal Pb [21].

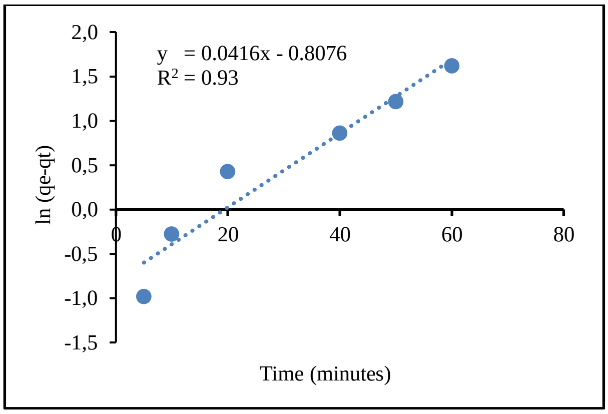

Figure 5. Graph of pseudo-first-order reaction kinetics.

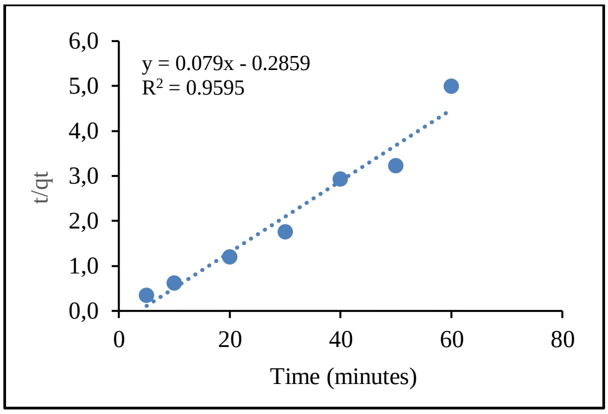

Figure 6. Pseudo-second-order reaction kinetics on a graph.

The pseudo-second-order reaction kinetics depicted in **Figure 6** has an R^2 value of 0.95, whereas the pseudo-first-order reaction outcome shown in **Figure 5** has a value of $R^2 = 0.93$. Humic acid's consistent rate of interaction with the heavy metal Pb suggests that the adsorption process is governed by a pseudo-second-order reaction that is affected by the characteristics of the adsorbent and the heavy metal ion Pb [21]. This suggests that the adsorption takes place chemically [22]. **Table 1** shows the outcomes of the calculations for the Pb adsorption kinetics of heavy metals.

Table 1. Heavy metal adsorption kinetics of Pb.

qt (mg/g)	qe (mg/g)	pseudo-first-order (ln qe-qt)	pseudo-first-order (t/qt)
5.32	14.68	-0.982	0.341
3.72	16.28	-0.280	0.614
3.34	16.66	0.426	1.200
2.96	17.04	0	1.761
6.33	13.67	0.858	2.926
4.49	15.51	1.214	3.225
8.00	12.00	1.616	4.999

Adsorption Process on Variation Concentration

The adsorption process may be impacted by concentration. More molecules will collect on the surface of the adsorbent at increasing concentrations [23]. In this experiment, variations in Pb concentration were carried out at 5, 10, 20, 30, 40, 50, and 60 ppm. To determine the concentration variation in adsorbing metal ions Pb, The optimum pH was 5, and the ideal contact period was 30 minutes. The adsorbent mass utilized was 20 mg.

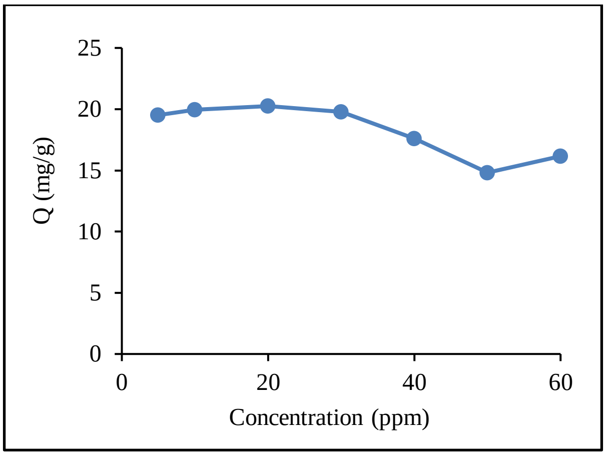

Figure 7. Graph showing the effect of concentration change on adsorption capacity.

The ideal point for Pb metal's adsorption capacity to fluctuate in concentration occurs at 20 ppm with an adsorption capacity of 20.25 mg/g, according to the graph of the relationship between concentration variation and adsorption capacity in **Figure 7**. The amount of the adsorbent that was adsorbing to the Pb metal increased from 5 ppm to 20 ppm in concentration. There observed a decline in the adsorption of Pb metal after achieving the optimum. This is due to the humic acid in goat dung having a higher adsorption capacity than it was designed to have for Pb. The effectiveness of adsorption may decrease due to the increasing Pb metal ion concentration. It is not proportional to the number of metal ions in the solution [17].

Figure 8. The outcomes of the heavy metal Pb adsorption at different concentrations.

Adsorption Isotherms

The two adsorption isotherms that are most frequently utilized are the Langmuir and Freundlich isotherms. Plotting the x-axis and y-axis will allow you to find the linear regression equation and estimate the adsorption isotherm, which will help you comprehend the isotherm model that was utilized. **Table 2** shows the computed value of the Pb adsorption isotherm.

Table 2. The isotherm of Pb's heavy metal adsorption.

Ce	qe	Langmuir		Freundlich	
		1/qe	1/Ce	ln qe	ln Ce
0.024	4.976	0.201	41.446	1.605	-3.724
0.390	9.610	0.104	2.561	2.263	-0.941
0.553	19.447	0.051	1.809	2.968	-0.593
0.923	29.077	0.034	1.083	3.370	-0.080
5.212	34.788	0.029	0.192	3.549	1.651
8.331	41.669	0.024	0.120	3.730	2.120
11.288	48.712	0.021	0.089	3.886	2.424

By comparing the correlation coefficient (R^2) value, it is possible to find the adsorption isotherm equation. Monolayers are necessary for the Langmuir isotherm adsorption process, but several surface layers can support the Freundlich isotherm (multilayer) [24]. The equation curve for the adsorption isotherm on heavy metal ions Pb has the findings $R^2 = 0.8528$ for the Langmuir isotherm and $R^2 = 0.9166$ for the Freundlich isotherm, as illustrated in **Figure 9** and **Figure 10**. Chemical and physical adsorption processes are demonstrated using the Langmuir and Freundlich adsorption isotherm equations. The Freundlich isotherm equation, however, often holds regardless of the adsorption type. This is because the Freundlich isotherm's R^2 value is higher than the Langmuir isotherm's R^2 value. Based on the data, it can be shown that the Van Der Walls force or hydrogen bonds are how the adsorbate particles approach the surface of the adsorbent [25].

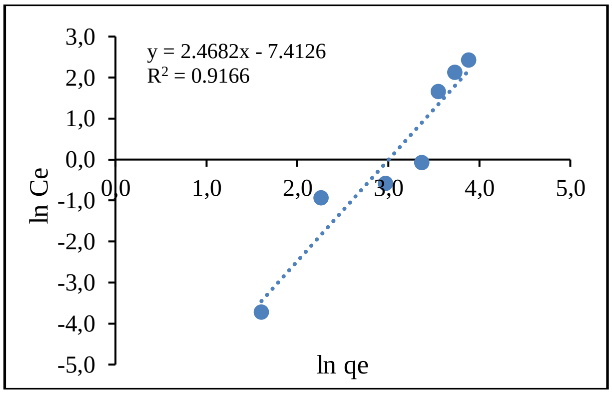

Figure 9. Graph of Freundlich adsorption isotherm.

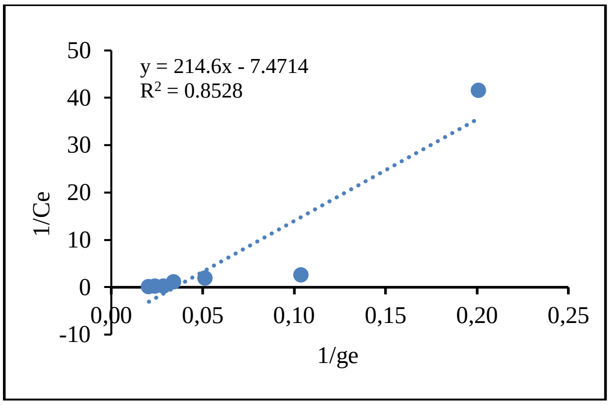

Figure 10. Graph of Langmuir adsorption isotherm.

CONCLUSION

Based on the study's findings, it can be said that humic acid from goat dung may be a very effective adsorbent to absorb the heavy metal Pb at an optimal pH of 5, contact period of 30, and metal concentration of 20 ppm with an adsorption capacity of 19,784 mg/g. For the adsorption of the heavy metal Pb using humic acid from goat dung, the Pseudo-second-order kinetics model and the Freundlich isotherm model, with $R^2 = 0.9595$ and $R^2 = 0.9166$ values, respectively, served as the foundation.

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