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Wastewater Treatment by Using Fruit Waste Derived Adsorbents

Kholdarova Gulsanam Akramjon qizi
Student, Namangan Institute of Engineering and Technology

Abstract: *Numerous studies have been reported to find the applications of fruit-based waste materials for wastewater treatment, and several advanced composite materials with fruit waste have been engineered for specific applications. There are various wastes of fruits such as peels, shell and hulls, pulp, stalk, seeds, bunch, pomace, etc. These wastes come with different elemental compositions and inherent structures and morphologies, which ultimately affect the product. Moreover, among different fruit waste derived adsorbents, the fruit waste peels are considered as promising fruit waste sources for the development of bio-adsorbents due to their high lignocellulosic properties, which facilitate in high elemental composition of carbon. Furthermore, it is found that the use of peels as absorbents can help to adsorb the heavy metals due to presence of polar-organic compounds, which result in formation of chelate with metal ions. Therefore, since the year of 2000, the research interest on fruit peels derived bio-adsorbents has been on the rise gradually.*

Keywords: *wastewater, derived adsorbents, peel, carbonyl, carboxyl, electro conductivity, orange peel, pineapple peel, pitaya peel.*

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Fruit's peel is known as outer protective layer, commonly called as skin or rind, which contains many organic compounds such as carbonyl, phenolic, carboxyl. It is believed, the use of peels as absorbents can help to adsorb the heavy metals due to presence of polar-organic compounds, which can facilitate to form chelate with metal ions. Scientists synthesized chemically activated adsorbents from pomelo peel (PP) to adsorb the chromium (Cr (VI)) heavy metal from aquatic solutions. In their study, to modify PP, they used different types of solid and liquid modifiers. The FeCl3 integrated PP revealed high adsorption efficiency with environmental friendless because of presence of iron ions that helped to precipitate the Cr(VI) ions due to high electrostatic attraction between Fe and Cr(VI). Although, it is well observed that liquid modifiers also show high percentage of Cr(VI) removal, but it is reported to be harsh due to toxic in nature compared to FeCl3. Therefore, F-PP were nominated for further investigation. Consequently, the pore size analysis revealed the presence of Fe ion in sample, where F-PP results exhibit high surface defect, and the porosity of material. As a result, the maximum adsorption of Cr(VI) reached to 93.7% or 21.55mgg^{-1}. We synthesized activated carbons from peels of orange, pineapple and pitaya for the removal of ammonium. These bio-adsorbents were synthesized at 573, 673, 773 and 873K with the residence time of 2h and 4h. The adsorbents were characterized for pH, electro conductivity, CHN elemental analysis, BET surface area and adsorption isotherms, surface composition, functional groups, surface morphology, surface element analysis zeta-potential, and stability. The bio-adsorbents of orange peel and pineapple peel showed better adsorption capacity compared to pitaya peels. Furthermore, the adsorption of ammonia followed pseudo second order reaction and the Langmuir model. Fig. 1 shows synthesis, characterization and utilization of orange, pineapple, and pitaya peel adsorbents. The untreated activated PAA exhibited comparatively high removal efficiency of dye than acid and base activation. The use of base in high concentration certainly results high adsorption, but its use would create alkaline impurities in water. On the other hand, the acid treatment did not convey high adsorption percentage, which might be attributed to the protonation of organic functional groups on PAA. Thus, to make process green and economical, the untreated activated PAA were continued for further assessment. The morphology of activated PAA comprised many pores and rough cracks, which are responsible for high percentage of dye removal. Subsequently, the bio-adsorbent revealed an adsorption efficiency of dye removal up to 80%. at pH (5.43). We developed of magnetized orange peel adsorbents for removal of crystal violet dye from water. The orange peels were washed and later dried, which were then passed through 80 BSS-mesh sieves to remove the coarse and agglomerated particles. Again, the powdered peels were washed, dried chemically treated in presence of 4.0g FeCl3 and 2.0g FeCl2·2H2O in 200mL of double distilled water. The precipitation of Fe3O4 nanoparticles on the orange peel was achieved by a drop wise addition of 10% ammonia. Fig. 2 presents a detailed exhibition of methodological order for the development of orange peel, magnetized orange peel bio-adsorbents and their application.

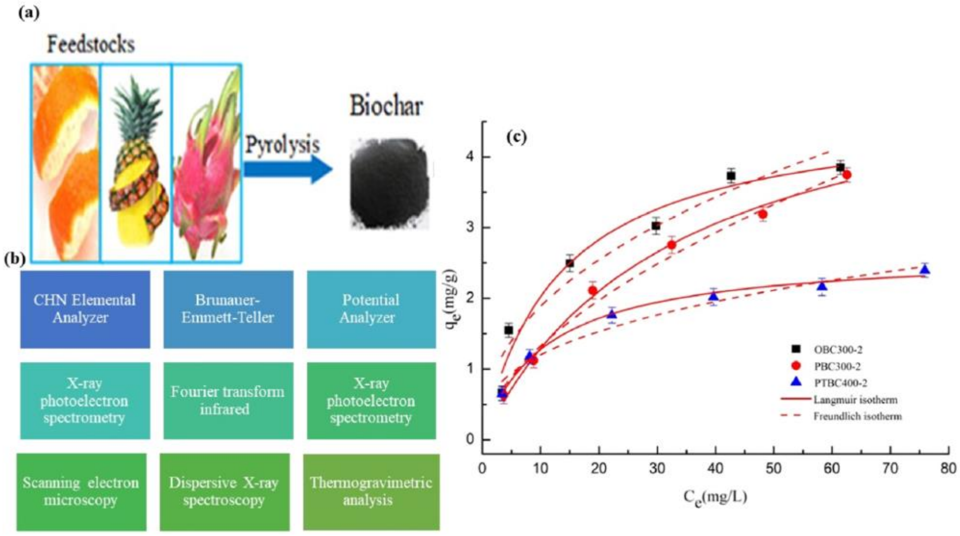

Fig. 1.(a) Synthesis, (b) characterization, (c) adsorption isotherm of three best bio-adsorbents

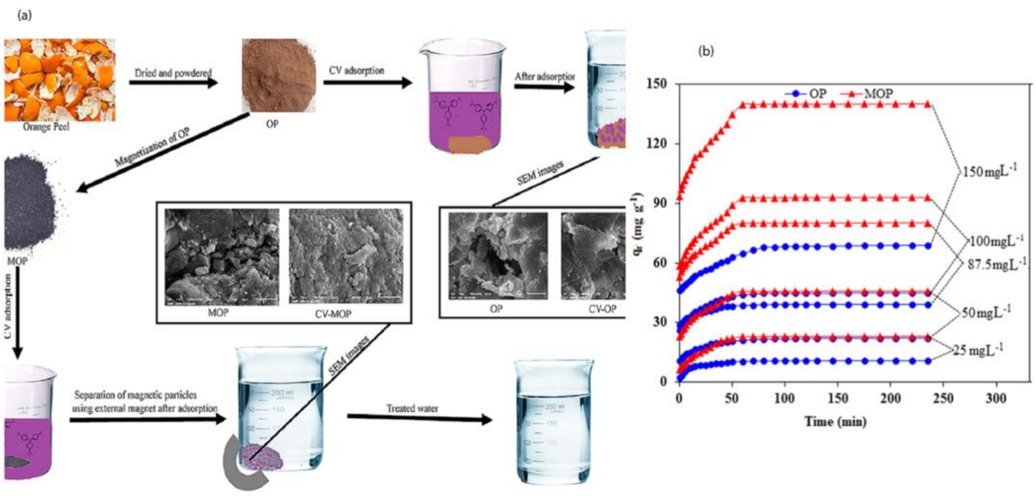

Fig. 2.(a) Methodological procedure for the development of orange peel and magnetized orange peel adsorbents and their application for removal of crystal violet dye from water. (b) Adsorption

capacities of various orange peel and magnetized orange peel adsorbents at 303K, using five different initial concentrations like 25, 50, 87.5, 100, 150mgL^{-1}

Fig. 3. shows comparison of removal of Cr(III), Zn(II) and Cd(II) by using banana, kiwi and tangerine peels powdered samples activated with NaOH at 301K and 2g adsorbent. Results show that highest removal of heavy metal ions was obtained by using Kiwi peel-based bio-adsorbents, followed by tangerine peel-based samples. However, lower adsorption was achieved by using banana peel-based bio-adsorbents. In addition to aforementioned examples, numerous similar adsorbents have been tailored from fruit peels in order to treat wastewater, such as banana, orange, lemon, Citrus maxima, papaya etc.

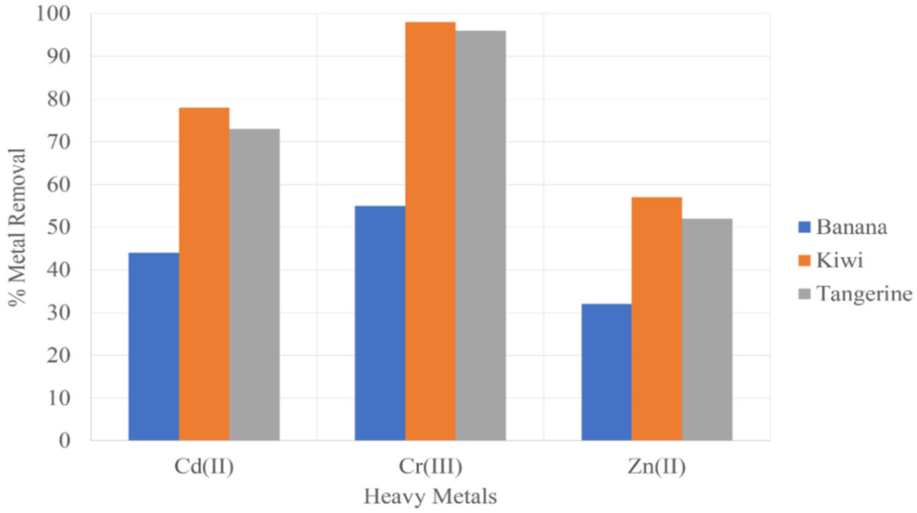

Fig. 3. Removal of heavy metal ions Cd+2, Cr+3 and Zn+2 by using banana, kiwi, and tangerine peel-based adsorbents.

Other fruit waste parts such as fruit stem, pulp, bunch, pomace, stalk have also been utilized for synthesis of bio-adsorbents for wastewater treatment. For instant, most scientists proposed removal of MB dye from contaminated wastewater by using oil palm bunch. In their method, initially cellulose membrane was prepared from oil palm bunch. To find the best cellulose type of membrane, two types of solvents were used with different cellulose to poly (vinylidene fluoride) (PVDF) ratio. Study reported that the optimized cellulose membrane can reject the dye up to 36%. Likewise, banana bunch were utilized for removal of heavy metal from wastewater. Samples were activated with NaOH for enhancing the porosity of bio-adsorbent at different weight percentages via hydrothermal method. Study reported that NaOH chemically interacted first with carbon and produced the C-OH based chemical compound, which further reacted with Cu(II) and trapped the metal impurity as a (CxO)2 Cu(II). After optimizing the reaction parameters, 95% adsorption of Cu (II) was achieved. Based on isotherms and kinetic models, it was reported that heterogeneous pores or multilayer adsorption of Cu(II) on surface loop of bio adsorbent takes place. Besides, we utilized the oil palm empty fruit bunch for the synthesis of nano cellulose (NC) based super-bio-adsorbents for wastewater treatment. The biomass derived activated carbons were functionalized with sulfuric and phosphoric acid via hydrolysis process. Their study reported that compared with phosphoric acid, the sulfuric acid based functionalized activated carbons as NCs delivered higher remediation capacities due to the formation of sulfonic group on the surface, whereas the removal percentage of Pb(II) metal was achieved up to 86%. Similarly, oil palm was uitilized empty fruit bunch for the synthesis of biodegradable adsorbents via physio-chemical activation for removal of cibacron blue 3G-A (CB) dye. Study revealed that prepared bio-adsorbents had smooth surface with high porosity, that is why almost complete removal of CB dye was achieved. Furthermore, the stem of cornulaca monacantha fruit was used for the preparation of bio-adsorbent by sharma and coworkers for the removal of congo red dye. Their study exhibited that the maximum adsorption percentage of dye reached up to 97.19% at 328K. Several other studies report the development of fruit leave derived BAs for efficient removal of water pollutants. Banana pseudo stems are well recognized for the development of bio-adsorbents. The pseudo stems of banana transport nutrients from the soil to its fruit. Once banana fruit is harvested, they turn into waste. The banana stem derived BAs have been used for the removal of Cu(II), Hg(II), Pb(II), safranin, methyl red, and several other pollutants from water synthesized banana stem fiber for the removal of Hg(II). The HCl modification of banana stem fiber increased the cellulose accessibility leading to more interaction of Hg(II) and banana stem fiber. The activation of banana stem fiber with HCl in vacuum at 373K increased adsorption capacity of Hg(II) from 28 to 372mgg^{-1}. Fig. 4 presents XRD and FTIR analysis of raw and chemically modified banana stem fiber adsorbents.

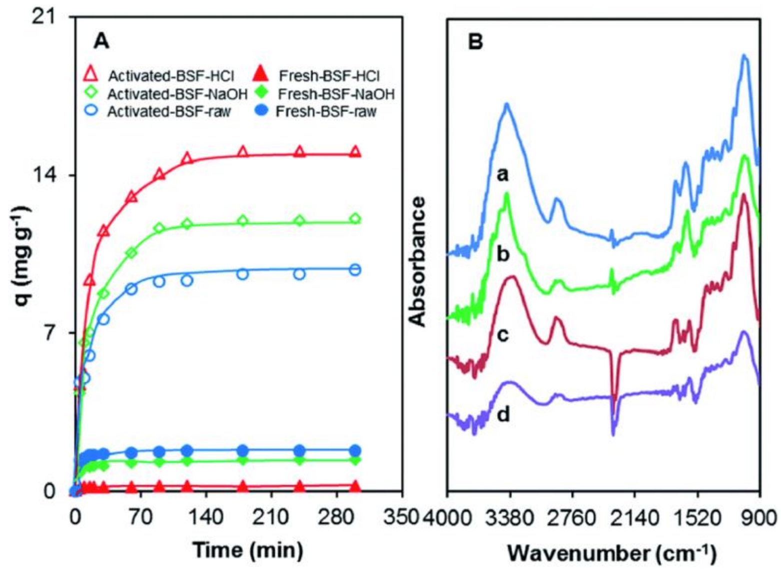

Fig. 4.(A) XRD and (B) FTIR spectra of (a) banana stem fiber raw (BSF-raw), (b) banana stem fiber-sodium hydroxide (BSF-NaOH) and (c) banana stem fiber- hydrochloric acid (BSF-HCl).

Fruit shell and hull-based bio-absorbents. The shell and hulls of fruits also play an important role as adsorbent materials due to their rigid structure, which provide the long-life cycle adsorbents. ZnCl2 activated carbon composite materials were prepared for removal of MB by using shell of cola. In our method, the cola shell was carbonized with $ZnCl_2$ at 773K under inert atmosphere. Subsequently, the black powder was neutralized by washing with acidic solution, then dried for further use as an adsorbent. The optimization parameters included reaction time, adsorbent dosage, and pH for the prepared adsorbent. The maximum removal of up to 90% or 87.37mgg^{-1} of MB was obtained at the dosage of 0.1g and 3hr. reaction time at pH of 3.5. Furthermore, the comparative study between each adsorption isotherm models were reported, which suggest that a monolayer sorption proceeds over a surface having a finite number of adsorption sites, which is reported as suitable pore structure to deposit the organic impurities.

Likewise, to other parts of fruit, fruit seeds and stones have also been utilized to purify the contaminated water. It is reported that the fruit stones and seeds are rich in lignin source, which can provide adsorbents materials with carbon range of 45–50%. Seeds and stones of several fruits such as apricot, cherry, corn cob, dates, peach, olive have been used to develop the bio-adsorbents for wastewater treatment. The olive stones have been widely used with physical and chemical activation to remove the organic pollutants and heavy metals. The olive oil assimilated with KOH were used to remove heavy metal impurities such as Cu, Cd, Zn, Fe and Ni. Synthesis of K_2CO_3 activated-olive stones is reported for MB removal. Similarly, for the removal of phenol, the olive stone derived activated carbons with the mixture of CO_2, HCl and $ZnCl_2$ have also been investigated. Fig. 5. presents SEM micrographs and EDX spectra of Putranjiva roxburghii seed, modified Putranjiva roxburghii seed and Ni(II) adsorbed modified Putranjiva roxburghii seed adsorption. Where the chemical modification was carried out by using epichlorohydrin and NaOH. Figure shows carbon content more than 50% in the samples. The application of three types of fruit seeds such as Carica papaya (CP), nephelium mutabile (NM), and euphoria malaiense (EM) were investigated for wastewater treatment. Among them, CP seed-based coagulants revealed excellent coagulation, which removed turbidity up to 95.5% at 7.5pH. A single step carbonization method with NaHCO3 for the removal of MB. We synthesized natural core-shell structure activated carbon beads from Litsea glutinosa seeds. Their study revealed that the as prepared bio-adsorbent were exhibited highly porous structure having size of 5mm. The bio-adsorbent exhibited high cycling stability, which could maintain more than 90% after five repeated cycles of use. Removal of Cr(VI) is reported up to 98% at 2pH and 120min by using BAs derived from yellow mombin seeds.

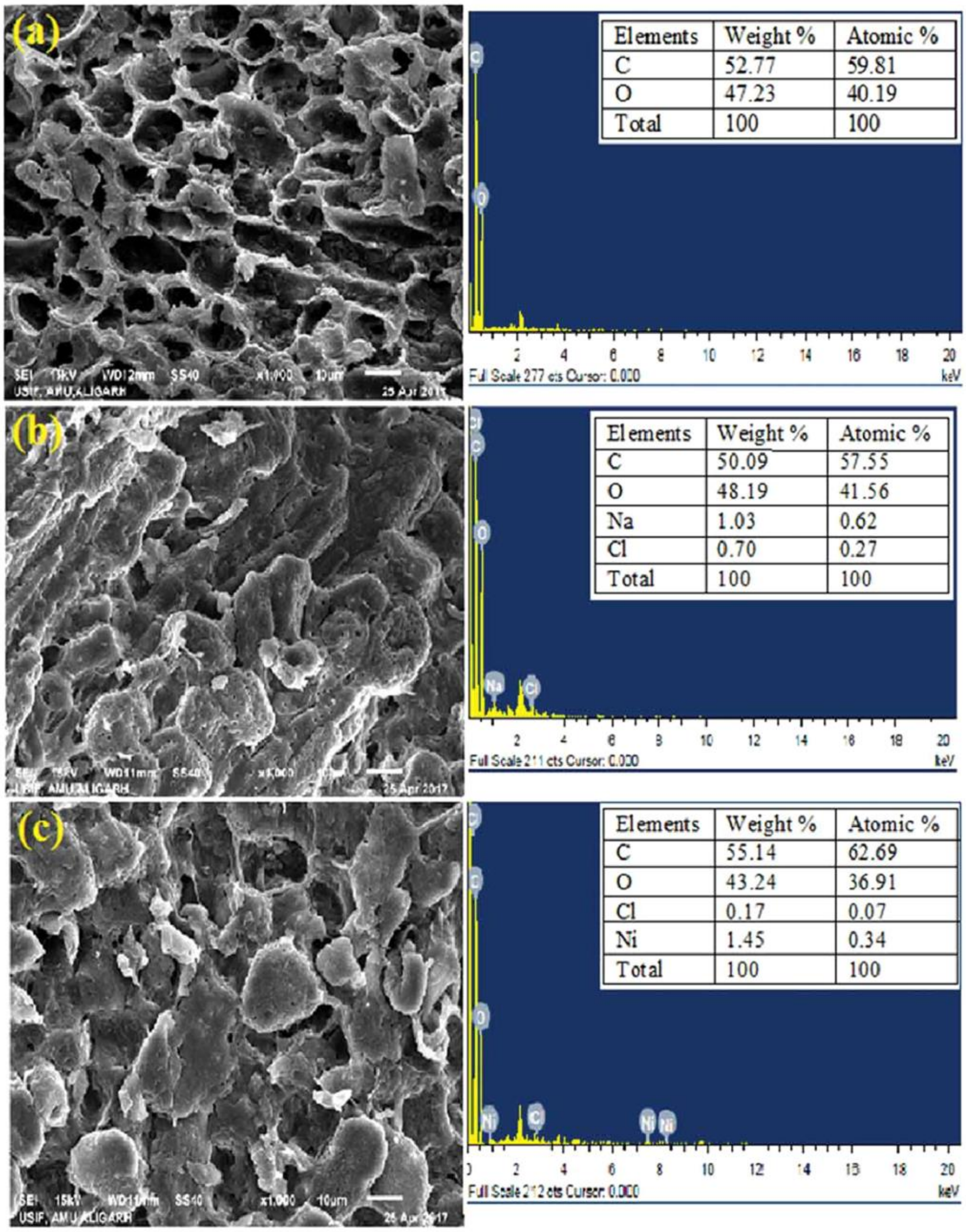

Fig. 5. Morphology and ultimate analysis of (a) Putranjiva roxburghii seed (b) modified Putranjiva roxburghii seed (c) Ni(II) adsorbed modified Putranjiva roxburghii seed adsorption.

Furthermore, the activated carbons were synthesized derived from papaya seeds. We found that prepared bio-adsorbents possess high potential toward MB removal from wastewater. Similarly, the use of papaya seeds based bio-absorbent to remove Pb+2 and Cd+2. And synthesis of bio-adsorbents from yellow mombin fruit stones for the removal of textile dye Dianix® royal blue CC. The ground stones of yellow mombin fruit were washed, dried, and later activated with phosphoric acid and sodium hydroxide above 773K. Influence of various parameters, such as pH, reaction time, and temperature. Study reported a maximum monolayer adsorption capacity of 147.47mgg^{-1} and 82.28mgg^{-1} for the acidic and basic treatments of activated carbons, respectively.

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