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ADSORPTION STUDIES OF HEAVY METALS AND DYES USING CORN COB: A REVIEW

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Highlights

- The heavy metals and dyes prevalent in wastewater are treated via adsorption process with the aid of corn cob as an adsorbent
- Adsorbents are treated with various chemicals such as phosphoric acid, citric acid, sodium hydroxide, and hydrochloric acid to enhance the adsorption capacity
- Equilibrium isotherm models discusses the adsorption characteristics in the interaction between adsorbent-adsorbate
- Kinetic models shows the movement of the adsorption process

Abstract

In the process, a variety of adsorbents have been treated and modified to increase its efficiency, effectivity, and capabilities to be applied for the major pollutants namely effluent dyes, heavy metals, and organic contaminants. Agricultural wastes, however, showed full utilization because of its abundance in nature. Even though its low-cost, it can compete with other synthetic adsorbents that are highly expensive. The review aims to comprehensively list and discuss adsorbents made of biomass and their adsorption capacity under diverse conditions which will then be compared to corn cob which is the focus of the review. The review literature presented in this paper aims to provide the potential of corn cob as an adsorbent to remove various pollutants from wastewater. However, the practical utility of such adsorbents needs to be further explored before they can be commercially applied.

Keywords: Adsorption, Adsorbents, Corn Cob, Review, Wastewater

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1. Introduction

In the present time, excessive released and production of wastewater as a product of various industries and other human activities is one of the major concern. This is due to the increasing demand of clean and potable water needed for various activities, human needs, and industrial production that in return produces a vast amount of wastewater. Wastewater contains contaminants such as heavy metals, biological and organic contaminants that can harm the animals, health of the human beings, and has a great effect on the environment when exposed in enormous and even trace amounts of those contaminants when left untreated.

Organic contaminants can be classified into 3 categories oxygen demanding wastes, synthetic organic compounds, and oil[1]. That can results in dissolved oxygen depletion that affects aquatic life. Most of these organic compounds are toxic and makes the water unfit for various activities. It can also endanger birds and coastal plants when there is an oil spillage and affecting the activities of aquatic plants due to the reduction of light transmission[1]. Examples of synthetic organic compounds are higher order alcohols, aldehydes, ketones, and some of miscible and immiscible organic substances that are necessary for resins lacquers and paints industry can be considered toxic for the environment[2].

Dyes are essential in industries such as textile, paper printing, food, pharmaceutical, cosmetics, and leather industries[3]. Textile industries are considered as one of the biggest consumers of water and complex chemicals during textile production[4]. Different types of dyes are present in the effluents from textile industries, which has high molecular weight and complex structures that shows a low biodegradability[5]. When released into bodies of water, can pollute the water and can cause aesthetic pollution. The reason why the process of reducing the amount of residual dyes in the textile effluent is one of the major concern these days.

Heavy metals, are metals who has a density of 5 g/cm^3, highly water soluble, toxic, and considered as carcinogenic agents. Metals such as copper, silver, zinc, cadmium, gold, mercury, lead, chromium, molybdenum, iron, nickel, tin, arsenic, selenium, cobalt, manganese, and aluminum are considered heavy metals. Heavy metals can affect the human health, and the fauna and flora of the receiving water during wastewater discharge in the bodies of water[6]. It is reported that when heavy metals are absorbed in the human body can caused serious health effects such as organ damages, cancer, or even death. It is also associated with the problems regarding growth and development among children[7]. Heavy metals such as arsenic, cadmium, chromium, copper, lead, nickel, zinc, and mercury are generated by manufacturing industries such as electroplating, phosphate and fertilizer, paints and textile, and tanning[8]. Heavy metals waste like Tin, lead, and nickel are products from printed circuit board manufacturing, while in the wood processing and in inorganic pigment manufacturing produces arsenic, chromium, and cadmium containing waste. In the petroleum refining and photographic operations industries hazardous wastes containing nickel, vanadium, chromium, silver, and ferrocyanide are generated. These industries produces and releases a great amount of wastewater, residues, and sludge that can classify as hazardous wastes that undergoes various waste treatment processes[9].

Wastewater from different industries undergoes treatment processes before releasing to reduce its potential effect to the environment, to the point that the environment can tolerate its effect and does not harm any possible animals, humans, and plants living in the area. Wastewater treatment methods includes physic-chemical methods, chemical precipitation, coagulation and flocculation, electrochemical treatments, ion exchange, membrane filtration, electrodialysis, and adsorption. But, some of this treatment processes can be expensive and ineffective at low metal concentrations[7].

Adsorption is the attachment of molecules to a surface, wherein the solid surface where adsorption occurs is called adsorbent, while the substance that adsorbs is the adsorbate and the reverse process of adsorption is called desorption[10]. It is considered that one of the most common and effective treatment nowadays is the adsorption process that involves low cost adsorbents such as agricultural waste, industrial by-products, modified polymers, and other biological materials in the removal of various contaminants in water. Some of the synthetic adsorbent are considered effective, but their cost is expensive, the reason why low cost adsorbent is one of the trend today. Some of the low cost adsorbent are made of biomass such as fruit peels, rice husk, corn cob, sugar bagasse, plant leaves and many more, studies investigating the potential of these adsorbents obtained a results which are closely similar to those synthetic adsorbent.

In this article, the efficiency and potential of corn cob as an adsorbent in removing water contaminants in aqueous and wastewater solutions is reviewed.

2. Adsorption Equilibrium Isotherm and Kinetics Models for Adsorption using Corn Cob

Kinetics and isotherm models are important in adsorption studies as it provides information to the mechanisms and principles of the adsorption process. Equilibrium isotherm models of adsorption are used to describe the surface properties, adsorption mechanism and interaction occurs between the adsorbent and adsorbate. On the other hand, kinetic models provides information on the mechanism of adsorption process[11]. Some of the models are discussed below[11], which are frequently used in the adsorption of corn cob.

2.1 Adsorption Kinetics Models

In the adsorption of corn cob, kinetic models can provide information to various factors such as the availability of sites, pH of the solution, particle size of the corn cob, and the initial concentration of the solution[13].

2.1.1 Based on Order of Reaction

1. Pseudo-First-Order Kinetic Adsorption Model

The non-linear equation of pseudo-first-order kinetic equation from the Lagergren's equation[13] was given by equation no. 2.1:

$$q_t = q_e(1 - exp^{\frac{k_i}{2.303}t}) \qquad [2.1]$$

Where, q_t is the amount of adsorbate adsorbed at the given time t (mg g^{-1}), q_e is the equilibrium adsorption capacity (mg g^{-1}), k_i is the pseudo-first-order rate constant (min−1), and t is the contact time (min).

2. Pseudo-Second-Order Kinetic Adsorption Model

The nonlinear kinetic equation from the Lagergren's equation was given as,

$$q_t = \frac{k_s \cdot q_e^2 \cdot t}{1 + q_e \cdot k_s \cdot 1} \qquad [2.2]$$

where, k_s is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

2.1.2 Elovich Kinetic Model

Elovich equation[12] is applied to chemisorption processes and given in the form of,

$$qt = \frac{1}{\beta}\ln(\alpha \cdot \beta) + \frac{1}{\beta}\ln(t) \qquad [2.3]$$

where α is the initial adsorption rate (mg g−1 min−1) and β is related to the extent of surface coverage and the activation energy involved in chemisorption (g mg−1).

2.1.3 Intraparticle Diffusion Model

Intraparticle diffusion resistance that affects adsorption process can be describe using the inraparticle diffusion model given as,

$$q_t = k_{id} \cdot \sqrt{t} + C \qquad [2.4]$$

Where, q_t is the amount of adsorbate adsorbed by adsorbent at a given time, t (min), k_{id} is the intraparticle diffusion rate constant (mg g−1 min−1), and C is a constant related to the thickness of boundary layer (mg g−1)

2.2 Equilibrium Isotherm Models

Adsorption isotherm are used to determine the metal uptake per unit weight of the adsorbent to attained the equilibrium concentration of the adsorbate. Adsorption isotherm models such as the Langmuir and Freundlich isotherm models were used in the adsorption of corn cob to determine the amount of adsorbate on the adsorbent[14].

2.2.1 Langmuir Isotherm Model

Langmuir equation was given as,

$$q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad [2.5]$$

Where, q_e is the amount of adsorbate adsorbed at the equilibrium (mg g^{-1}), C_e is the adsorbate concentration at the equilibrium (mg L^{-1}), K_L is the Langmuir equilibrium constant, and Q_{max} is the maximum adsorption capacity of the adsorbent(mg g^{-1}). Assuming that the adsorbates are chemically adsorbed at a fixed number of known sites, formation of adsorbate monolayer will form when the adsorbent becomes saturated, each site can only hold one species of adsorbate, the sites are energetically equivalent , and there are no interactions between the adsorbate.

2.2.2. Freundlich Isotherm Model

The Freundlich equation was given in the form of,

$$q_e = K_F \cdot C_e^{1/nF} \quad [2.6]$$

Where K_F is the Freundlich equilibrium constant (mg g^{-1}(mg $L^{-1})^{-1/n}$), while n_F is the Freundlich exponent which is dimensionless. Unlike the Langmuir isotherm equation it was given in an exponential form, and has the assumptions that adsorbate concentration on the adsorbent surface increases as the adsorbate concentration increases, there is an infinite amount of adsorption will occur, and lastly, the adsorption could occur via multiple layers instead of a single layer.

3. Methodology

Different studies used corn cob as adsorbent in removal of organic contaminants and heavy metals, wherein the researchers used various chemicals such as sodium hydroxide, hydrochloric acid, phosphoric acid, citric acid, etc. to modify the adsorbent. Other studies also investigated the adsorption capacity of corn cob without chemical modification. The adsorption process that involves the used of corn cob as adsorbent are discussed below.

3.1 Preparation of Unmodified Adsorbent

The corn cobs were collected, washed, air/sun and oven-dried, ground into powder into the desired particle size using different size mesh-sieved. Adsorption kinetics of heavy metals such as cadmium, nickel(II), iron, manganese, and lead ions using corn cob adsorbent in aqueous solution and industrial effluent solution was investigated[13-17]. Atomic adsorption spectrophotometer(AAS) was used to determine the mineral content of the corn cob, scanning electron micrograph (SEM) and SEM-EDX were used to determine the porosity and structure of the powdered corn cob. Adsorption capacity was determined using various kinetic models such as Levenberg Marquardt algorithm (Marquardt) pseudo first- and second-orders, Elovich and intraparticle diffusion models (Oke et al., 2008). Influence of pH, temperature and particle size in the adsorption of heavy metals were determined using batch adsorption experiments. After the adsorption process, the solution was filtered with the desired filter paper to separate the adsorbent and the concentration of metal ions were determined using various instrument such as UV-Vis spectrophotometer[13] or Atomic adsorption spectrophotometer (AAS)[14].

The adsorption capacity and percentage removal were calculated using equations 3.1 and 3.2[15], respectively:

$$Q = (C_o - C_e) \qquad [3.1]$$

$$percentage\ removal = \frac{C_o - C_e}{C_o} \times 100 \qquad [3.2]$$

Where,

Q is adsorption capacity of the adsorbent

C_o is the concentration of the metal ion before adsorption

C_e is the concentration of the metal ion after adsorption

Studies proved that powdered corn cob as adsorbent without undergoing any chemical treatment is a good adsorbent for iron and manganese[16], and even other metals and substances.

3.2 Preparation of Modified Adsorbent

The study of cadmium, copper, lead, nickel, and zinc, two types of acid were used to treat the corn cob for the adsorption process of the said metal ions in singular or binary system[17]. The singular system were the solutions containing individual metal ions while binary system for solutions containing mixed solution of each metal ions.The corn cobs were subjected to pre-treatment process through washing, drying, and sieving using different mesh sieve to obtain the necessary particle size. The grinded corn cobs were divided into two set-ups, one is for the phosphoric acid treatment and the other one is for the citric acid treatment. The powdered corn cobs were mixed with 1M Phosphoric acid and 0.6 M of citric acid separately. Unreacted citric acid was identified by collecting the liquid from the washed modified corn cob and evaporating in a forced air oven, while unreacted phosphoric acid was determined using ICP emission spectrometry. The adsorption efficiency of each modified corn cob adsorbent was compared to the commercialized resin. The adsorption capacity was measured using the Langmuir non-linear equation.

Another study involving treatment of citric acid in the powdered corn cob was investigated and determined its efficiency for the removal of Manganese(II) ions from aqueous solution[18]. The usual adsorption parameters such as effect of pH, contact time, and etc., were studied to exhibit the adsorption capacity of the adsorbent treated with citric acid in Manganese(II) removal.the metal concentration was observed using UV-Vis spectrophotometer with the aid of perpurine, and a presence of surfactant as a complexing agent for Mn(II) ions.

Treatment of citric acid was used to enhance the surface of powdered corn cob for efficient adsorption of Cr(VI)[19]. The corn cob was subjected to pre-treatment processes and treated with 0.5 M citric acid, and oven dried. To identify the functional groups present in the adsorbent, the researchers used the FTIR instrument. Another adsorption study using treated corn cob was studied in the removal of Cr(VI) in aqueous solution. Unlike, in the study of Abbas et.al, the researchers used NaOH, acetone, and HCl to modify the surface of the adsorbent, and used atomic adsorption spectrophotometer to determing the metal concentration[20]. The adsorption capacity was calculated using equation 3.3,

$$q = \frac{V\,(C_i - C_e)}{m \times 1000} \qquad [3.3]$$

where:
q Is the adsorption capacity (mg/g)
V is the volume of the metal solution
m is the mass or dosage of the adsorbent
C_i is the initial metal concentration
C_e is the metal concentration at equilibrium

In the study of Huawen Hu et. al, the polysaccharide was extracted from the powdered corn cob then treated it with 1M Phosphoric Acid and subsequently stirred at a constant temperature in a water bath to ensure the reaction between the surface of the corncob that contains cellulose and the phosphoric acid proceeds[21]. The corn cob was then oven-dried and wash with deionized water to remove remaining H_3PO_4 then oven-dried for the second time to yield the modified-corn cob. Unlike the previous studies above, they subjected the modified corn cob to Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Micrograph (SEM) Analysis to determine the morphology, structure and the functional groups present. These characterizations are very important when studying adsorption especially when it involves the enhancement of the surface of the adsorbent. It allows the researchers to identify changes on the surface of the adsorbent after the treatment. To test its adsorption efficiency, batch experiments with Malachite green as adsorbate were done; effect of pH, adsorption dosage and adsorption time were also determined.

Rabbani et. al [22] prepared their corn cob the same way like the other studies however the treatment was different. The biomass was hydrolyzed using sulfuric acid (98%) as a catalysis having a ratio of 2:5 (g/mL). Hydrolysis reaction was conducted at the temperature of 80 ^{o}C for 40 minutes. The acid concentration of the biomass subjected to hydrolysis was diluted to 68%. The liquid formed from the reaction was separated from the solid by filtration. After several washing of distilled water, the adsorbent was obtained. The characterization of adsorbent utilized SEM and XRD analysis in examining the surface morphology. UV/Vis spectrophotometer was used in the calculation of the absorbance of dye concentration at maximum absorption. Batch studies for adsorption with the common parameters and recyclability of the adsorbent were conducted.

3.3 Corn cob Immobilization

Immobilization/ bio-composite preparation became more popular in recent years, although natural adsorbents like agricultural wastes possess impressive capability of adsorbing heavy metals and dyes, we cannot overlook the fact that it lacks in some aspects. Environmentalists were attracted to physico-chemical properties and adsorption capacity of the modified adsorbent because natural adsorbents have disadvantages like un-even particle size, low density, poor mechanical strength, rigidity and instability under variable conditions. Manzoor et. al[23] investigated the efficiency of a corn cob immobilized in composite beads for the adsorption of Chromium in tannery wastewater and compared it to the adsorption efficiency using raw corn cob[23]. Parameters such as initial concentration of Cr, pH, dosage and contact time were also tested to get the optimal values. A 0.25 mm of oven-dried PCC was collected and used for the immobilization process. Sodium alginate was used as the composite beads where the 0.25 mm of PCC was encapsulated. The resulting bead (3 mm) was kept for adsorption experiment. Unlike the previous studies stated here, they also studied the desorption capacity of the adsorbent where the adsorbent was submerged in a 0.1 M NaOH solution and stirred constantly and adsorption-desorption capacity was recorded. Characterization of the adsorbent before and after the adsorption was done using SEM and SEM-EDX.

In a different study [24], the corn cobs were dehydrated and ashed at around 350-400^{o}C. From the ash, extraction of silica was carried out and was made to pass through a 200 mesh sieve. The extracted corn cob silica was added to a solution of sodium alginate (2% w/w) which was homogenized by ultrasonication. An addition of bacterial biomass, cultured from *Pseudomonas putida* sp., to the solution was mixed by agitation for immobilization of the biomass at the surface. Beads formed from the aforementioned steps were added to a solution of $CaCl_2$ solution.

4. Results and Discussion

A. Using Unmodified Adsorbent for Adsorption of Heavy Metals

Without chemical modification, the adsorption kinetics of cadmium ions was investigated using powdered corn cob (PCC)[13]. In this study, the researchers used AAS to determine the mineral content of the PCC. Scanning Electron Micrograph (SEM) and SEM-EDX with two different Magnifications were used to determine the porosity and structure of the Powdered Corn Cob. For determining the adsorption capacity, different kinetic models were used like Levenberg Marquardt algorithm pseudo first- and second-orders, Elovich and intraparticle diffusion models. Influence of pH, temperature and particle size in the adsorption of cadmium was also determined by batch adsorption experiments.

From the SEM and SEM-EDX analysis, it was found that the powdered corn cob adsorbent (PCC) was amorphous indicating its nature of porosity. It was also found in the analysis that the small openings in the surface indicated an increase in the contact area that facilitates pore diffusion during the adsorption process.

Results from the batch experiments done showed that the relationship between the remaining concentration of Cd^{2+} in the solution and time followed an exponential function with an R^2 value ranging from 0.8514 to 0.9290 for typical domestic-industrial wastewater and 0.9928 to 0.9993 for synthetic wastewater. The adsorption of Cd^{2+} from wastewaters were based on first order kinetics which can be attributed to many factors such as availability of sites, pH of the solution, particle size of PCC and initial concentration of Cd^{2+}. Based from the batch adsorption experiments, researchers found at that there is a direct relationship between the adsorption capacity of Cd^{2+} by PCC and time. A noticeable increase in the concentration of the Cd^{2+} in the solution was observed at the first few hours of the operation. An initial conc. of 20 ppm was decreased to 13.2 ppm at 5 hr. mark and reached equilibrium at the 18^{th} hr. of the operation. The same relationship was observed between the adsorption capacity and the adsorbent mass or dosage; The smallest PCC mass (0.3 g/300 mL) appeared to have reached the equilibrium faster after only 4 h, while higher PCC masses (1.0 g/300 mL) reached to the equilibrium after 7.5 h.

It was observed that the variation of particle size can influence the cadmium adsorption kinetics. From the batch experiment, it can be noticed that there is an inverse relation between particle size and adsorption capacity at equilibrium. As the particle size decreases its ability to adsorb Cd^{2+} increases. For particle size 0.075mm, the amount of cadmium removed was 13.46 mg/g and the time required to reach equilibrium is 4 h while for particle sizes that ranges from 0.212-0.300mm; the time required to reach equilibrium is 7.5 h and a removal capacity of 6.93 mg/g PCC.

Adsorption of Ni (II) from aqueous solution was investigated in the study by Arunkumar et. al [14]. Parameters such as adsorbent dosage, contact time, pH and initial concentration was studied by batch experiment and kinetics studies were investigated using the Langmuir and Freundlich isotherm models. The adsorbent dosage were varied from 1 to 7 grams maintained at pH 6, pH was varied from the range of 1 to 9, contact time at 15 to 90 minutes, and initial concentration from 25 to 150 ppm. Experimental data showed that with the adsorbent dosage of 6g the percentage removal was high with 70.08%, at pH 6 the maximum removal efficiency was obtained, at 90 minutes contact time the equilibrium was reached, and concentration of 25 ppm has 86.08% removal while for 150 ppm results in 67 % removal. Langmuir isotherm models gives an R_L value of 0.007 for the studied system at different dosage were found to be in between 0 to 1 which indicate favourable adsorption of Ni (II) onto the adsorbent[14].

Another study of maize cob was used as an adsorbent together with dowex which is a synthetic resin that served as a control in the removal of Pb(II) from aqueous solutions and effluent from battery and paint industries[15]. Adsorption experiments on equilibrium conditions on adsorbents weight, contact time, pH, and adsorbate conditions were studied by using standard solutions of Pb(II) and industrial effluents . The Lagergren's equation and Freundlich isotherm was used to determine the adsorption rate constant and adsorption pattern. Quality control measurements and statistical analysis were performed. Experimental data obtained shows that equilibrium was attained at 2 hours upon varying the contact time from 30 min to 3 hours with interval of 30 minutes. The result was compared to the other study which used Staphylococcus saprophyticus as adsorbent which also reported to attain equilibrium time within 2 hours[25] . The adsorption rate constants for maize cob and dowex(control) were 7.26 x 10^{-2} and 7.58 x $10^{-2}$$min^{-1}$, while the equilibrium ph value was 6; shaking at 150 rpm enhanced adsorption with maximum adsorption by both adsorbents in battery and paint effluents . Optimal weight at equilibrium for the adsorbents in Pb^{2+} solution was 16 mg/L of solution. Pb^{2+} removal by maize cob from battery effluent was 99.99% while it was 47.38% for Dowex. Corresponding values from paint effluents were 66.16 and 27.83%. The study concludes that maize cob has a potential to remove Pb^{2+} from industrial effluents it implies that it may also decontaminate wastewaters containing other divalent metal ions such as Zn^{2+}, Cd^{2+}amongst others. There is therefore the need for more extensive research on possibility of removing such metals using other crop residues since typical wastewaters contain mixed metal ions. This may increase the extent of use and applicability of the residues in wastewater remediation. An according to other studies Lead (II) suppresses the removal of other ions from mixed solution due to the greater stability constant of Pb^{2+} when bound to the surface of the ligands, in which other metals compete .

B. Using Modified Adsorbent in Adsorption of Heavy Metals

Cr (VI) uptake of the chemically-modified PCC was proven to be efficient with a removal percentage of 39.8% Ortiz et al[19] . Given data from the batch experiment proven that at lower pH, the removal efficiency is higher due to the protonation of the adsorbent's surface at acidic range. Optimal pH was determined to be at pH=2 where the highest removal percentage was observed. It was also proven that the smaller particle size used in the adsorption, the higher the removal percentage. This is due to the high surface area and available binding sites of the chemically-modified PCC Similar to the first study above; Freundlich was the isotherm model that best describes the adsorption process though Langmuir Model also fitted the experimental data but with higher sum of squared error. Maximum adsorption capacity of raw corn cob and modified corn cob were compared with values of 14.81 mg/g and 208.93 mg/g respectively.

Both studies revealed the efficiency of using PCC in adsorption of both dye and heavy metals; this efficiency was further enhanced by the study of Manzoor et. al [23] which immobilized the PCC in an alginate bead. The studies of Ortiz et. al [19] and Huawen Hu et. al[21] both followed the Freundlich model, whereas it should also be the case in this study because we presumed in the Freundlich isotherm model that adsorption takes place in the heterogeneous layer and the data given suggest that there is heterogeneity in the surface of the adsorbent . However, this is not the case for this study R^2 value of the Langmuir Model was higher than the Freundlich Model.

However, study on the biosorption of Cr (VI) from aqueous solutions was conducted using chemically treated *Zea mays* (corn) cob by Abbas et. al. [20]. The corn cobs were prepared and has various particle sizes ranging from 0.50 to 1.70 mm. The adsorbent was treated with acetone, HCl, and NaOH to modify its surface area. Batch experiment was carried out by varying those parameters that can affect the adsorption process such as biosorbent size and dose, initial metal concentration, pH, and kinetics were studied. Optimization of the biosorbent particle size and dose of biosorbent (0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 g) was performed without pretreatment of the adsorbent. The pH value was observed from 1.0 to 7.0. Initial metal concentrations in the range of 25, 50, 100, 200, 400, 600, 800, 1000 ppm were used. The contact time was varied in the range of 15, 30, 60, 120, 180, 240 min and 24 h. The experiments were carried out using 100 ppm stock solution for 24 hours with a mixing rate of 200 rpm. The metal ions were analyzed by atomic adsorption spectrophotometer. The results showed that, the optimum size for the adsorption process was 0.5 mm, while the adsorbent dose were 0.3 g. It is observed that the higher adsorption observed for chemically pretreated adsorbent with sodium hydroxide followed by acetone, then HCl has the lowest adsorption. The effect of pH, initial concentration, and contact time was carried out using pretreated adsorbent, and shows that maximum adsorption was observed at pH 2, 800 ppm, and 180 min. The data obtained were analyzed using Langmuir isotherm and Freundlich isotherm models, pseudo first- and pseudo second-order kinetic models. Following the Langmuir isotherm, the coefficient of determination(R^2) value of 0.9049, 0.9763, 9606, and 0.9833 for untreated,HCl, acetone, and NaOH treated adsorbent, while for Freundlich isotherm model coefficient of determination(R^2) value were 0.9672, 0.9085, 0.9012, and 0.9091 for untreated HCl, acetone, and NaOH treated adsorbent. Pseudo-first order kinetic model gives an R^2 value of 0.8005, 0.8234, 0.7199,and 0.7623 for untreated, HCl, acetone, and NaOH treated adsorbent 0.8005, 0.8234, 0.7199,and 0.7623 for untreated,HCl, acetone, and NaOH treated adsorbent, while the Pseudo-second order gives an R^2 values of 0.9938, 0.9997, 0.9999,and 0.9999 for untreated,HCl, acetone, and NaOH treated adsorbent From the result it follows that Langmuir isotherm and pseudo second-order kinetic model best fitted the experimental data having higher R2 value.

Adsorption capacity of immobilized PCC with optimized conditions was found out to be 277.57mg/g for Cr (III) and 208.6mg/L for Cr (VI). Removal efficiency in tannery wastewater was found to be to 64.52% and 55.98% for Cr (III) and (VI) respectively. Desorption of Cr (VI) was achieved up to 86% and 79% for Cr (III). Desorption process can take up to five cycles before the adsorbent becomes saturated.

C. Adsorption of Dyes using Corn Cob as Adsorbent

Corn cobs were used as an adsorbent in the removal of the azo dye Direct Yellow 27[26], reactive dye orange 16[28], malachite green[27], and methylene green[29]. The adsorbent does undergo pretreatment process such as washing, drying, and sieving and treated with phosphoric acid[29] and was subjected to various operational parameters such as effect of pH, particle size, contact time, and initial concentration. The results shows that the pH strongly affects the surface charge of the adsorbent and the biosorption capacity, surface charge can be determined by the point of zero charge (pH), and the pH of the corncob was identified to be 6.83 which means that below this value the corncob particles carry positive charges, the value obtained from this study can be compared to the study of Leyva-Ramos et. al[30] which has a value of 6.2 and close enough with the value in this study[26]. Adsorption by reactive dye was found to be strongly dependent on pH having its maximum removal at pH=1, and its sorption capacity was found to be 25.25 mg dye g^{-1} corn cob at 18 °C.

In the study, thermodynamics parameters was investigated and the results showed that the dye sorption on corn cob is spontaneous having a negative value of ΔG and the process was considered to exothermic by having negative values ΔH. Among the Freundlich, Langmuir, Dubinin-Radushkevich and Tempkin isotherm models, the Langmuir isotherm model was best suited for the adsorption process which has a monoloyer sorption capacity of 25.25 mg g^{-1} was obtained at 18°C[28]. For the adsorption of methylene blue and malachite green the adsorption capacity was found to be 75.27 and 76.42 mg/g for raw corn cob, while 271.19 and 313.63 mg/g for activated corn cob, respectively[29]. In the study of adsorption of malachite green in aqueous solution, the adsorption process was not affected by the changes in pH of the solution at the experimental range and there is no changes in adsorption capacity after 100 min,in this study the dye concentration was determined using uv vis spectrophotometer at 617 nm[27].

In the study of Huawen et al (2018), they found out that the usage of Phosphoric acid causes the morphology of the PCC to change into a coarsened surface and more porous structure with crack formations compared to the sheet-like bulk morphology of the original corn cob. Results from the FTIR analysis show that the –OH stretching vibration broadened due to the chemical modification. According to the researchers, the large pores can immobilize the Malachite Green molecules; coarse surface and the cracks can also facilitate the adsorption. From the data gathered through the batch experiments, they found out that the optimal pH is 7.00 where the removal percentage of Malachite green is 92% and optimal adsorbent dosage is 1.0 g/L. The adsorption process reaches the equilibrium at 90 minutes. Two kinetic models were used based from pseudo-first and pseudo second order reactions to get the equilibrium adsorption capacity and the adsorption capacity at time *t* respectively. Experimental value of 148 mg/g was closer to (q_{2e}=152.19 mg/g) rather than the (q_{1e} =141.13 mg/g) of the pseudo-first order kinetic model. R^2 values of the two kinetic models showed that pseudo-second order best describes the adsorption process which tells us that the interaction between the malachite green and the adsorbent is strong because it is assumed that the rate determining step of the pseudo second order kinetic model is chemical interactions. Freundlich isotherm model best describes the isothermic process of the adsorption, which tells us that multilayer adsorption takes place and that inhomogeneously active sites are present in the surface of the adsorbent. It was also suggested that both chemical and physical interactions takes place during the adsorption process.

D. Adsorption using Corn Cob-alginate Beads

In the study of J. Shim et. al[24] the prepared beads were characterized as rough due to the surface containing silica and microorganism in contrast of sodium alginate beads having smooth and soft surface. The large surface area contributed by the corn cob silica provided more sites for contaminant adsorption and reaction. In identifying the alginate beads structure, the before and after equilibrated aqueous solution containing phenol, Cu, and Cd was analyzed using FTIR analysis. The FTIR analysis indicated -OH stretching near 3445 cm-1. Asymmetric and symmetric stretching vibrations of alginate-COO- were observed at 1424 and 1601 cm-1, respectively. Peaks observed at 1072 and 1025 cm-1 can attributed to O-glycosidic bonding between (1-4)-β-D-mannunoric acid and (1-4)-α-L-guluronic acid, which indicates stability of the linear chain in the alginate beads. Characteristic Si-O-Si stretching was observed near 1100 cm-1 in beads containing silica. Stretching of silanol (Si-OH) occurs near -OH, the 3000-3700 cm-1 band is largest in beads containing both silica and the strain. The removal of copper and cadmium revealed that with increasing pH the heavy metal removal by the composites beads is significantly increased by 99.3% for Cu and 83.5% for Cd. However, the alginate beads containing silica dominate for being most effective, results obtained as 84% (4.73 mg/g) for the removal of Cu and 83% (4.60 mg/g) for the removal of Cd within 3 hours of equilibrium. Using EDS analysis, confirmed the presence of Cu and Cd on the surface of the beads. In a mixture containing 114 mg phenol, 43 mg Cu, and 51 mg Cd, in the treatment 93% of phenol was degraded within 96 hours, and for Cu and Cd the removal was 98% and 99% respectively, critically reduced the toxicity in the strain. Available alginate carboxylate groups would also be more limiting in the multiple contaminant mixture and some competition between Cd and Cu for adsorption sites was apparent. The Langmuir isotherm model gave a better fit to the Cu and Cd adsorption data than the Freundlich model having an adsorption capacity of 4.07 mg/g for Cu and 4.24 mg/g for Cd. Regeneration or desorption experiments showed that HCl is way more effective rather than distilled water in desorbing the metals from the beads. The regenerated beads removed 64% of the Cd content and 56% of the Cu content from the solution in the second reuse. Further experimentation will be required to optimize regeneration even though these tests indicate that the beads have some potential for reuse.

Table 1. Adsorption Capacity and Percentage Removal of the Corn Cob Adsorbent to Various Metals and Dyes.

Type of Adsorbent	**Adsorbate**	**Percentage Removal**	**Adsorption Capacity**	**Particle Size**	**Studies**
Corn Cob (Not chemically treated)	Cd^{2+}	_	6.93 mg/g	0.212-0.300 mm	Ismail et. al[13]
	Ni^{2+}	70.08 %	_	250 micron	Arunkumar et. al[14]
	Pb^{2+}	66.16 %	-	-	Opeolu et. al[15]
	Orange 16	-	25.25 mg dye g^{-1}	<800 µm	Suteu et. al[28]
Corn Cob (Treated with Phosphoric Acid)	Malachite Green	92%		-	Hu et. al[21]
	Malachite Green	-	313.63 mg/g	-	Farnane et. al[29]
	Methylene Blue	-	271.19 mg/g	-	
Corn Cob-alginate beads	Copper	84%	4.73 mg/g	-	Shim et. al[24]
	Cadmium	83%	4.60 mg/g	-	
	Cr^{3+}	64.52%	_	_	Manzoor et.al[23]
	Cr^{6+}	55.88%	_	_	

E. Adsorption of other substances using corn cob

Corn cobs were used as an adsorbent for the adsorption of amino acids such as phenylalanine (Phe) and tyrosine (Tyr), in this study the adsorbent was activated by phosphoric acid with particle size ranges of greater than 0.15mm but not greater than 0.85 mm. And the results showed that the adsorption capacities are in the range of 14.28 to 66.01 mg/g for Phe, and from 1.96 to 9.11 mg/g for Tyr, which indicates that corn cob adsorbent can be used as an alternative for reducing the amount/costs in the production of Phe-depleted protein hydrolysates[31].

4. Adsorption Capacity of other Agricultural Biomass Adsorbent Compared to Corn Cob

Aside from corn cob, other agricultural biomass are also used as adsorbent due to its affordability and availability when being compared to synthetic adsorbents. Adsorption capacity of other agricultural biomass adsorbent are discussed below to show the capability of other biomass on adsorbing various substances.

4.1 Adsorption using Sunflower Stalk

In the recent years, sunflower stalk has been use as a good adsorbent for heavy metals. Study of adsorption using sunflower stalk with a particle size of 2mm as adsorbent was prepared without any chemical treatment shows that in adsorption of Pb and Cd the adsorption rate was high at lower concentration of added Pb and Cd, while at higher levels of added Pb and Cd the percentage removal of the two metals were decreased. At low concentration of Pb and Cd (5mg/L) the amounts of metal adsorbed were 1.1 ppm Pb (88.4%) and 1.2 ppm Cd (96%). Whereas, at higher concentration of Pb and Cd such as 1700 ppm and 1000 ppm, the amounts adsorbed by the adsorbent were 150 ppm Pb (35 %) and 62.5 ppm Cd (25%), which shows that at higher concentration the percent removal was less. The Freundlich, one site Langmuir, and modified two-site Langmuir isotherm models were used to describe the adsorption equilibrium. Based on the experimental data, the model that suited well with the process was the modified two-site Langmuir having R^2 value of 0.991 and 0.993 for Pb and Cd, respectively , while the other models has an R^2 value less than the modified two-site Langmuir. On the other hand, the optimum pH value was found to be at pH 5.0 whereas, the percent removal for Pb and Cd are 99.2 and 99.1 %. The effect of contact time shows that at 240 min the two metals attained saturation and the removal of the metals also increases with time. The kinetic model to describe the adsorption process is suited with the pseudo-second order and has a linear fit which has an adsorption capacity(q_e) of 0.174 and 0.357 mg g^{-1} for Pb and Cd and has an R^2 value of 0.9994 and 0.9996 respectively, that indicates that the adsorption process for the adsorbent and the metals are involves in rate determining step[32,35] and may be considered as chemical adsorption[32,36].And lastly, one of the parameters that affects the adsorption capacity is the adsorbent dose which in this study shows that the percent removal of metal ions increases with the increasing dosage due to the greater availability of the surface area at higher concentration of the adsorbent. Adsorption capacity of sunflower stalk was used in the study of Sun et al.[33] , adsorption of cadmium(II), copper(II), chromium(III), and zinc(II) from wastewater. The concentration of metals were determined by ICP AES and the adsorbent was sieved in 25-45 and 60 mesh. Kinetic studies showed that cadmium has the highest adsorption having 80 % removal, while chromium being the lowest one having 50% removal. Competitiveness of each metal were studied and shows that when the four metals are mixed together, cadmium has the lowest adsorption rate and copper has the highest. On the adsorption of Congo Red (CR), Direct Blue 71 (DB), Methylene Blue (MB), and Basic Red 9 (BR) on sunflower stalk, the results showed that the sunflower stalk has the maximum adsorption capacities on Basic red 9 and methylene blue and lower on Congo red dye and direct blue dye[34].

Table 2. Adsorption Capacity of Sunflower Stalk as an Adsorbent for Dyes and Heavy Metals

Adsorbate	Particle Size	Adsorption capacity (mg g^{-1})	Source
Pb	2mm	182.90	Jalali et al.[32]
Cd		69.80	
Cu^{2+}	>60 mesh sieve	29.3	Sun et al.[33]
Zn^{2+}		30.73	
Cd^{2+}		42.18	
Cr^{3+}		25.07	
Methylene Blue	>60 mesh sieve	205.41	Sun et al.[34]
Basic Red 9		317.34	
Congo Red		37.78	
Direct Blue 79	25-45 mesh sieve	26.84	

4.2. Adsorption using Cucumis melo

Adsorption properties of Cucumis melo (C.melo) rind for the removal of Fe and Pb ions from groundwater solutions was studied[37] . The C. melo rind was treated with 15% nitric acid and has a particle size less than <150µm. The adsorption capacity was determined by addition of 0.05 g of the adsorbent and by adjusting the pH to the desired value using glacial acetic acid and sodium hydroxide, with a mixing rate of 125 rpm for 45 minutes at room temperature. After the adsorption process, the adsorbent was separated from the metal solution by filtration through 0.45 µm nylon cellulose membrane filters. The metal concentration residue was detected by ICP-MS. The optimized pH of Fe and Pb was at pH 7.0 and 6.5. Adsorption experiment done under Fe-optimized conditions yielded an average removal for Fe and Pb of 90.73% and 88.36%. While, the study under Pb optimized conditions resulted in an average removal of 90.94% and 82.44% for Pb and Fe. It was concluded that C.melo rind has a potential low cost adsorbent for the removal of Fe and Pb ions from groundwater . Plotting the data results from the experiment, it was shown that the adsorption process was fitted with the Langmuir isotherm with a maximum adsorption capacity 5.3505 mg/g and 0.0830 mg/g for Fe and Pb, while the kinetics study showed that the process follows the Pseudo-second order kinetics.

4.3 Adsorption using Durian Leaves

Potential of durian leaves as a low cost bioadsorbent for the removal of Fe(II) ions in aqueous solution was investigated in the study of Abayati et al.[38]. The effects of parameters such as pH, initial metal concentration, contact time, mixing rate , and particle size of the adsorbent was observed in a batch experiment at room temperature. The prepared durian leaf powder was used as an adsorbent, which is held constant for every test (1.5 g). The effect of pH was observed at pH ranges from 2-8 for 2 hours with 1.5 g durian leaves, mixing rate of 100 rpm for solutions of Fe(II) having concentrations of 10 mg/L. Effects of initial concentration and contact time was studied by varying Fe(II) solutions having concentrations of 3.0 mg/L, 10 mg/L, 20 mg/L and 30 mg/L, while the effects of contact time was observed by various periods such as 5, 10, 20, 30, 60, and 120 minutes for Fe(II) solution of 5 mg/L, both experiments were carried out at a mixing rate of 100 rpm. The effect of mixing rate on the adsorption process was held at various mixing rate of 50, 100, 150 rpm for time periods of 5, 10, 20, 30, 60, and 120 minutes for Fe(II) solution of 5 mg/L. And lastly, the effect of particle size adsorbent was determined by manipulating the particle size of the durian leaf powder by < 0.600 mm and > 0.600 mm. The adsorption isotherm used in the adsorption of Fe(II) ions onto durian leaves are the Freundlich and Langmuir isotherm models. Experimental data shows that the maximum metal uptake was around pH 6 with 81.0 % Fe(II) removal. Having an initial concentration of 5 mg/L has a removal of 83.0 %, however, metal concentration of 30 mg/L has 46.3 % removal. As to the mixing rate, the adsorption capacity increases, the percent removal was 49.0%, 61.0%, 66.0% for the mixing rate 50rpm, 100rpm and 150 rpm after the initial 5 minutes. And lastly, by using different particle size which were less than 0.600 mm and the other was greater than 0.600 mm, the adsorption process was able to remove 59.0% and 48.0% during the initial 5 minutes. The results shows that removal of metal increased upon decreasing the particle size because smaller particles have larger surface areas and requires shorter time to reach equilibrium[39]. The isotherm models that fits into the adsorption process is the Langmuir isotherm model which gives a correlation coefficient of 0.7736 and maximum adsorption capacity is found to be at 3.914 mg/g, which has a higher value than the Freundlich isotherm model which has a correlation coefficient of 0.7397. The study concluded that the removal of Fe (II) ions in the solution is highly dependent to the ph of the solution, contact time, and by the other parameters tested in the study. And said that durian leaves is an effective biosorbent for the removal of Fe(II) ion in aqueous solution.

4.4 Adsorption using Sporopollenin

Adsorption of Cu(II), Pb(II), and Cd(II) onto sporopollenin has been studied [40]. Sporopollenin, a natural biopolymer which can be found in the outer membrane of moss and fern spores, and also found in most pollen grains. In this study, *Lycopodium clavatum* spores was used as an adsorbent with a particle size of 20 µm without any chemical treatment. Parameters that affects the sorpion capacity such as the pH of the solution, adsorption time, initial metal ion concentration, and temperature was investigated and the experiment was conducted in acetic-acetate medium to represent to represent complexing agents that are present in industrial wastewaters together with complex forming organic compounds. Initial and equilibrium metal concentration were observed using flame atomic adsorption spectrophotometer (FAAS). Adsorption kinetics used in the study are the pseudo-first-order kinetic model, pseudo second-order kinetic model and, intra particle diffusion model, while Freundlich, Langmuir, and D-R isotherms was used to describe the adsorption isotherm. Experimental data shows that the adsorption process follow and best fitted to Freundlich adsorption isotherm and determines the adsorption capacities for Cu(II), Pb(II) and Cd(II) metal ions to be 0.0195, 0.0411 and 0.0146 mmol g−1. From the results obtained, it shows that for the three metal ions the adsorption process follows the pseudo-second order type adsorption kinetics. Thermodynamics parameters such as ΔH, ΔS, and ΔG was also calculated and investigated in the adsorption process. For the adsorption of Cu(II), Pb(II) and Cd(II) ions onto the adsorbent, the standard heats of adsorption ΔH were found to be endothermic and the calculated ΔS were positive for the adsorption. Negative ΔG values describes the adsorption process for the three metal ions onto the sporopollenin which indicates spontaneous process. The calculated mean free energies (E) of the adsorption were found to be between 8 and 16 kJ mol^{-1}. It was concluded that the adsorption process of these metal onto sporopollenin occurs as an ion-exchange process.

4.5 Adsorption using Rice husks, Wheat straw, Green algae

In the study, removal of copper, nickel, cadmium, and lead ions from simulated contaminated water by using raw wheat and soybean straws, corn stalks and corn cobs as adsorbent was investigated[41]. To increase the adsorption capacity, and decrease the leaching of organic matter in the biomass it was subjected to pretreatment. The biomasses were modified with formaldehyde in acid medium, sodium hydroxide with and without previous modification with formaldehyde, acid solution , or water washed.. Batch adsorption experiment was studied at constant temperature by addition of 5 g/L of adsorbent to the containers having various metal salt solutions. Experiment using heavy metal concentration of 0.8 mmol/L and observation for 3 hours was carried out to determine the equilibrium time. The adsorbent was separated using vacuum filtration then analysing the filtrate using atomic adsorption spectrophotometer. The results shows that different plants have a different adsorption capacities in adsorbing heavy metal ions. Corn cob was a good adsorbent for cadmium and nickel, while these metals are adsorbed less by corn plant and soybean straw. On the other hand, corn cob adsorbed less copper ions, while soybean straw showed high removal rate. It is also reported that soybean straw and corn stalk adsorbed lead in great amount. Chemical composition and anatomical structure of the various adsorbent are responsible to their differences in adsorption characteristics. The results shows that after treatment of formaldehyde in the acidic medium the adsorption capacities of the adsorbents decreases. Nevertheless, usage of formaldehyde in the treatment process is not advisable due to the large amount of waste produced after the treatment process. However, Adsorbents modification with 1% NaOH and water washing gave a good results, but using the raw/native materials were still quite efficient.

Toxic heavy metals adsorption such as As, Cd, Cr, and Pb from aqueous solution using rice hulls and green algae as an adsorbent has been studied[42] . The rice husks was dried and pulverized to maximize its surface area. Batch and desorption experiments were carried out to determine the adsorption capacity of the adsorbent in the removal of heavy metals. The ph was adjusted using HCl and tetramethylammonium hydroxide, and the metal concentration was observed using inductively coupled argon plasma. Experimental data shows that the percentage removal of metals from aqueous solution using rice hulls biomass for Pb, Cd, and Sr were 99.43%, 97.96%, 94.11% , while for Cr and As were 98.93% and 98.95%, respectively . The resulted adsorption capacity of rice hulls for As, Cd, Cr,and Pb is $8.21x10^{-3}$, $1.9X10^{-4}$, $3.16x10^{-3}$, and $5.5x10^{-5}$ mmoles/mg adsorbent. The metal desorption from the rice hull adsorbent was reported to be 9.5%, 6.9%, and 5.2% for Cd, *Sr,* and Pb. Concluded that the adsorption equilibrium was rapidly established within minutes, and by lowering the pH to 1.55 the rice hulls was able to desorb cationic metal ions.

Heavy metals adsorption using the green alga (Chlorella minutissima) in aqueous solution was investigated[42]. The algae were washed, centrifuged, then dried. Batch adsorption and desorption experiment was carried out to investigate the adsorption capacity of metals such as Cd, Pb, Zn, Ni, and Co. The algal biomass was added to PIPES(piperazine N N' bis (2 ethane sulphonic acid) buffer) before the adsorption process. The effect of initial concentration of heavy metals (varying the initial concentration of different heavy metals) such as Cd, Zn, Pb, Ni, and Co (in increasing concentration) was observed with an algal concentration of 3.5 mg/mL at pH 7. The results shown that the rate of adsorption for Cd, Pb, and Zn was rapid, reaching the equilibrium in the span of 3 minutes, while it takes 15-20 minutes for Co and Ni to attain the equilibrium. From the experimental data, it shows that Ni has the lowest percentage removal having 77%, while Pb has the highest percentage removal having 99%. On the molar basis, removal of Cd, Zn, Pb, Ni, and Co were reported to be $1.5x10^{-6}$. $1.2x10^{-5}$, $4.7x10^{-5}$, $2.65x10^{-4}$, and $7.1x10^{-4}$ mmoles/mg cell mass. From these results, it can be concluded that increasing the initial metal concentration results with an increase of metal removal. Comparing the percentage removal of Ni and Pb with Ni having a greater concentration than Pb, by analysing the results it was suggested that Ni and Pb has a different adsorption site and the number of adsorption sites for different heavy metals per unit of biomass is different. The desorption process was carried out by reducing the pH using HCl to 1.55. The metal desorption from the adsorbent was reported to be high for Pb and Zn having 90.2 % and 91.5 %, while Ni and Cd has 1.2% and 0.3%.

Zn(II), Cd(II), and Fe(II) adsorption on rice hull, sawdust, sugarcane bagasse, and wheat straw was studied[43]. The dried samples of was sieved to 1mm sieve. The adsorption process was studied by using raw and modified adsorbents and investigated in wastewater solution. The modified adsorbent was treated with nitric acid then dried afterwards. The experiment was carried out in a batch and column adsorption procedure. The batch sorption experiment was studied by adding 1 g of adsorbent in 100 mL wastewater, while the column procedure has a column internal diameter of 15 cm with a length of 15 cm. For the batch experiment, the instrument used to detect the concentration of the metal is the atomic adsorption spectrophotometer. The results shows that highest metal adsorbed by the adsorbent is the Fe >Zn>Cd and the adsorbent that has a higher adsorption capacity is the ricehull followed by saw dust, sugarcane and wheat hull having the least. In line with the study of Crystian et al.[44], which concluded that rice straw was an effective adsorbent for divalent Cu(II), Zn(II), Cd(II) and Hg(II) removal from aqueous solutions in a very rapid adsorption process. And demonstrates a good ability for removing metallic ion from industrial effluent containing the said metal ions. Upon their application on the treating wastewater, modified adsorbents showed a higher percent removal than the raw adsorbent.

4.6 Adsorption using Fruit Peels

The adsorption of heavy metals like heavy metals using modified orange peels were studied by Feng et al.[46] and Annadurai et al.[47]. Orange peels (OP) were treated with Sodium Hydroxide and mercapto-acetic acid [45] to enhance the adsorption capacity of the sample. Particle size 1-5mm and lower than 0.45 mm and were used for all the batch experimentation in the studies. Various instruments like SEM, FT-IR Spectrometer, Infrared C–S analyzer were used in the studies to characterize the modified orange peel adsorbent[45][46]. Zeta potential of the modified OP was measured using Malvern instrument.

Reusability of the product was taken into consider; after the adsorption, metal-loaded adsorbent was analyzed in AAS then soaked in a 0.1 M HCl to start the desorption process. Adsorption-desorption process was repeated several times using the same adsorbent. They had observed that the surface of the modified OP (treated with NaOH) has irregular shape and more porous that the untreated OP indicating that there are more active sites where Cu (II) can bind.
Zeta potential showed that after the adsorption process, less negative potential was observed compared to the zero potential before the adsorption [47] and is mainly due to the -COOH and -OH attached on the adsorbent where the binding of metal ions takes place [46].

Maximum adsorption efficiency for NaOH-treated OP is 91.6% at initial conc. of 50 ppm, pH of 5.4 and adsorbent dosage of 4 g/L. Langmuir isotherm model best fitted the equilibrium data. Maximum adsorption capacity is 50.23 mg/g, where it followed the pseudo-second order rate of reaction indicating a chemical interaction between the adsorbent and the adsorbate. Adsorption capacity for Cu (II) and Cd (II) using the mercapto-acetic acid treated OP were found to be 70.67 and 136.054mg/g, respectively. It also followed Pseudo-second order rate of reaction. Pb^{2+}> Ni^{2+}> Zn^{2+}> Cu^{2+}> Co^{2+} is the order of adsorption for orange peels. Adsorption capacity of all the heavy metals was also determined: 7.75 (Pb2+), 6.01 (Ni2+), 5.25 (Zn2+), 3.65 (Cu2+), and 1.82 mg/g (Co2+). Freundlich isotherm model best fitted the data. Adsorption was high for two regeneration cycle. Study of the efficiency of banana peel as an adsorbent was also studied by Annadurai et al.[47]. Same procedure was done for the banana peel. Batch experiments were also conducted to investigate the effect of the parameters used. In comparison to the orange peel adsorption of various heavy metals, Banana peels showed slightly higher adsorption capacities: 7.97 (Pb^{2+}), 6.88 (Ni^{2+}), 5.80 (Zn^{2+}), 4.75 (Cu^{2+}), and 2.55 mg/g (Co^{2+}). Freundlich isotherm was also the best fit for the data gathered.

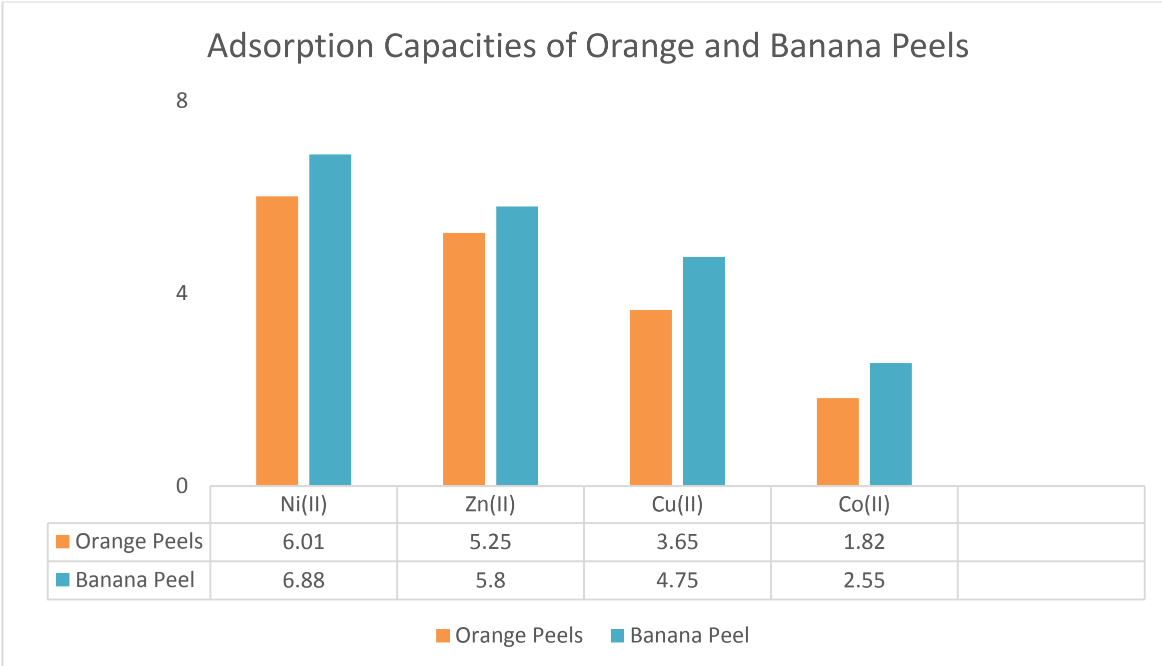

Figure 1. Comparison of Adsorption Capacities of Orange Peels and Banana Peels.

Removal of Methylene blue; a deep blue colored compound that can be either use in medication and as a dye use in textile industry using Citrus peels was studied by Kučić et. al [48]. Different components of orange and lemon peels contain functional groups that are involved in the adsorption process. Without modification, orange and lemon peel powders were used to adsorb methylene blue in simulated wastewater. Adsorption capacity of the adsorbent was compared to the adsorption capacity of mineral adsorbents like zeolite. Results showed that OP and LP produced higher adsorption capacity compared to 20mg/g of mineral sorbent. It was also found that adsorption in the pH ranging from 2-3 was weaker than the adsorption on pH 3-6 because of the poor dissociation of carboxyl group [47]. Approximately 100% adsorption efficiency was achieved during the experiments when 50-1000 ppm concentration of methylene blue. Data showed that it also followed the pseudo-second order rate of reaction just like the treated OP from the above studies.

Banana Peel as modified adsorbent was proven to be very efficient based from the studies above. P.Kumari[49] and Hossain et. al[50] aimed to prove the efficiency of unmodified banana peel. Both studies excluded the use of instrument to characterize the adsorbent. It was observed from the study that maximum adsorption of Pb is 82% that can be achieved when pH is 7, 80 mins. contact time with an initial concentration of 10 ppm and 0.5 mg/100mL of adsorbent. For the Adsorption of Cu (II), optimum pH is 6 where it followed the second order model and fitted both Langmuir and Freundlich isotherm models. Monolayer adsorption capacity is 27.78 mg/g.

4.7 Adsorption using Almond shell and Apricot waste

Both studies made by researchers Duran et. al[51] and Deniz[52] showed potential and feasible results in the removal of dye in aqueous solutions using almond shell as an adsorbent. The adsorption characteristics of the basic dyes onto the almond shells were investigated with respect to the effect of parameters including effect of pH, initial concentration, temperature, etc. The adsorption kinetics of methylene blue, methyl violet, and toluidine blue[51]were analyzed using intraparticle diffusion model, pseudo first order, pseudo second order, and Elovich isotherm model and the pseudo first order model was remarkably described by the adsorption data. The equilibrium adsorption data were shown in terms of Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Tekim isotherm models. The Langmuir isotherm model equation determined the adsorption capacity of almond shell to be 51.02 mg/g for methylene blue, 76.34 mg/g for methyl violet, and 72.99 mg/g for toluidine blue. The adsorption kinetics for methyl orange[52] best fit to the pseudo second order isotherm model. The equilibrium data points out to the Langmuir isotherm model which excellently fits. The maximum monolayer adsorption capacity of the almond shell was found to be 41.34 mg/g for methyl orange.

Önal[53] studied in a batch system, with respect to contact time and temperature, the adsorption of three dyes, namely, methylene blue, malachite green, and crystal violet onto the activated carbon in aqueous solution. The kinetics of adsorption of the three dyes have been studied using six kinetic models, i.e., the pseudo first order, pseudo second order, intraparticle diffusion model, the Bangham equation, Elovich equation, and the modified Freundlich equation. The pseudo second order kinetic equation has shown the best fit for describing the adsorption kinetics of the three dyes. The adsorption capacities of the three dyes decreases in order of malachite green > methylene blue > crystal violet. The amount of adsorption the adsorbent was capable was 79.28 and 90.5 mg/g for methylene blue, 88.75 and 100.77 mg/g for malachite green, and 52.86 and 63.53 mg/g for crystal violet. Erdoğan et al.[54] investigated the removal of Ni (II) ions in the aqueous solution with the use of activated carbon and the adsorption properties under various conditions such as pH, activation temperature, etc. Langmuir isotherm model best fitted in determining the adsorption parameters. The maximum Langmuir adsorption capacity of the activated carbon prepared at 900^{o}C was 101.01 mg/g which is effective at the removal of Ni (II) in an aqueous solution by a 100%. In contrast with the first study, the activated carbon here has got the highest adsorption capacity.

4.8 Adsorption using Alginate Beads

Adsorption study of copper into alginate beads were studied by Mahmoud et al.[55], batch adsorption studies were used to investigate different operational parameters in adsorption process. Results showed that maximum metal ions removal was obtained at pH 5 and for every increase of initial concentration adsorption capacity decreases. The isotherm models used to demonstrate the adsorption were the Langmuir and Freundlich isotherm models where the Langmuir isotherm model suited well having R^2 value of 0.9959 and maximum adsorption capacity was found to be 17.5 mg/g having 87.5 % at room temperature. Immobilization of other plant biomass and materials by calcium alginate as adsorbent has been investigated in various studies[56,57]. Zn(II) and Cu(II) adsorption on immobilized rice bran from aqueous solution was investigated, results showed that at pH 4 and contact time of 120 minutes were the optimum optimum condition for the process[2]. The percent removal of Zn from the aqueous solution was 86.63% while, Cu has 80 % . The results were higher compared to the ca-alginate and activated rice bran adsorbent. Sorption capacity of 67.0 mg/g and 60 mg/g were obtained for Cu(II) and Cd(II) having greater than 90% removal efficiency from the adsorption using alginate immobilized Moringa oleifera[57] .

Table 3. Adsorption Studies using Different Types of Agricultural Biomass as Adsorbent

Type of Adsorbent	Particle Size	Adsorbate	Percentage Removal	Adsorption Capacity	Source
Cucumis melo	<150μm	Fe Pb	90.73% 88.36% (pH 7)	5.3505 mg/g 0.0830 mg/g	Othman et. al[37]
Durian Leaves	-	Fe(II)	81.0 % (pH 6)	3.914 mg/g	Abayati et. al[38]
Sporopollenin	20 μm	Cu(II) Pb(II) Cd(II)	- - -	1.24 mg/g 8.52 mg/g 1.64 mg/g	Unlu et. al[40]
Rice Hulls	-	Pb Cd Sr Cr As	99.43% 97.96% 94.11% 98.93% 98.95%	-	Dipak et. al[42]
Green Alga	-	Ni Pb	77 % 99%	-	

4.9 Other Adsorption Studies using Agricultural Biomass

Tannin, a naturally occurring organic compound that can be found in plants is proven to be a good adsorbent for heavy metals. Investigation of the efficiency of the tannin-based adsorbent on the Adsorption of Cr and Zn metal was studied [58]; Saba Banana (Musa paradisiaca L) a common plant in the Philippines was the main material for this study. The procedure was based on (Hagerman, 2012) where the sample was washed with distilled, sun-dried, ground into powder and treated with 70% acetone. The filtrates obtained from the filtration using Whatmann no. 2 Filter paper where subjected to rotary evaporator. To test the presence of tannin in the sample; Gardiner test, Ferric Chloride test, and Ferrous Sulfate test were all used. Gelated form of the oven-dried filtrate was done by cross-linking of the filtrate with 37% formaldehyde and stirred in an alkaline solution. Tannin resin adsorbent was washed with nitric acid and distilled water to remove all unreacted materials and oven- dried for 80° C. Batch experiments were also done to get the optimum values for pH, initial metal concentration, and adsorbent dosage and contact time. For the Kinetic modeling of the adsorption, two of the most common equation (pseudo-first order and pseudo-second order) were used. Data gathered were fitted to three isotherm models: Langmuir, Freundlich, Dubini-Radushkevich to check the best model to described the adsorption isotherm process. Changing of color for both reference and the sample were observed on the tests that were conducted. Positive results for all the three tests indicate presence of tannin in the extracted sample. Samples from Saba banana bud tannin extract, cross-linked tannin resin adsorbent before and after adsorption of heavy metals were analyze with FT-IR instrument. The IR-spectra from the three samples showed wide and sharp peaks at the –OH stretch phenol. Conversion of –OH to C-O caused the spectra of the cross-linked tannin resin adsorbent to have narrower peak when compared with a normal tannin resin while the IR-spectra of the metal-loaded tannin resin adsorbent showed a broader peak for –OH peak due to possibility of overlapping signals between Metal-O-H and free O-H groups. Researchers found out from the results of the batch experiments that at pH 6 and adsorbent dosage of 0.12 g maximum removal percentages for both metals could be attained.Adsorption slowed down after 40 mins.of contact between the adsorbent and the adsorbate due to the binding sites becoming exhausted thus, achieving equilibrium. Data gathered from the experiments were fitted to different isotherm model to describe the adsorption isotherm process. Langmuir isotherm model best fitted the data from the Cr adsorption with a regression of .9097 while Temkin model having the highest regression value of 0.7185 best fitted the data of Zinc. Both metals followed the Pseudo-second order of reaction.

Utilization of treated rice husk as an adsorbent in the adsorption of Co^{2+} and Fe^{2+} metals was studied[59]. The process of rice husk treatment is started by washing the rice husk with water for the removal of impurities and dried in an oven at the temperature of 50^{o}C for 12 hours. The dried sample was then alkali treated using NaOH in an oil bath for 3 hours. The filtrate was washed several times and halted upon reaching pH 7. The treated rice husk was oven dried at 105^{o}C for 12 hours. Further, the treated sample was carbonized in a furnace, washed with deionized water, and homogenized using mortar and pestle. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used in characterizing the morphology of the rice husk ash (RHA). As for the metal ion analysis, Atomic Absorption Spectroscopy (AAS) was used. Batch experiments were done to obtain the effect of pH of Co^{2+} ions, and adsorbent dosage. In studying the adsorption kinetics, the zeroth, first, second, and pseudo-first order kinetic models were used in describing the adsorption of cobalt (II) and iron (II). In describing the equilibrium data of adsorption of cobalt (II) and iron (II), the isotherm models Langmuir adsorption isotherm and Freundlich adsorption isotherm were used. Characterization of rice husk ash using XRD showed that RHA is mainly amorphous in nature. Surface characterization by SEM showed that RHA is highly porous and have a pore size of approximately 13 micrometers. The porous structure of RHA has a relatively large specific surface area that is favorable for the uptake of metals. The researchers found about the optimum pH of Co^{2+} is 10 and the optimal adsorbent dosage for Co (II) and Fe (II) were 0.2 g and 0.5 g, respectively. From the data gathered, the Langmuir isotherm model best fitted the Co^{2+} adsorption rather than the Freundlich isotherm model with a regression value of 0.9335. However, no isotherm model fitted for Fe^{2+} adsorption.

In the study of Chromium (VI) and Cadmium (II) using human hair as an adsorbent[60]. The collected hair does not undergo any chemical treatment before subjecting to the experiment. Effect of contact time varying from 10 to 120 minutes, and pH such as 2, 4, 7,and 9 was tested using 100 ppm of metal ions for 30 minutes. The adsorption process was describe using Langmuir and Freundlich Isotherm models, while the kinetic rate was describe using pseudo-first and pseudo-second order rate. Experimental data shows that equilibrium was achieved at 70 minutes contact time for Cadmium and the favored ph was at 4 and 7.

Another study was conducted by using acetylated coconut (Cocos nucifera) shell powder based fixed column for the removal of Cr(VI) from inorganic and organic waste[61]. The coconut shell was treated with glacial acetic acid. Fixed-bed column studies were investigated by varying the inlet flow rate, column bed height, initial concentration. The fixed bed column was described using Thomas Model, Adams-Bohart, and Yoon-Nelson Model. Experimental data shows that the highest percent removal was high at flow rate of 0.3 mL/ min., bed height of 18 cm and influent concentration of 20 ppm. Thomas model gives R^2 values ranging from 0.964-0.99, while Adams-Bohart model was in the range of 0.815-0.981. Yoon-Nelson model gives an R^2 values of 0.966, 0.9638, and 0.982 for an inlet flow of 0.3, 0.5 and,1.0 mL/min., for initial concentration varying from 20, 50, and 100 it gives 0.9904, 0.9865, and 0.9813 values, while varying the bed height (12 cm, 15 cm, and 18 cm), R^2 values of 0.966, 0.9357, and 0.9744 was observed. The study shows that from the waste with initial concentration of 12 and 145 ppm the adsorption capacity were 0.737 and 0.085 mg/g. From the experimental data, the researchers concluded that adsorption of metal ions was higher at lower flow rate, higher bed height, and lower initial concentration.

Comparative study on the adsorption capacity of alkali treated peels of saba (Musa acuminata × balbisiana) and lakatan banana (Musa acuminata) was investigated by Carlos et. al[62]. The peels were washed and treated with NaOH solutions. Batch dsorption was performed by varying the pH (3-5) and the adsorbent dosage. The adsorption isotherm used to describe the adsorption process was investigated using the Langmuir and Freundlich isotherm models. The results shows that the optimum pH of $Pb^{2+}$for saba and lakatan banana was at pH 3.0. The Langmuir equation gives an R^2 value of 0.9933, while freundlich gives an R^2 value of 1 for alkali treated lakatan banana. The study shows that the amount of lead decreases as the mass of the adsorbent increases due to the piling of the adsorbent particles reducing its surface area for adsorption.

Study on adsorption of Co(II) and Ni(II) ions using Rambutan peel (Nephelium lappaceum) was investigated by Arbuis et. al. The rambutan peels was treated with 90% ethanol and grinded using 100 mesh sieves. Batch adsorption studies were investigated by varying the contact time for 30 minutes with 3 minutes interval, effect of biosorbent dosage from 0.025g to 5.0 g, and effect of pH such as 4, 7, and 10. Kinetic and isotherm studies were investigated by varying the contact time and the initial concentration. Kinetic models such as Zeroth order, First-order, Second-order, Pseudo-first, and Pseudo-second, while isotherm models such as Langmuir, Freundlich, and Elovich were used. The results showed that the optimum time was 21 minutes for the adsorption, biosorbent dosage of 1.0 g for Ni(II) and 0.5 g for Co(II), and pH 10 was the optimum for the adsorption. The Langmuir adsorption isotherm gives an R^2 value of 0.952 and 0.958 for Co(II) and Ni(II) with a maximum adsorption capacity of 4.878 mg/g and 6.25 mg/g , respectively. The Freundlich equation gives an R^2 value of 0.834 and 0.9596 for

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Co(II) and Ni(II), while the Elovich equation gives a maximum adsorption capacity of 1.2987 and 1.642 for Co(II) and Ni(II). Kinetic studies shows that Ni(II) has an R^2 value of 0.9910 for Pseudo-second order and Co(II) which has an R^2 value of 0.9931[63].

Table 3. Other Types of Adsorbent used in Adsorption Studies.

Type of Biomass adsorbent	**Metal Adsorbate**	**Optimum pH**	**Optimum adsorbent dosage**	**Type of kinetic model**	**Type of isotherm model**	**Adsorption capacity (mg/g)**	**Removal percentage (%)**
Hagonoy leaves (Chromolana Odorata L	Copper (Cu^{2+}) Lead (Pb^{2+})	4.0 4.0	-	-	Thomas Model Yoon and Nelson	-	98.57% 99.64%
Coconut Coire (cocosnuefera)	Cadmium (Cd^{2+}) Cobalt (Co^{2+})	-	1.0 g 0.5 g	Pseudo- 2nd order Zeroth order	Temkin isotherm Dubinin-Radushkevich isotherm	-	75.56% 23.51%
Rice Husk Ash (*Oryza sativa Linn.*)	Cobalt Co^{2+} Iron Fe^{2+}	10 -	0.5 g 0.2 g	Zeroth order 1st order 2nd order Pseudo-1st order	Langmuir isotherm Freundlich isotherm	2.1802 0.8370	-
Saba and Lakatan banana	Pb(II)	3.0	-	-	Langmuir isotherm Freundlich isotherm	-	-
Rambutan Peel	Co(II) Ni(II)	10	0.5 g /1.0 g	Zeroth order 1st order 2nd order Pseudo-1st order Pseudo 2nd order	Langmuir Freundlich Elovich	-	-

5. Conclusion

The journal review attempts to identify and study the corn cob as an efficient and effective adsorbent and compare it to wide range of agricultural waste for their adsorptive capability for the removal of major pollutants such as effluent dyes, heavy metals, and organic contaminants being prominent in aqueous and wastewater solution. These adsorbents poses advantages that are of economic value, generates zero-waste and eco-friendly as it utilizes the waste by products, and abundant in nature. From the published literatures, it was observed that the kinetics of adsorption and mechanism is dependent on the characteristics of the adsorbent surface as well as the operational parameters such as effect of pH, adsorbent dosage, contact time, temperature, and initial concentration. Further, the Langmuir isotherm model along with Freundlich isotherm model best discussed the determination of sorption capacity of corn cob compared to other adsorbents made from biomass. The pseudo second order adsorption kinetics has shown to be best fitted in describing the adsorption kinetics of the corn cob and other biomass adsorbents.

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