

Mechanisms of solution pH effects on the adsorption process efficiency: A theoretical and experimental study

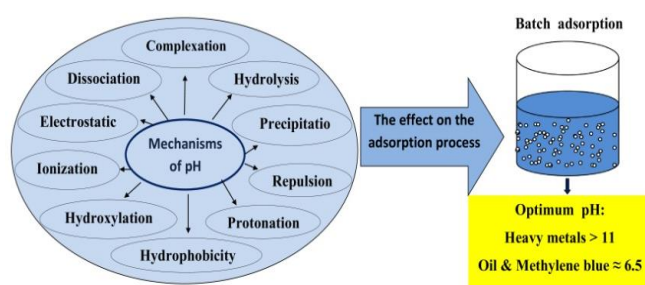
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ABSTRACT

The study aims to show the role of pH value and the feasible mechanisms that affect the adsorption capacity by the theoretical concept and experimental work. The protonation, ionization, hydrophobicity, dissociation, precipitation, hydrolysis, hydroxylation, electrical repulsion or interaction, ion exchange, and complexation and chelating are effective mechanisms that have been studied theoretically to show their essential role in the adsorption process and how they are affected by the pH value. Moreover, using varied pH values (2, 4, 6.5, 9, 11, and 13) to verify experimentally the role of the studied mechanisms on the adsorption capacity utilizing the recycled bentonite waste as adsorbent to adsorb the heavy metals, methylene blue dye, and engine oil as adsorbates from aqueous solution. It was apparent that the pH solution has an influential role in the adsorption capacity and from the difficulty in predicting the effect without making the experimental investigations due to the nature of the adsorbent and adsorbate that affected the ten mechanisms where the pH of the high adsorption capacity for heavy metal was alkaline (>11) and for the methylene blue and engine oil was neutral (≈ 6.5).

1. Introduction

In recent decades, it was apparent that dissolved pollutants like organic or inorganic pollutants have increased due to the high quantities of discharged industrial wastewater into the water sources to assemble essential crucial in environmental management. The threats of these pollutants on the environment are varied and associated with the characteristics of discharged wastewater possessing contaminant concentration, temperature, alkalinity, and acidity (Owhonka, Fubara and Otto, 2023).

The adsorption process includes the transport of the adsorbates or dissolved contaminants in the bulk solution into the surface of the adsorbent or solid material by physical or chemical mechanisms due to physical forces like Van der Waals forces or chemical bonds like ionic bonds or covalent bonds (Alaqarbeh, 2021).

These characteristics have a significant role in selecting the type and the efficiency of the treatment and degree of the treated water. One of the most affecting characteristics that have an influential role in the performance of the treatment is the pH value, especially the adsorption process. The solution pH effect is present in both the adsorbent and

adsorbate material in the adsorption process system. Numerous active materials are adsorbents like activated carbon, clay, organic clay, thermally modified clay, chemically modified clay, industrial solid waste, agricultural solid waste, and so on. On the other hand, the removed adsorbates or contaminants in the wastewater effectively using the adsorption technology are varied as heavy metals, dyes, pesticides, pharmaceuticals, and medical contaminants.

From the many previous types of research, it was apparent that there is no fixed context to determine the optimum pH in the adsorption process due to the complexity and unpredictable effect of the pH degree on the adsorbent material or adsorbed contaminants that result from many mechanisms such as ionization, hydrolysis, precipitation, electrostatic interaction or repulsion, dissociation, hydroxylation, and protonation.

The objectives of this research are to explain the effect of the solution pH on the efficiency of the adsorption process depending on the results of the previous studies and also use the recycled bentonite waste as an adsorbent to remove the heavy metals, engine oil, and methylene blue dye as adsorbed contaminants from aqueous solution with different degree of solution pH as a case study.

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2. Theoretical concepts

All mechanisms are affected by changes in solution pH and then affect the adsorbent materials or adsorbed contaminants in the adsorption process as:

2.1. Ionization

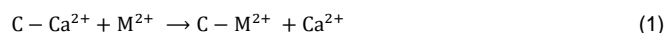
A chemical process by which the electrons are transported from or into the neutral molecules or atoms to convert into ions. The ionization is a significant process in the adsorption technique and has a crucial role in transferring the dissolved contaminants from a bulk solution into a solid adsorbent. The solution pH affects the chemical composition of the adsorbent by ionizing the molecules on the surface (Soliman and Moustafa, 2020). At elevated pH, the adsorbent surface will be negatively charged due to the ionization process to organic or inorganic functional groups like carboxylate, phosphate, and hydroxyl in the adsorbent surface and then increase the adsorbing of positive metal ions (Farhan and Khadom, 2015; Zhou *et al.*, 2016). Each functional group has a specified range of pH. For example, the group of carboxyl groups ranges from (3 to 4), which has maximum ionization and then achieves high adsorption (Ahmad *et al.*, 2016).

Also, the pH value of the solution affects the ionization degree of the ionizable organic and inorganic functional groups, where an increase in the pH increases the ionization and then increases the adsorbing of positive ions (Gu and Lan, 2021), which are different from one to another depending on the ionization energy of the adsorbed ion (Shtepliuk *et al.*, 2017). Moreover, the ion exchange between adsorbates and the ions of the adsorbent surface depends on the various ionization potentials that affect the selectivity of the investigated metal ions like $Pb^{2+} > Cd^{2+} > Cu^{2+}$ (Choi, Yu and Kim, 2016).

2.2. Ion exchange

The ion exchange is a chemical process that includes replacing the ions in the solution with another ion in the adsorbent having the same charge, where it is either a cation exchange that means replacement between the positively charged ions or an anion exchange that specifies for negatively charged ions (Qiu *et al.*, 2021).

The study of Qiu *et al.*, (2021) explained the adsorbing of heavy metals by the cation exchange with Ca^{2+} on the biochar adsorbent surface with an acidic medium (pH < 6.5) as in the reaction of the below formula. Clay is one of the most used adsorbents due to high cationic exchange that can remove contaminants having positive charges like heavy metal ions (Maleki and Karimi-Jashni, 2020).



2.3. Hydrolysis

Hydrolysis is a decomposition reaction between two reactants, and water is an essential reactant that converts the other reactant into smaller molecules or atoms by breaking the chemical bonds due to separating water molecules into hydrogen and hydroxide ions (Antonetti, 2025).



The hydrolysis reaction is one of the significant methods to prepare the adsorbent, especially from organic materials such as converting the chitosan to chitosan-oligomers (Ibrahim *et al.*, 2016). The pH has a necessary role in the hydrolysis reaction where the final products of the reactions are affected by the pH level because the acid hydrolysis with a neutral pH or acid (less than < 3) and the base hydrolysis with a pH more than ≥ 10 (Tollini *et al.*, 2022).

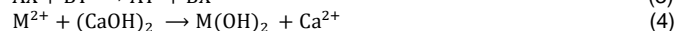
H^+ ions are elevated in acidic hydrolysis, while OH^- ions are higher in base hydrolysis reactions. Usually, the hydrolysis reaction affects both the adsorbent and the adsorbate simultaneously, and the solution pH plays an evident role in this reaction, especially the acidic solution that activates the hydrolysis and increases the adsorption capacity (Deng *et al.*, 2010). Another research shows that the high concentration of H^+ will promote the hydrolysis of $C = N$ into $C = NH^+$ and $-NH^2$ into $-NH_3^+$ to lead to an increase in the number of surface positive charges and then increasing the adsorbing on anionic dye on the surface of the salicylaldehyde-chitosan Schiff base (Huang *et al.*, 2021).

Hydrolysis is a significant process in modifying biosorbents due to the increases in the adsorption capacity with low pH by removing the sugar components and increasing the organic carbon content from plant residue (Kong *et al.*, 2020). (Schiewer and Patil, 2008) demonstrated that pH plays an influential role in the change of the adsorbent characterization and then increases the adsorption capacity

as hydrolysis of metal ions with an increase in pH value to form the mono-hydroxyl species. The change in pH affects the pre-hydrolyzed adsorbent due to the release of the OH^- ions into the solution as reported by "Y. Yang" approved that an increase in pH leads to an exchange process between the phosphates and the OH^- ions in the surface of alum-sludge (Yang *et al.*, 2006).

2.4. Precipitation

The precipitation reaction results from a combination of two different soluble in charge to produce insoluble ions and depends on significant factors such as pH, temperature, and concentration of the reactants (Kim, Kim and Youn, 2018).



The pH is considered a crucial factor in the precipitation and may enable or inhibit the reaction to control the solubility of the product and affect the other processes such as hydrolysis, protonation, and ionization. The adsorption process by the precipitation mechanism is through depositing the contaminants on the surface of the adsorbent, especially for the inorganic material such as heavy metals in an alkaline solution (Ambaye *et al.*, 2021). Moreover, some adsorbents release anions to the solution to react with the presented adsorbates (if cations) to form the precipitated ions, such as the biochar adsorbent release CO_3^{2-} to solution reacting with Pb ion to form $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$, and $2PbCO_3$ depending on the pH level (Wu *et al.*, 2021). Another research approved the presence of $CdSiO_3$ or Cd_2SiO_4 , $Cd_3(PO_4)_2$, and $Cd(OH)_2$ resulting from adsorbing Cd ions on the surface of biochars by precipitation mechanism (Gao *et al.*, 2019).

The optimum pH level to precipitate the malachite green dye on the ZnO surface was 6 to achieve the maximum adsorption attributed to the decrease in pH level may cause the decomposition of the adsorbent while the increase leads to an enlargement in the concentration of H^+ ions in the solution (Zhang *et al.*, 2016).

2.5. Electrostatic interaction

Electrostatic interaction is a physical mechanism that depends on the existing opposite charges on the adsorbent surface and the adsorbates (contaminants). Fig. 1 shows this mechanism. The temperature, pH, zeta potential, and ionic strength are essential factors in the strength and magnitude of electrostatic interaction (Eliasquevic and Bernardino, 2024).

For example, adsorbent particles having negatively charged functional groups such as (SO_3^-) and contaminants in solution with positively charged metal ions (M^{2+}) are attracted to these functional groups by electrostatic forces.

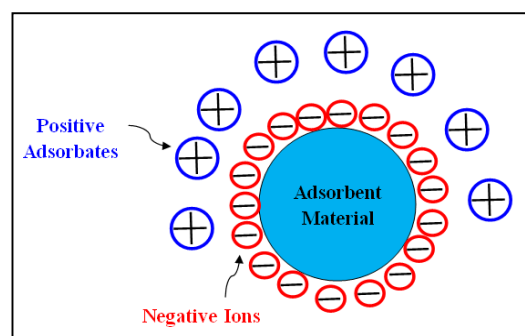


Fig. 1. The Electrostatic mechanism (Adapted from Ambaye *et al.*, 2021).

The pH affects the zeta potential where a specified level of the pH achieves minimum magnitude of zeta potential to create maximum electrostatic interaction and then high adsorption capacity as reported by He *et al.* (2017) that approved the maximum adsorption capacity of Pb, Cu, and Cd on the β -cyclodextrin (β -CD) polymers in pH equal to 8, 7, and 10, respectively due to the high electrostatic interaction.

Researchers assessed the zeta potentials of cellulose-based bioadsorbents with different pH values. They approved that it was always negative with the minimum value in the alkaline solution to achieve high adsorption for anionic and cationic due to high electrostatic interaction (Liu *et al.*, 2015). Another researchers used porous starch citrate to adsorb the Pb ions from an aqueous solution, and they found that the electrostatic interactions were from the crucial factors in the adsorption process due to the carboxylate groups that

create sorption sites having negative charges to adsorb the positively charged ions (Ma *et al.*, 2015).

2.6. Dissociation reaction

Dissociation reaction is one of the crucial chemical reactions that appear on the material surface due to the separation of molecular bonds to form new chemical bonds between atoms, ions, or metals. The pH plays an essential role in improving the performance of the organic adsorbents due to the high number of the acid functional groups on the surface that are dissociated with the change of pH degree (Bartczak *et al.*, 2018).



The pH affects the dissociation level of the functional groups on the adsorbent surface and then creates more adsorption sites, where the pH of 5 was a suitable level to dissociate the carboxylic groups of the carbon surface and then achieve high removal efficiency of Cu(II) (Hotová *et al.*, 2020). Dhaouadi *et al.* (2021) found that the dissociation degree of the carboxylic and phenolic functional groups of avocado seed hydrochar adsorbent has a significant role in the adsorption of the heavy metals (Ni, Cu, and Pb) with a pH equal to 5. Also, the dissociation of the carboxyl groups on the surface of the carnauba fruit biomass adsorbent was apparent with pH equal to 5 and an essential factor in the adsorbing of Pb from aqueous solution (Oliveira *et al.*, 2021).

2.7. Protonation reaction

Protonation reaction results from adding hydrogen ions to another atom or molecules due to a change in the degree of pH solution and then causes a change in the charge and the hydrophobicity of the protonated species.



The degree of pH solution affects the protonation and deprotonation process due to the change in the concentration of H⁺ ions in the solution to affect the chemical composition to change the adsorption capacity of the adsorbent (Wagner *et al.*, 2021) or protonation of the functional groups such as the carboxylic and amino groups to charge the molecule's surface of the adsorbates (Cermakova *et al.*, 2017). When the pH solution decreases or increases compared to the point zero charge (pH_{pzc}) of the adsorbent, the functional groups of the adsorbent either protonated or deprotonated and then increase the electrostatic attraction to remove the cationic or anionic adsorbates, respectively (Tatarchuk, Soltys and Macyk, 2023). The adsorption of methylene green on the adsorbent surface of the activated charcoal was stable even with a pH solution less than pH_{pzc}, and this was due to the protonation of the acidic groups such as (COOH and OH) on the adsorbent surface that equal in the efficiency with other mechanisms like electrostatic attraction (Tran *et al.*, 2017).

2.8. Complexation and chelation interaction

The complexation results from covalent or non-covalent reactions between two or more molecules having different surface charges to produce complexes (polyatomic structures) as reacting between metal (M) ions (as cationic) with ligands (L) (as anionic) (Behzadipour and Hemmati, 2024).



Chelating is one type of complexation but is more stable and results from binding more than one atom of molecules with a central metal ion through a multidentate ligand (Svanedal *et al.*, 2024). The reaction between the metal ions and the oxygen-containing groups (as COOH functional groups) on the surface adsorbent of biochar can convert into a complex and then increase the adsorption capacity (Wang *et al.*, 2020). Complexation of natural organic matter with cations is with different pH levels due to the types of present functional groups where the carboxyl group complex with pH > 4.4 while the phenolic group with pH > 9.5 and this attributed to deprotonation of functional groups and availability of active sites to bind with investigated cations (Adusei-Gyamfi *et al.*, 2019).

Medeiros Borsagli *et al.* (2015) used the chitosan as an adsorbent to remove the Cd ions from aqueous solution and found that at (pH = 3) the amine groups are protonated and the Cd ions competing with H⁺ ions for forming complexes with non-protonated amines, with high pH degree (pH = 6), the role of the amine groups increase in the adsorption capacity due to the dative bonds of amines with Cd ions that reduce the electrostatic repulsion. However, with an alkaline medium (pH = 10) and

although from the presence of the hydroxyl group, the overall result of the uptaking was less.

2.9. Hydroxylation reaction

The hydroxylation reaction is a chemical bonding between the hydroxide ion and a molecule or an ion as adsorbent or adsorbate. The hydroxylation of the adsorbent increases the adsorption capacity and creates a hydroxyl functional group on the surface that enhances the active site, the chemical formula below of organic and inorganic reaction, respectively (Wang *et al.*, 2019).



Moreover, the hydroxylation of the adsorbates increases with pH to form insoluble hydroxides to increase the chance of the precipitation process to minimize the adsorption capacity where it was apparent that increased pH converts the metal ion such as Zn(II) from Zn⁺² and Zn(OH)⁺ in pH < 7 into Zn(OH)₂ after pH > 9 and so on for other metal ions (Vijayaraghavan *et al.*, 2009).

2.10. Hydrophobicity

The hydrophobicity is a physical reaction that has a significant role in the adsorption process that binds between the non-polar contaminants (such as oil and fat) and adsorbent by van der Waals force.



The energy of this reaction decreases with a decrease in the pH level due to the protonation of the active sites of the adsorbent, and the study of (Ibrahim, Wang and Ang, 2010) explained that the oil molecules are more adsorbing with a high pH level. Also, the study of (Li and Wei, 2022) showed that the hydrophobic reaction is one of the main adsorbing mechanisms for organic pollutant removal.

2.11. The experimental work

This section conducts preparation to perform the work of the experimental adsorption where the procedure of the adsorption experiment and the used adsorbent detailed in (Shubber and Kebria, 2023), where the adsorbent was thermal recycled bentonite waste. The adsorbates were heavy metals (Pb, Cd, Cr, Zn, and Ni), methylene blue dye (MB), and emulsified engine oil (EEO), utilizing the HCl and NaOH to determine the required degree of pH solution. Six levels of pH solution were (2, 4, 6.5, 8, 10, and 12) in the experimental work.

3. Results and discussion

3.1. Adsorption of heavy metals

Five metal ions (Pb, Cd, Cr, Zn, and Ni) were used as adsorbates in the experimental investigations to know the effect of the various pH levels on the adsorption capacity and the behavior of each metal ion. From Fig. 2, the difference in adsorption capacity between the metal ions was noticeable due to the self-electrochemical characteristics of the metal ions. However, the behavior of the metal ions was similar in that the removal efficiency of all metal ions increased with the increase of the pH.

The change in the adsorption capacity of the Pb ion was low, where the increase was 6.5 % when the pH increased from 2 to 6.5, and this indicates that the Pb ion has electrochemical characteristics that permit high removal efficiency compared with other metal ions for varied pH levels. The increase beyond pH equal to 6 leads to the form of the Pb(OH)⁺, Pb(OH)₂, and Pb(OH)₃⁻ and this is one of the indicators to create a hydroxylation reaction and then increase the adsorption capacity (Soliman and Moustafa, 2020). However, the decrease in the adsorption capacity beyond pH 13 > pH_{pzc} of the adsorbent is attributed to the electrostatic repulsion with surface functional groups having negative charges.

Cd ion has the same behavior as the lead Pb with lower adsorption capacity due to the electrochemical characteristics. The percentage of the increase when the pH elevates from 2 to 9 was 15 %, and then the uptaking was stable after pH > 9, where the hydroxide forms of Cd start beyond pH equal to 8 (Ji *et al.*, 2022). Zn ion has a different behavior in that the removal increment was more than Pb and Cd ions until the pH = 11, when the pH increased from (2 to 11) increased the removal percentage to 75% to be an indicator that the pH has a high effect on the adsorption capacity of Zn ion. The Zn²⁺, Zn(OH)⁺, and Zn(OH)₂ are the main species with a pH between 8-9, and the Zn²⁺ is at pH less than 7 (Vijayaraghavan *et al.*, 2009).

Cr ion adsorption increases with an increase in pH degree where the increase in the pH from 2 to 13 increases the removal from 25.5 to 50 % where the increasing percentage reaches 96%, and this an indicator that the Cr ion continuously was affected in the pH level, where the change in the pH level create more than form of the Cr species (Uysal and Ar, 2007).

Ni ion adsorption capacity was stable with pH < 6.5 approximately then after that sharp increment between pH (6.5 to 11) and to be stable with pH > 11, where the removal percentage when pH arranged from (6.5 to 11) was 65%, the form of Ni change with increase the pH level where it converts to NiOH^+ and H_2NiO_2 with pH arrange from (9 to 13) (Çelebi, Gök and Gök, 2020).

From Fig. 2, it was apparent that there are many essential factors by which the pH affects the adsorption metal ions behaviors as previously mentioned as the ionization, hydrolysis, precipitation, electrostatic interaction, protonation, and, and hydroxylation reactions.

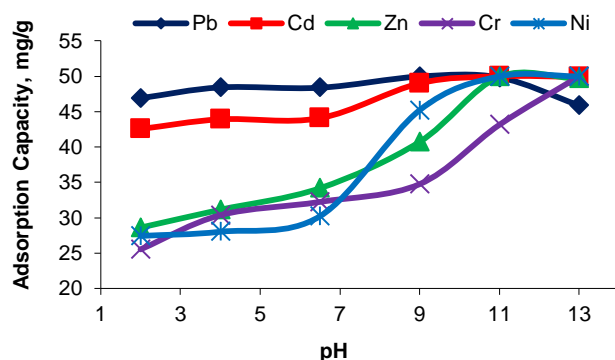


Fig. 2. The effect of pH on the adsorption capacity of heavy metal ions.

More than one of these reactions can affect the adsorption capacity by changes in the adsorbent surface and composition of the adsorbate or by incentivizing and inhibiting specified reactions between the adsorbent and adsorbate. The adsorbent TRBW has many surface functional groups such as Si-O-Al , Si-O-Mg , Si-O-Si , Al-O , Si-O , H-O-H , C-H , and H-OH (Shubber and Kebria, 2023) that likely react with ions adsorbate and then increase or decrease the adsorbing depending the condition of the pH. The change in the degree of pH affects the surface functional group by hydrolysis, precipitation, dissociation, complexation, and hydroxylation reactions and then binding with adsorbate or finding sites for the adsorbate on the surface of the adsorbent. Also, the protonation of the surface functional group of the adsorbent in the acidic medium due to the high concentration of the H_3O^+ ions ion, and the adsorbent became cationic to create an electrostatic repulsion with cationic adsorbates. In the base solution, the negatively charged metal oxides are more attractive to the positive surface of the cationic adsorbent, especially after the deprotonation of the adsorbent surface with $\text{pH} < \text{pH}_{\text{pzc}}$ as reported in (Islam, Awual and Angove, 2019). Increasing the adsorption capacity means providing suitable conditions (active sites) to transport the adsorbates from the solution into the sites that are present on the surface of the adsorbent and then creating a chance for the physical or chemical adsorption that is reversible or irreversible depending on the mechanism of the adsorption.

3.2. Adsorption of MB and EEO

MB removal was stable with all pH degrees where the change percentage was much lower and did not exceed more than 6 %, and this is due to one of two probabilities: the first is the change that happened not affect the adsorption capacity, or there does an equivalent role for each mechanism of the mention reactions in each one change of the pH level that the increase or decrease is not apparent in the adsorption capacity. The positively charged surface of TRBW having pH_{pzc} equal to 10.4 and the MB was cationic then the acidic solution was not a motivator medium for the adsorption due to the electrostatic repulsion between the adsorbent and adsorbate and the competition between the H^+ ion and the MB molecules, in increasing the pH solution, there are many influential mechanisms such as dissociation or hydrolysis of adsorbent functional group, ionization or complexation of the MB molecules (Khan, 2020), all these reactions contribute to making the average of the adsorbing MB stable for the high extent of pH solution. The results were compatible with (Khan, 2020); (Ethaib and Zubaidi, 2020). EEO adsorbing has a different behavior as in Fig. 3, where the adsorption capacity increases by increasing the pH from 2 to 6.5 to achieve the high adsorption capacity

and then decreases to reach the minimum adsorption with a pH equal to 9 to raise slowly in pH of 13. The EEO molecules are electrically neutral and then have a lower effect by the electrical interaction, a low adsorption capacity in an acidic medium due to the solubility of the EEO molecules that may lead to desorption. Also, the acidic and alkaline medium cause dissociation of the adsorbent surface functional group (Sarran *et al.*, 2024). It was apparent that there was a change after pH reached pH_{pzc} where the adsorption capacity started to increase due to the surface of the adsorbent converting to negatively charged. Also, increasing the pH increases the hydroxylation reaction due to the availability of the hydroxyl group on the surface of the adsorbent to form a highly active site to increase the chance of the adsorption capacity.

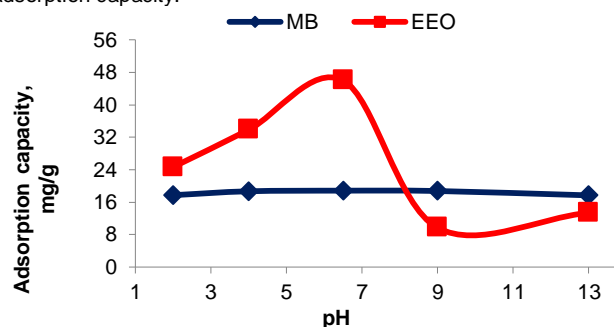


Fig. 3. The effect of pH on the adsorption capacity of MB and EEO.

Overall, the mentioned mechanisms like ionization, hydrolysis, precipitation, electrostatic interaction or repulsion, dissociation, hydroxylation, and protonation reactions are significant factors in determining adsorption efficiency where they affect both adsorbent and adsorbate. All these mechanisms are affected by solution pH due to possible changes in chemical composition during the adsorption process.

Table 1. Comparison between the optimum pH solution for different adsorbents and adsorbates.

Adsorbent	Adsorbate	Optimum pH solution	pH_{pzc} of the adsorbent	Ref.
Raw bentonite	Cu^{+2}	5.5	6.1	(Almeida Neto, Vieira and Silva, 2012)
Calcined bentonite			5.4	
Na-bentonite	MB	10	2	(Puchongkawarin, Mattaraj and Umpuch, 2021)
Purified clays	MB	3	4.8	
Bentonite – zeolite	Cu^{+2} Zn^{+2}	6	3.63	Cao <i>et al.</i> , 2019
	Zn^{+2} , Pb^{+2} , Cr^{+2} , Ni^{+2} , and Cd^{+2}	>12		
RBWC	MB	6.5	10.4	This study
	EEO	6.5		

From Table 1, it was apparent there is no constant value for the pH solution to achieve the optimum adsorption capacity due to the nature of the used adsorbent and the investigated adsorbates that may be affected by different reactions resulting from the mentioned mechanisms.

4. Conclusions

The effect of pH on the adsorption capacity is a complex and significant factor. It was an important issue to conclude that:

- The pH influences ten mechanisms and reactions such as protonation, ionization, hydrophobicity, dissociation, precipitation, hydrolysis, hydroxylation, electrical repulsion or interaction, ion exchange, complexation, and chelating to be assistant factors to provide the highly active site on the adsorbent surface.
- The effect of pH is variable depending on the characterization of the adsorbate materials, where it was obvious that the alkaline ($\text{pH} > 11$) was the optimum condition for adsorbing the heavy metals, and the methylene blue dye and emulsified engine oil was neutral ($\text{pH}=6.5$).
- The pH affects the gained surface charge of the adsorbent depending on the pH_{pzc} value, and it is an essential reason for activating mechanisms like ion exchange and ionization.

-The pH value changes the aquatic medium into acidic or alkaline to increase the H⁺ or the OH⁻ ion, respectively, and then the type of activated mechanism is varied.

Author Contributions

Mukhtar Dhajir Shubber: Manuscript writing, performing calculations, and collecting relevant information.

Mohammed Kadhum Al kasser: Reviewing and editing of the manuscript.

Daryoush Yousefi Kebria: Conducting the experimental work, Reviewing and editing.

Conflict of Interest

The author declares no conflict of interest.

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Data Availability Statement

Data will be available on request due to privacy and ethical restrictions.

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