Nigerian Research Journal of Engineering and Environmental Sciences 8(2) 2023 pp. 403-418
p ISSN: 2635-3342; e ISSN: 2635-3350

Nigerian Research Journal of Engineering and Environmental Sciences
Journal homepage: www.rjees.com

Review Article

Simultaneous Removal of Heavy Metals and Organics using Biosorbents: A Review

***[1]Agbale, N.R., [2]Arinkoola, A.O., [2]Ogunleye, O.O. and [2]Agarry, S.E.**

[1]Department of Chemical Engineering, Faculty of Chemical Engineering, Delta State University Oleh Campus, Nigeria.
[2]Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomosho.
*agbalenr@delsu.edu.ng

http://doi.org/10.5281/zenodo.10441900

ARTICLE INFORMATION

Article history:
Received 13 Aug. 2023
Revised 28 Oct. 2023
Accepted 10 Nov. 2023
Available online 30 Dec. 2023

Keywords:
Biosorbents
Multi-component adsorption
Heavy metal
Organics
Modified isotherms

ABSTRACT

This work is a compilation of the studies done over the past decade on the simultaneous removal of co-existing heavy metals (HMs) and organics using biosorbents. A summary of the origin and classification of biosorbents were compiled. The mechanisms of biosorption of HM and organics were also studied, with emphasis on the effects of the functional groups of the biosorbents. Furthermore, the optimum operating conditions of the solution pH, kinetics and isotherms were also investigated. An attempt was made to investigate the synergistic and antagonistic effects of the pollutants on each other. The biosorption process were mostly suited to the Langmuir and Freundlich isotherms, while the pseudo second order (PSO) kinetics provided the best fit for most of the adsorption studies. The study also revealed that while adsorption capacities are usually higher in single component adsorption (SCA) systems, adsorption of HMs and organics in multi-component adsorption (MCA) systems can be more than that in their individual SCA systems. The study showed the non-utilization of the modified isotherms for the equilibria studies of multi-component adsorption system, this may lead to the inaccuracy of the results obtained.

1. INTRODUCTION

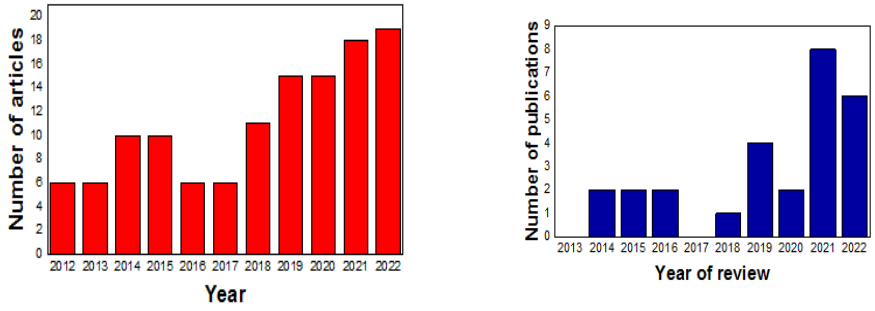
The activities of man in his quest for improved lifestyles culminate into the depletion and contamination of the resources of the environment, which are essentially tailored to provide the habitat and food for the sustenance of its flora and fauna. These consequently affect the organisms in the food chain adversely. Industrialization comes with its perks, but not without the discharge of recalcitrant and harmful wastes into

water bodies, landfills and dumpsites (Sigdel et al.,2016). These wastes which constitute environmental pollutants may be organic (dyes, hydrocarbons, pesticides, antibiotics, etc.). or inorganic (heavy metals, chlorides, phosphates, nitrates etc.). These harmful substances are responsible for diverse disease conditions in humans. Dye causes skin and eye inflammation, are harmful to the respiratory system and carcinogenic (Salih et al., 2019). Heavy metals such as Cd damage vital organs of the body. Cr (VI) and Pb (II) are carcinogenic and disrupt the nervous system (Luo et al., 2016). Benzene and other organics disrupt the normal structural and numerical arrangement of the human cells (Sigdel et al., 2016). The simultaneous sequestration of these pollutants in waste water constitutes serious treatment procedural problem such as the affinity of the adsorbates towards a particular adsorbent, as well as the synergistic and antagonistic effects of the adsorbates towards each other (Luo et al., 2016; Ajiboye et al., 2021).

It becomes imperative therefore, to design multifunctional adsorbents that are suitable for removing the mixed components, and also to include the interactive factors of the components in the equilibrium models. To address the former, research studies on the use of biosorbents which are synthesized from wastes of plants and animals, and microbes have been extensively conducted, while the application of extended isotherms are employed in the study of MCA equilibria for the later. These green low-cost materials can be modified to improve their adsorptive properties, mechanical properties, handling, and reuse properties (Rosales et al., 2017). The design of real life processes will be less cumbersome with the use of extended isotherms for multi-compnent adsorption.

Presently, the methods employed in the treatment of waste water are coagulation, flocculation, membrane separation, chemical precipitation, electrochemical oxidation, ion exchange and adsorption processes (Wisniewska and Nowicki, 2019). Adsorption is generally a preferred route, since the other processes are characterized by problems which have limited their applications in waste water treatment. Chemical precipitation and electrochemical treatment are effective only in waste water with a high concentration of metal ions and chemical consumption is high. A large quantity of secondary pollutants are also generated in these processes (Wang and Chen, 2006). Ion exchange and membrane technology require a high cost of operation and complex operational technology are encountered (Gautam et al., 2014). The merits of adsorption process include low cost, ease of operation, availability of materials and efficient output (Lambert, 2019; Arif et al., 2021).

This review covers a broad study on the use of biosorbents for the multi-component adsorption of heavy metals and organics. Empirical findings have been presented on the sources, modification, and adsorptive characteristics of biosorbents. The adsorptive behaviour of these class of pollutants in multicomponent adsorption of heavy metals and organics are also studied. Special attention has been paid to the interactive effects of the pollutants in multi-polluted systems, with the view to elucidate the research trends and gaps in knowledge. An extensive search of the studies carried out on this subject in the last decade was conducted on Google Scholar. Figure 1 (a) and (b) are the numbers of researches articles and reviews respectively published on the simultaneous adsorption of heavy metals and organic in the last decade.



(a) (b)

Figure 1: (a) Number of published articles in the past decade on the simultaneous removal of HM and organics on biosorbents, (b) Review articles on the simultaneous removal of HM and organics on any type of adsorbent and by different processes

2. BIOSORBENTS

Biological based adsorbents of different genre have been used extensively for the sequestration of pollutants in the environment (Wang and Can, 2009). The biosorption process has been given great attention in researches because biomass is abundant, cheap and the modification processes are relatively cost effective (Gupta et al., 2015). The precursor used for the syntheses of bioadsorbent can be classified according to their origins as plant, animal and microorganisms .

Figure 2 is the chart showing the percentage of different biomass used in studying the simultaneous adsorption of HM and organics on biosorbents obtained from studies conducted from 2012 to 2022 on Google Scholar.

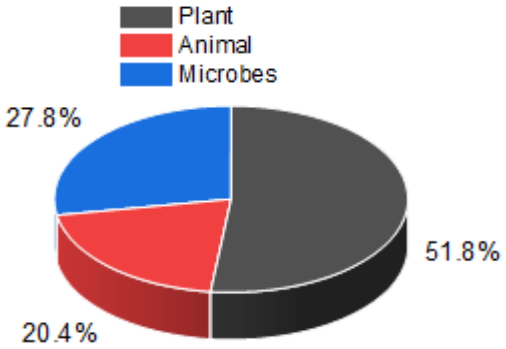


Figure 2: Ratios of biomass used as precursors of biosorbents for the study of simultaneous adsorption HM and organics in the articles published in the past decade

2.1. Biomass of Plant Origin

Biomass from plants are mostly agricultural wastes like rice husks (Xiang, et al., 2018; Ramola, et al., 2019), bagasse (Yao, et al., , 2014; Hoang, et al., 2022), shells of pods (Shakya and Vithanage, 2022), fruit and vegetable peels (Vigneshwaran et al., 2021), stems (Thines et al.,2017), barks (Ighalo and Adeniyi, 2020) , pseudo stems of banana (Chakhtouna et al., 2021) and many others. The preference for these materials as adsorbents is due to their biocompatibility, availability, and low cost. Modifications method include physical (Gautam et al., 2014) thermal conversion into biochar or hydrochar (Zhang et al, 2017), chemical activation (Ranasinghe et al., 2018), immobilization into hydrogels, and treatment with magnetic or electropositive metals

The conversion of biomass to biochar is a commonly used pathway to the modification of biomass which is necessitated by the need to produce a low-cost substitute of activated carbon. Biochars are modified by engineering processes for further valorization of their surface and chemical properties (Yao, et al., 2014; Wang, et al., 2021). The methods of modification include ball milling (Xiang, et al., 2020), fabrication of engineered biochar, in which the biochar is combined with other organic or inorganic materials before or after thermal treatment (Arif, et al., 2021). The different constituents of biochar composites are mineral (Yao et al., 2014; Premarathna et al., 2019; Liu et al., 2021) metals (Li et al., 2018; Creamer et al., 2016) microorganisms (Feng, et al., 2020), Layered Double hydroxide (LADH) (Li et al., 2016). Biochar is also immobilized in hydrogels to improve on their mechanical stability (Wang et al., 2018).

In the study conducted on Google Scholar, there were no results returned for the multicomponent adsorption of pollutants onto ball milled biochars. The use of pristine ball-milled biochar was predominantly for the removal of organics like methylene blue (MB) (Lyu et al., 2017) antibiotics (Huang, Zimmerman et al., 2019), volatile organic Carbons (VOC) (Xiang et al., 2020). Ball-milled biochar showed great improvement in surface area, pore volume, zeta potential, and an increase in oxygen containing functional groups of the biochar (Lyu et al., 2017). Biochar-mineral composites are composites of biochar with small quantity of

minerals such as clays, calcite, $CaCO_3$, layered double hydroxides (LDH), Zeolites (Ahmad et al., 2019; Vithanage et al,. 2020; Arif et al., 2021). The surface functional groups, surface charge, surface area, ash content which are generally altered in the process of modification of biochar result in the change of the adsorption efficiency. Other procedures used for the modification of plant based biosorbents include the acid and alkali treatment of the biomass. The acids used include HNO_3, HCl and H_2SO_4, H_3PO_4 (Zafar et al., 2007; Gautam et al., 2014). These treatments were reported to valorize the adsorptive power of the biomasses.

2.2. Biosorbents of Animal Origin

Biosorbents of animal origin are synthesized from the wastes of animals, which include the shells of mollusk (Popoola, 2019; Mukkanti and Tembhurkar, 2022) and crustaceans (Jeon, 2019; Zhang et al., 2020), egg shell (Slimani et al., 2014; Wang et al, 2021), bones of vertebrates (Ghiaci et al., 2014) and keratin proteins of furred and feathered animals. Exoskeletons of mollusk and crustaceans are good sources for the synthesis of chitosan and chitin and their derivatives, they are composed of chitin (15-40% for crustacean), calcite (20-50% for crustacean) and proteins (20-40% for crustaceans) (Yan and Chen 2015; Dai et al., 2017). Hydroxyapatite (HA), a biosorbent that has been widely used for the adsorption of pollutants such as heavy metal (Ghiaci et al., 2014) is a major inorganic component of animal bone.

2.3. Microorganisms Biosorbents

Microorganisms are a class of biosorbents which have been used in the bioremediation of heavy metals and organics. A wide range of microorganisms of the prokaryotes and the eukaryotes family have been used, and these include *Pseudomonas sp*. (Singh, et al., 2013; Al Disi et al. 2022), Bacillus *sp, Neopestalotiopsis clavispora* (Hassan et al. 2018), *Streptomyces rimosus*., (Wu et al., 2018), micro algae. Different methods of the modification of microorganism are employed to improve on the adsorptive properties of the biosorbent. Zhang et al. (2020) synthesized magnetized chitosan immobilized *Aspergillus sydowii* for the simultaneous biosorption of Cd(II) and trichlorofon in waste water. The characterization of the chitosan immobilized *Aspergillus sydowii and* showed differences in morphology, functional group and surface areas., these also enhanced the adsorption efficacy of the Aspergillus sydowii based biosorbents. Their surface area was increased by more than one third the surface area of the magnetized chitosan, while biosorption efficiency increased for Cd (II) and trichlorofon. Microorganisms are also used in their pristine form for environmental sequestration of HM and organics. *Pleurotus mutilus*, fungal waste was used to remove Cr(II) and congo red dye from aqueous solution in its dried and communited form. The surface functions contained both basic and acidc group which increased its affinity for the adsorption of dyes and heavy metals. (Alouache, et al., 2021).

3. MECHANISM OF ADSORPTION OF ORGANICS AND HEAVY METALS ON BIOSORBENTS

The mechanism of the co-adsorption of pollutants on biosorbents is important for evaluating the process efficiency. It is dependent on the physical and chemical characteristics of the biosorbents, these include chemical composition, reactivity, hydrophilicity, surface charge, molecular size, and solubility (Elgarahy et al., 2021). Results from instrumentation analyses such as the Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and X-Ray diffraction (XRD together with the pH, equilibrium and kinetics studies are used to validate the techniques of the biosorption system. The shift of the peaks of functional groups and the change in biosorbent composition are considered (Gupta et al., 2015). Numerous mechanisms can also take place at the same time in the process of biosorption and these are physisorption, (E.g. van de Waals forces of interaction), chemisorption such as electrostatic attraction, chelation and complexation coordination (Bhattacharje et al., 2020). Chemisorption requires that there is an abundant of surface functional group that aid in binding the pollutants to the biosorbents (Renu et al., 2017), Electrostatic attractions (ion exchange) occurs through the interactions between charged groups (anions or cations) of the biosorbent and those of the pollutants. The concentration of ions and electroneutrality determine the transfer of ions from both the biosorbent solid phase and the sorbate liquid phase (Rashed and Palanisamy, 2018). The formation of complex compounds by the reaction of cations with solvents, molecules or other simple

ions is chelation. The compounds formed comprise a centralized atom which may be charged or not, and a group of ions and neutral molecules surrounding it. (Amilton et al,. 2019), The process is beneficial for the sequestration of heavy metals in the environment.

4. EFFECTS OF pH ON THE SIMULTANEOUS ADSORPTION ORGANICS AND HEAVY METALS ON BIOSORBENTS

One important parameter for the optimization of the MCA process is pH on which the nature of the biosorption mechanism is dependent (Gupta and Balomajumder, 2015; Bashir et al., 2019). pH is a function also of the surface functional groups of the adsorbents, the extent of ionization of these functional groups, as well as the physiochemical interaction of species in the multi-component system (Bashir et al., 2019). Functional groups which are affected by the pH include the hydroxyl, amides, amines, carbohydrates, calcites

4.1. Effect of pH on the Simultaneous Adsorption of HMs and Dyes

The pH of a solution, apart from modifying the surface charge of the biosorbents also affects the degree of ionization of adsorbents in solution (Tanzifi et al., 2016). The pH studies for the removal of Cu (II), Cd (II) and amido black on chitosan/diatomaceous earth (CSDE) biosorbent was affected at a pH of 2-9. The maximum adsorption capacity of Cd (II) and Cu (II) were 77 and 88 mg/L at pH of 7 and 8 respectively. This is in contrast to the adsorption efficiency of the amido dye which decreased as the pH decreased from 112 to 40.33 mg/L at pH 2 and 9. The HMs started precipitating at pH 7, so 7 was the optimal pH for the adsorption of the cations. The pH_{PZC} of the adsorbent was 5.8, at low pH between 1-6, its surface is positively charged because of the protonation of the --NH_2 group. This causes a repulsion between the cations and the adsorbents thereby limiting its precipitation out of solution. Also, in alkaline solution, the adsorbent becomes negatively charged which enhances the repulsion between the anionic dye and the adsorbent which reduced the removal of the dye (Salih et al. 2019). The study of the effect of pH on the adsorption of Cu (II) and Reactive Green (RG) 6 dye on immobilized mixed fungal biomass showed an increased adsorption capacity of the pollutants from pH 2-5, after pH of 5, the capacity reached a constant value then gradually declined from pH 6 to 9. This occurrence was attributed to the presence of strong electrostatic forces between adsorbent and pollutants in the acidic medium, and repulsive forces in the alkaline solution (Saravanan et al., 2021).

4.2. Effect of pH on the Simultaneous Adsorption of HMs and Antibiotics

The co-adsorption of tetracycline (TC), Zn (II) and Cu (II) was investigated using hybrid silicate-hydrochar (MgSi-HC) composite. The pH study on TC was carried out at pH values of 2-11. The adsorption capacity of the biosorbent on TC increased steadily from pH 2 and remained unchanged in the pH range 4-7. Thereafter, a waning of the adsorption capacity started at pH greater than 8, due to the repulsive forces between negatively charge MgSi-HC and negatively charge TC species. pH values of 2-7 were used to study the effect of changing pH on the adsorption of C(II) and Zn (II). This pH range was used to inhibit the formation of insoluble salts of Cu (II) and Zn (II) at pH > 7 (Deng, et al., 2019). The adsorptive power of MgSi-HC for Cu(II) and Zn(II) increased from pH 2 -5, and remained constant from pH 5-7. At pH > 3.3 (which is the PZC of the biosorbent), the surface of MgSi-HC becomes negatively charged, this leads to greater electrostatic for of attraction between the metallic adsorbates and the biosobent. The presence of TC (+) and a positively charged surface of MgSi-HC at pH 3.3 causes electrostatic repulsion between MgSi-HC, the metallic ions and TC(+), therefore limiting their adsorption (Deng, et al., 2019).

4.3. Effect of pH on the Simultaneous Adsorption of HMs and other Hydrocarbons Compounds

The study of pH on the adsorption of heavy metals and organics showed that pH had greater effect on the adsorption of HM than the polar organic compounds because the solubility of the HMs in solution is depended on the pH (Simantiraki and Gidarakos, 2015). For some of the biosorbents, HM uptake coexisting with HCs in solution was found to increase with increase in pH. However, at pH > 7, the precipitation of metallic hydroxides hinders the efficiency of the biosorbent towards the removal of HM (Pap et al., 2017;

Qu et al., 2020). The organics which also exhibited higher adsorption capacity at higher pH were adversely affected after the optimum pH due to the ease with which they are degraded (Chen et al. 2011). The study conducted by Gupta and Balomajumder (2015) on the simultaneous adsorption of Cr (VI) and phenol on *Bacillus* sp. immobilized onto tea waste showed that the optimum pH for the adsorption of both pollutants in their binary solution was 5. It was posited that the similar pH uptake mechanism could be due to the nature of the chemical interaction of the components with the cells present on the surface of the tea waste. The low adsorption capacity of biosorbents at low pH is also attributed to the presence of H^+ ions, which compete with the HMs on the biding sites they easily get adhered to. While the Cr (VI) removal was facilitated by the affinity between the ions and biosorbents, the phenol removal depended on the Van der Waals force and Π-Π attractive forces between the phenol rings and the microbes on the biomass surface (Gupta and Balomajumder, 2015). There is no result recorded in the studies to show that pH affects HM and organics in different ways in SCA and MCA systems.

5. KINETICS OF THE SIMULTANEOUS REMOVAL OF HM AND ORGANICS ON BIOSORBENTS

The adsorptive behavior of adsorbents is a function of the kinetic and equilibria models of the system. Table 1 shows the correlated kinetics and equilibrium models of some MCA systems on biosorbents. The adsorption kinetics are also employed in describing the mechanism of the adsorbents in the process and aid in the determination of the kinetics rate controlling steps (Wu et al,. 2018; Liu et al. 2020) The best fitted rate model amongst those considered is determined by statistical analysis of either the linear or no-linear regression of the kinetics.

5.1. Kinetics of the Simultaneous Removal of HM and Dyes

The kinetics of most of the systems in which heavy metals and dyes were removed simultaneously followed the PSO models. This was established by the low values of the error functions and the closeness of the correlation coefficient to 1 as well as the closeness of the evaluated adsorption capacity (q_{calc}) to the experimental one. q (exp). Higher values of the rate constant, K meant that the adsorbate requires a shorter time to be adsorbed (Albadarin et al., 2017; (Ramalingam et al., 2018; Keshawy et al., 2022).

5.2. Kinetics of the Simultaneous Removal of HMs and Antibiotics

The kinetics of the simultaneous removal of antibiotics and heavy metals were studied either in SCA or MCA systems. The kinetic study by Cuprys et al (2021) on the simultaneous removal of As, Cd, Pb and Ciprofloxacin (CIP) on chitosan functionalized Pine biochar (CH-PB) was conducted for the single and multi-component polluted water. From the R^2 and Chi squared vales, the study showed that the PSO mechanism was well suited to the adsorption of CIP alone in solution and with metallic mixture. The kinetics for As was best described by the PFO alone in solution, with the other metals and with the metals and CIP. The kinetics for the adsorption of Cd were PSO individually and with the metals and CIP, while the best fit for it in metallic mixture solution was the Elovich model. The adsorption of Pb were well suited by the Elovich model in the SCA and MCA system of metallic ions in solution, while the PFO provided a good fit for the mixed metal and TIC solution (Cuprys et al., 2021).

5.3. Kinetics of the simultaneous removal of HM and Hydrocarbon Compounds

The study on the simultaneous removal of HC and their derivative and HM also entails the study of the kinetic behavior to establish the mechanism of adsorption. The kinetics of the adsorption study of a multi polluted a solution made up of 114 mg phenol, 43 mg Cu and 51 mg/L using corn cob biochar silica-alginate had a better correlation with the PSO model than the PFO model (Shim et al., 2014). Also, the co-removal of Cu (II) and pitch-pine biochar encapsulated in alginates show that the kinetics followed the PSO model in which the q_{calc} were close to the q_{exp} (Park, et al. 2022). The application of *Bacillus sp.* supported on tea waste for the simultaneous removal of Cr (VI) and phenol was well fitted to the PFO, PSO and intraparticle models. (Gupta and Balomajumder, 2015).

Table 1: Equilibrium adsorption models, kinetics adsorbent of the simultaneous biosorption of Heavy metals and organics

Adsorbent	Pollutants	Equilibrium model	Kinetic	Interactive s effects	References
Bacillus sp. immobilized tea waste tea waste biomass	Phenol and Cr (VI)	Freundlich model and Redlich–Peterson for phenol and Cr(VI) in MCA system non-modified competitive Redlich–Peterson and extended Langmuir were very suitable for Cr(VI) and phenol,	PSO for phenol and Cr (VI)	Synergistic effect of Cr(VI) in the MCA system	(Ankur and Balomajumder, 2015)
Steam-activated bamboo-derived biochar	Cu and tetracycline	Langmuir in the MCA for both of the pollutants			(Wang et al., 2019)
Corn cob silica alginate beads	Phenol, Cu(II), Cd(II)	Langmuir for Cu(II) and Cd(II)	PSO for Cu(II) and Cd(II)	.	(Shima et al. 2014)
Chitosan biochar beads	Ciprofloxacin, Pb(II), As(II) and		PSO for CIP, Pb, AS, Cd in the mixed mixture		(Cuprys et al., 2021)
Wood residue	Cu Reactive blue cyprodinil	Cu Langmuir RB and cyprodinil Sips	PSO		(Velinov et al., 2019)

6. EQUILIBRIUM STUDIES OF MULTI-COMPONENT ADSORPTION OF HM AND ORGANICS

The equilibrium studies of adsorption process are conducted to determine the efficiency of the adsorbents in a set of given conditions under constant temperature. Isotherms are used to define the efficiency and behavior of the adsorbents, and are dependent on the type of adsorbent, adsorbates, pH of the solution and temperature (Abin-Bazaine et al. 2020). The isotherms provide information on the interactive relationship between the adsorbents and adsorbates, as well as that between the adsorbates of a multi-polluted water. Isotherm models obtained from experimental data are used in the design of industrial processes (Girish, 2017; Al-Ghouti and Da'ana, 2020). Table 2 is a representation of the isotherms models commonly used in the co-adsorption of HM and organics on biosorbents. Also shown in Figure 3 are the ratios of MCA and SCA equilibrium studies in the last decade on the adsorption of HM and organics on pollutants from results obtained on Google scholar.

Some of the equilibrium studies conducted in literature for SCA process were modelled with the MCA isotherms, while in some other studies, no mention was made if the study were carried out in the MCA or not. The commonly used isotherms in literature for the isotherm modelling of the simultaneous biosorption of heavy metals are the Langmuir and the Freundlich isotherm, the modified competitive and non-competitive forms of these isotherms are available in literature but not widely used.

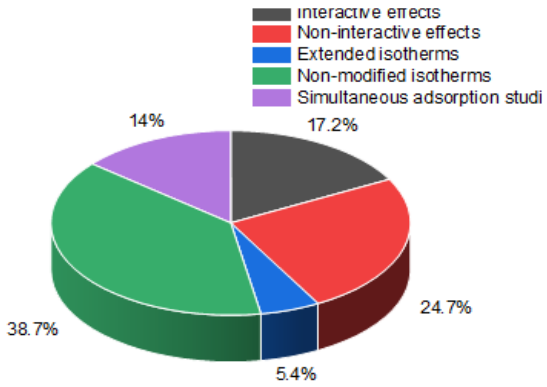


Figure 3: The percentages of multicomponent studies in which the interactive and non-interactive effects of pollutant, modified isotherms, non-modified isotherms and simultaneous adsorption experiments

6.1. Equilibrium Behaviour of Simultaneous Biosorption of dye and HM

The interactive effects of the pollutants on each other can be determined from the equation

$$I_{\varepsilon} = \frac{q_{m,i}}{q_{s,i}} \quad (1)$$

Where:

I_{ε} = interactive effect and $q_{m,i}$ and $q_{s,i}$ (mg/g) are the adsorption capacity in the MCA and SCA solutions at equal initial concentrations.

When $\frac{q_{m,i}}{q_{s,i}} > 1$, there is synergistic interaction meaning that there is an increase of the adsorption capacity of the pollutants in the presence of other pollutants.

When $\frac{q_{m,i}}{q_{s,i}} < 1$, there is antagonistic interaction, meaning that there is a decrease in the adsorption capacity of the pollutants in the presence of other pollutants.

When $\frac{q_{m,i}}{q_{s,i}} = 1$, there is no interaction and the adsorption capacity remains unchanged (Girish, 2017; Yu et al., 2018).

The adsorption of MB and Co (II) on banana peel biochar, as demonstrated by Yu et al., (2018) followed the Langmuir isotherm. At low initial concentration of Co (II) in the multicomponent system, Iε =1for Co (II) indicated that there was no interaction between Co (II) and MB in the MCA system. However, at high initial concentrations, Iε >1 for Co (II), the adsorption of Co (II) in the presence of MB was enhanced. Functionalized chitosan from shrimp shell was used to study the simultaneous removal of Pb^{2+} ions and alizarin red S dye. Langmuir, Freundlich and Temkin isotherms were used to conduct the equilibrium adsorption studies, Langmuir isotherm also had a good fit with the experimental data of the adsorption of Pb^{2+} ions and alizarin red S dye, maximum capacities were 50.25 and 57.14 mg g−1 for ARS and Pb^{2+} respectively. However, the multicomponent isotherms, nor the interactive effects of the dye and HM were not studied (Poorebrahim et al., 2016). The commonly used isotherms for MCA processes are shown in Table 2.

Table 2: Commonly extended used isotherms in the simultaneous adsorption of HM and organics on biosorbents

Isotherm model	Model Equation	Brief description	References
Extended Langmuir	$q_{e,i} = \frac{q_m K_L C_{e,i}}{1 + \sum_{i=1}^{N} K_L Ce}$	This model describes the Langmuir isotherm in MCA solutions	(Singh and Balomajumder, 2016)
Modified competitive Langmuir	$q_{e,i} = \frac{q_m K_{L(} C_{e,i}/\eta i)}{1 + \sum_{i=1}^{N} K_{L(} Ce/\eta i)}$	The interactive factor, η_i is included	(Gupta and Balomajumder, 2015)
Extended Freundlich	$q_{e,1} = \frac{K_F, 1. Ce, 1}{C_{e_{1}^{1}}^{x_1} + y_1 C_{e,2}^{z_1}}$	This is the Freundlich for MCA modified for binary adsorption	(Gupta and Balomajumder, 2015)
Non-modified Redlich Peterson	$q_{e,i} = \frac{K_{P,C_p,i}}{1{:}.1{:} \sum_{J=1}^{N} \begin{pmatrix} \alpha_{RP,J} \cdot C_{e,J}^{\beta 1J} \\ 1 \end{pmatrix}}$		(Gupta & Balomajumder, 2015)
Modified Redlich Peterson	$q_e = \frac{q_{m,i} K_{L,i} (Ce, i/\eta_{L,i})}{1 + \sum_{J=1}^{N} K_{L,J} \left(C_{e,J} \Big/ \eta_{L,J} \right)}$		(Gupta and Balomajumder, 2015)

6.2. Equilibrium Behaviour of Co-existence of Antibiotics and HM

Reports on the study of the equilibrium behavior of HMs and antibiotics coexisting in solution on biosorbent were not readily available. The available studies were conducted by Inyang et al. (2015) and Wang et al. (2010). In both studies, the modified isotherms were not used to study the equilibrium models of MCA systems, even if the adsorption occurred in MCA systems. The adsorption of lead and sulfapyridine on carbon nanotube-modified biochar was well correlated to the Langmuir-Freundlich isotherm, but there was no available information to indicate if the process occurred in MCA or SCA adsorption system (Inyang et al.2015). The Langmuir and Freundlich models were used predict the equilibrium behaviour of Cu^{2+} and TC adsorbed on steam activated bamboo-derived biochar, and the Langmuir isotherm provided the best fit for the two adsorbates in the binary and single solutions. The K_L values of the SCA system were lower than those of the binary adsorption, suggesting a better affinity of both pollutants towards the adsorbent in the binary system (Wang, et al., 2019).

6.3. Equilibrium Behaviour of the Co-existence of HC and HM

A few articles had included equilibria studies in the studies of the simultaneous adsorption of HM and HCs. Although Pap et al (2017) studied the effect of initial concentration, there was no mention made of the equilibria behavior of the system. The equilibria studies of most of the MCA systems on biosorbents were not reported (Shima et al., 2014; Lou et al., 2016; Wang et al., 2017; Yasmin et al, 2019; Al Wi´sniewska et al., 2021; Disi, et al 2022). However, Sulaymon et al (2012) reported the equilibria behavior of the adsorption of Pb (II) and phenol on dead and living microbes by the application of Langmuir, Freundlich and R-P isotherms to the SCA systems, while the extended forms of these isotherms were applied in the MCA systems. The modified Langmuir was not used, so the correction factor could not be accounted for. The maximum adsorption capacities were more for all the components in the SCA systems, 16.56 and 27.15 mg/L of phenol and Pb (II) respectively on the active microbes, 41.48 and 83.43 mg/L of phenol and Pb (II) respectively on the dead microbes. The q_m of the pollutants in the MCA were 30.20 and 36.79 mg/L of phenol and Pb (II) respectively on the live microbes 70.0183 and 89.878mg/L of phenol and Pb (II) on the dead microbes. The affinity of the adsorbates towards the biosorbents were in the same range in the MCA and SCA, 0.05 for Pb (II) in the MCA and SCA, (on dead microbes) 0.08 – 0.09 for Pb (II) in MCA and SCA (on dead and living organisms), and approximately 0.08 for phenol in the MCA and SCA on living microbes. The reduction in the removal of phenol was affected by the presence of Pb (II) due to the increased attraction of Pb (II) towards the adsorption sites, which were negatively charged.

7. COMPETITIVE ADSORPTION OF HMS AND ORGANICS IN AQUEOUS SOLUTION

Generally, the interactive effects of the adsorption of HMs and organics could either be antagonistic, synergistic or of non-effect on the adsorption of either of them. Studies have been carried out in which the concentration of one pollutant is kept constant while the other(s) is / are increased. Most of the competitive adsorption studied where in binary systems while a few took place in ternary system and quaternary systems. In the study on the simultaneous removal of Cu (II), sulfamethoxazole (SMX) and tylosin (TY) were conducted on nano-hydroxyapatite modified biochar in aqueous solution, the removal of TYL and SMX in the MCA systems differed. The adsorptions of TYL was repressed by thepresence of Cu (II) and SMX, while the adsorptions of the SMX was enhanced by Cu (II) and limited by TYL. The reduction of TY in the presence of Cu (II) was more than that caused by the presence of SMX. Since the adsorbed mass of Ty reduced by 13.36% and 41.04% and by 9.92 and 38.69% with Cu (II) only, and a mixture of Cu (II) and SMX respectively. This occurred because there HM and antibiotics had to compete for the available sites. The pH of the solution at which the studies were carried out was 6, which implied a surface negative charge on the biosorbent. Since TYL and Cu (II) had the same charges at this Ph, there would be a competition for the available sites, from the electrostatic interactions between TYL and the sorbent. The interactions between the biosorbent and TYL, are the same as for SMX and the biosorbent too, this also will result in the competition between the two antibiotics for the available sites. As a result, the antagonism suffered by TYL in the presence of Cu (II) and SMX increased tremendously. The adsorption efficiency of SMX followed the order SMX with Cu (II) > SMX with TYL (simultaneously) >SMX (alone) SMX with TYYL This is because the adsorbed Cu(II) provided an extra sites for the adsorption of the SMX. The adsorption of Cu (II) was enhanced by the presence of SMX and TYL, however, the adsorption increased more in the presence of TYL to 18.15 and 51.62 mg/g while it was 9.85 and 44.53 mg/g in the presence of SMX. The presence of TY). The competition between SMX and TYL results in the reduced efficiency of TYL and SMX, and with Cu (II) in the same solution (Li et al. 2020).

In another study, the competitive adsorption of Co (II) and MB on banana peels biochar was evaluated. The ratios of the adsorption capacities were used to determine the interactive relationship between the pollutants. The study revealed that the sorption capacity of Co (II) at low concentration in solution with MB had I_{eff} approximately equal to 1, implying that the adsorption efficiency of Co (II) in SCA system was the same as for the MCA system at low concentrations. This, however, is different for the interactions of the pollutants which occur at high concentrations of MB solution with Co (II). The I_{eff} for Co (II) was > 1, implying that MB exerted a synergistic effect on the adsorption of Co (II) at its high concentration in together in solution with MB. The adsorptive power of the biosorbent for the adsorption of Co (II) in the HM MCA system was 105,63 mg/g while it was 115.93 mg/g in the Co (II)/MB system at high concentrations of Co (II) (C_i values are from 60 mg/L and more) (Yu et al., 2018).

There are studies which have shown that the removal capacity of the biosorbents is the same for the SCA and the MCA systems. Velinov et al (2019) reported that the multi-component adsorption capacity of Cu (II), reactive blue 19 and cyprodinol from aqueous solution on lignocellulose biosorbent were the same in the MCA as in the SCA of each of the components (Velinov, et al., 2019). Another phenomenon which occurs in the co-removal of pollutants on biosorbents id the reduction of adsorption capacity of the HM in MCA systems and, while the adsorption of the organic remains the same in the MCA as in the SCA system. Lou et al observed that the adsorption of Cr (VI) in the SCA solution of the metal was 1.13 times greater than in the MCA solution of Cr(VI) and trichloroethylene. While the adsorption of trichloroethylene both the MCA and SCA systems remained the same. The adsorption was conducted on agarose-Fe nanoparticles hydrogel (Luo et al. 2016). The multicomponent biosorption studies of Cu(II)/Zn (II) and tetracycline conducted by Deng et al. (2020) also indicated the improved adsorption efficiency of the HMs in the co-adsorption of HMs and high concentration of TC. The presence of HM at low concentration also increased the adsorption capacity of the biosorbent for TC. This was attributed to the chelation of TC with HMs for the formation of complexes, which limits the water affinity of the TC, thereby resulting in a lower electrostatic repulsion between the biosorbent and the antibiotic.

8. CONCLUSION AND FUTURE PROSPECTS

Environmental remediation processes proffer solutions to the abatement of increasing environmental distress caused by the emissions of effluents. Process and materials deployed for the removal of these pollutants are also studied in-depth for an optimal throughput better removal and minimization of secondary wastes. This has necessitated the attention given to the application of biosorbents in the sequestration of waste water, however, studies are focused more on the removal of single solutes. In cases where multi-pollutants were simultaneously removed, attention was not given to the interactive effects of the pollutants in solution. This may constitute some problems in the adaptation of such studies to real waste water, since waste water from most industries are multi-polluted. The investigations conducted in this study revealed that biosorbents are effective in the co-sorption of HM and organics polluted water, although most studies were on binary MCA systems. Looking forward, efforts should be put into synthesizing biosorbents that are well suited for the removal of multiple pollutants from waste water. Also, attention should be given to the study of the removal of more than two pollutants simultaneously. Finally, this could be achieved by conduction a field application of the biosorbent by using them to treat real waste such as produced water. The application of the extended isotherms should be used in the equilibrium studies of the MCA systems, and an inclusion of the interaction effects is needed in the equilibrium study of the MCA adsorption systems. These will ensure better results in the analyses of the processes and ease the design for industrial applications.

9. ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Prof. Jean Mulopo of the Department of Chemical and Metallurgical Engineering, University of Witwatersrand for the use of his laboratory facilities.

10. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

Abin-Bazaine, A., Trujillo, A. and Olmos-Marquez, M. (2022). Adsorption Isotherms:Enlightenment of the Phenomenon of Adsorption IntechOpen, doi: 10.5772/intechopen.104260.

Adeniyi, A. and Ighalo, J. (2019). Biosorption of pollutants by plant leaves: an empirical review. *J.Environ.Chem.Eng, 7*(3),

Ahmad, M., Usman, R. R. and Al-Wabel, M. (2019). Engineered biochar composites with zeolite, silica, and nano - zerovalent adsorbent iron for the efficient scavenging ochlortrecycline from aqueous solution. *Environmental Science and Pollution, 2615*, pp. 15136-15152.

Ahsana, M. A., Jabarib, V., Islama, T., Kim, H., Hernendez-Viezcasa, J., Lin, Y., . . . NoveronaJ.C. (2018). Green synthesis of a highly efficient biosorbent for organic, pharmaceutical,heavy metals pollutants removal:Engineering surface chemistry of polymeric biomass of spent coffee waste. *Journal of Water Processing, 25,* pp. 309-319.

.Ajiboye, T., Oyewo, O. amd Onwudiwe, D. (2021). Simultaneous removal of organics and heavy metals from industrial waste water: A Review. *Chemosphere, 262*(2021), //doi.org/10.1016/j.chemosphere.2020.128379.

Al Disi, Z., Al-Ghouti, M. and Zouari, N. (2022). Investigating the simultaneous removal of hydrocarbons and heavy metals by highly adapted Bacillus and Pseudomonas strains. *Environmental Technology & Innovation, 27*(10253),

Al Sagheer, F., Al-Sughayer, M., Muslim, S. and Elsabee, M. (2009). extraction and charaterization of chitin and chitosan from marine sources in Arabian Gulf. *Carbohydrate Polym, 77*(2), pp. 410-419.

Albadarin, A., Solomon, S., Kurniawan, T., Mangwansi, C. and Walker, G. (2017). Single, simultaneous and consecutive biosorption of Cr(VI) and Orange II onto chemicall modified massau stone. *Journal of Environmental Management, 204*(2017), 365-374.

Alexander, R., Filho, J., A. M., de Assis, I. and de Olivera, T. (2020). Influence of pyrolysis temperature and feedstock on the properties of biochars produced from agricltural and industrial wastes. *Journal of analytical and applied physics*.

Al-Ghouti, M. and Da'ana, D. (2020). Guidelines for the use and interpretation of adsorption isotherm models: A. *Journal of Hazardous Materils, 393*,

Alouache, A., Selatnia, A., Sayah, H., Khodja, M., Moussous, S. and Daoud, N. (2021). Biosorption of hexavalent chromium and Congo red dye onto Pleurotus mu mutilus biomass in aqueous solutions. *International Journal of Environmental Science and Technology*..

Amilton, B. B., André de Albuquerque, V. and Denise, C. R. (2019). Recovery of metals by ion exchange process using chelating resin and sodium dithionite. *Journal of Materials Research and Technology,, 8*(5), pp. 4464-4469.

Arif, M., Liu, G., Yousaf, B., Ahmed, R., Irshad, S., Ashraf, A., . . . Rashid, M. (2021). Synthesis, characteristics and mechanistic insight into the clays and clay minerals -biochar surface interactions for contaminants removal. *Journal of Cleaner Production.*

Bashir, A., Malik, L., Ahad, S., Manzoor, T., Bhat, M., Dar, G., & Pandith, A. (2019). Removal of heavy metal ions from aqueous system by ion-exchangeand biosorption methods. *Environmental Chemistry Letters, 17*, pp. 729-754.

Bhattacharje, C., Dutta, S. and Saxena, V. (2020). A review on biosorptive removal of dyes and heavy metals from wastewater using watermelon rind as biosorbent. *Environmental Advances*. doi:.

Chakhtouna, H., Benzeid, H., Zari, N., Qaiss, A. and Bouhfid, R. (2021). Functional CoFe2O4-modified biochar derived from banana pseudostem as an efficient adsorbent for the removal of amoxicillin from water. *Separation and Purification Technology, 266*. doi:.

Chen, L., Liu, F., Liu, Y., Dong, H. and Colberg, P. (2011). Benzene and toluene biodegradation down gradient of a zero-valent iron permeable reactive barrier. *J.Hazard.Mater, 188*, pp. 110-115.

Creamer, A., Gao, B. and Wang, S. (2016). Carbon dioxide capture using various metal oxyhydroxide–biochar composite. *Journal of Chemical Engineering, 283*, pp. 826-832

Cuprys, A., Maletskyi, Z., Rouissi, T., Ratnaweera, H., Brar, S., Knystautas, E. and Drogui, P. (2021). Insights into the Simultaneous Sorption of Ciprofloxacin and heavy metals using functionalized biochar. *Water, 13*(2768). Doi;.

Dai, L., Tan, T., Li, H., Zhu, N., He, M., Zhu, Q., . . . Zhao, J. (2017). Calcium-rich biochar from the pyrolysis of crab shell for phosphorus removal. *Journal of Environmental Management, 198*, pp. 70-74.

Deng, J. L., Weia, X., Liua, Y., Lianga, ,. J., Songa, B. and Huang, W. (2020). Hybrid silicate-hydrochar composite for highly efficient removal of heavy metals and antibiotics: Coadsorption and mechanism. *Chemical Engineering Journal*,

Deng, J., Li, X., Wei, X., Liu, Y., Liang, J., Tang, N. S. and Cheng, X. (2019). Sulfamic acid modified hydrochar derived from sawdust for removal of benzotriazole and Cu (II) from aqueous solution: adsorption behavior and mechanism,. *Bioresour. Technol, 290*(2019),

Deng, J., Zhang, X., Zeng, G., Gong, J., Niu, Q. and Liang, J. (2013). Simultaneous removal of Cu(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. *Chemical Engineering Journal, 226*, pp. 189-300.

Dong, F., Yan, L., Zhou, X., Huang, S., Liang, J., Zhang, W., . . . H. (2021). Simultaneous adsorption of Cr(VI) and phenol by biochar-based iron oxide. *Juornal of Hazardous MAterial, 416*.

Elgarahy, A., Elwakeel, K., Mohammad, S. and Elshoubaky, G. (2021). A critical review of biosorption of dyes, heavy metals and metalloids from waste water as an efficient and green process. *Cleaner Engineering Technology*. doi:https://doi.org/10.1016/j.clet.2021.100209.

Feng, F., Chen, X., Wang, Q., Xu, W., Long, L., Nabil El-Masry, G., . . . Yu, X. (2020). Use of Bacillus-siamensis-inoculated biochar to decrease uptake of dibutyl phthalate in leafy vegetables. *Journal of Environmental Management*, pp. 1-8.

Gautam, R., Mudhoo, A., Lofrano, G. and Chattopadhyaya, M. (2014). Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. *Journal of Environmental Chemical Engineering, 2*(1),pp. 239-259.

Ghiaci, M., Dorotskar, N. and Gil, A. (2014). Chicken bone ash as an efficient metal biosorbent for cadmium, lead, nickel, and zinc from aqueous solutions. *desalination and water Treatment, 52*(16-18), pp. 3115-3121.

Girish, C. (2017). Various isotherm models for multicomponent adsorption: A review. *International Journalmof Civil Engineering, 8*(10), pp. 1-7

Gupta, A. and Balomajumder, C. (2015). Simultaneous removal of Cr(VI) and phenol from binary solution using Bacillus sp. immobilized onto tea waste biomass. *Journal of Water Process Engineering, 6*(2015), pp. 1-10.

Gupta, V., Nayak, A. and Agarwa, S. (2015). Bioadsorbents for remediation of heavy metals: Current status and their gfuture propects. *Environ. Eng. Res, 20*(1), pp. 1-18.

Han, J., Du, Z., Zou, W., Li, H. and Zhang, C. (2015). In-situ improved phenol adsorption at ions-enrichment interface of copper ions and phenol. *chemical Engineering Journal, 262*(2015). Doi

Han, X., Liang, C., Li, T., Wang, K., Huang, H. andYang, X. (2013). Simultaneous removal of cadmium and sulfamethoxazole from aqueous solution by rice straw biochar. *Bioremediation and Biotechnol, 13*(7), pp. 640-649.

Hassan, S., Kout, M., Nafady, N., & Hassan, E. (2018). Potentiality of Neopestalotiopsis clavicpora ASU1 in biosorption of cadmium and zinc. *Chemosphere, 202*, pp. 750-756.

Hoang, L. P., Nguyen, T., Van, H., Yılmaz, M., Hoang, T., Nguyen, Q., . . . Nga, L. (2022). Removal of Tetracycline from aqueous solution using composite adsorbent of ZnAl layered double hydroxide and bagasse biochar. *Environmental Technology & Innovation, 28*, doi:

Huang, J., Zimmerman, A., Chen, H. and Gao, G. (2019). Ball milled biochar effectively removes sulfamethoxazole and sulfapyridine antibiotics from water and wastewater. *Environmental Pollution, 258*. doi:

Ighalo, J. and Adeniyi, A. (2020). Adsorption of pollutants by plant bark derived adsorbents: An empirical. *Journal of Water Process Engineering, 35*,

Inyang, M., Gao, B., Zimmerman, A., Zhou, Y., & Cao, X. (2015). Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars. *Environ Sci Pollut Res, 22*, pp. 1868-1876.

Jeon, C. (2019). Removal of Cr(VI) from aqueous solution using amine-impregnated. *Journal of Industrial and Engineering Chemistry, 77*, pp. 111-117.

Keshawy, M., Kamal, S., & Abdel-raouf, M. (2022). Synthesis and investigation of green hydrogels for simultaneous removal of of mercuric cations and methylene blue from aqueous solutions. *Egypt. J. Chem, 65*(5), pp. 325 -33.

Lambert, J. (2019). Organic pollutants Adsorption on Clay minerals. In *Developments in Clay Science*, pp. 195-253).

Li, R., Wang, J., Gaston, L., Zhou, B., Li, M., Xiao, R., . . . Zhang, X. (2018). An overview of carbothermal synthesis of metal–biochar composites for the removal of oxyanion contaminants from aqueous solution. *Carbon, 129*, pp. 674-687.

Li, R., Wang, J., Zhou, B., M.K, A., Ali, A., Zhang, Z., . . . Mahar, A. (2016). Enhancing phosphate adsorption by Mg/Al layered double hydroxide functionalized biochar with different Mg/Al ratios. *Science of the Toital Environment, 559*, pp. 121-129.

Li, Y., Wang, Z., Xie, X., Zhu, J., Li, R., & Qin, T. (2016). Removal of Norfloxacin from aqueous solution by clay-biochar compositee prepared from potato stem and natural attapulgite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. doi:.

Li, Z., Wang, Z., Wu, X., & Li, M. (2020). Competitive adsorption of tylosin, sulfamethoxazole and Cu(II) on nano-hydroxyhapitite modified biochar in water. *Chemosphere, 240,*

Liu, G., Liu, L., Zhou, J., & Jin, R. (2021). Interaction between hexavalent chromium and biologically formed iron mineral-biochar composites: Kinetics, products and mechanisms. *Journal of Hazardous Material, 405*, doi:.

Liu, J., Yang, X., Liu, H., Cheng, W., & Bao, Y. (2020). Modification of calcium-rich biochar by loading Si/Mn binary oxide after NaOH activation and its adsorption mechanisms for removal of Cu(II) from aqueous solution. *Colloids and Surfaces, 201*,.

Luo, F., Chen, Z., Megharaj, M. and Naidu, R. (2016). Simultaneous removal of trichloroethylene and hexavalent chromium by green synthesized agrose-Fe nanoparticles hydrogel. *Chemical Engineering Journal, 204*(2020), pp. 290-297.

Lyu, H., Gao, G., He, F., Zimmerman, A., Ding, C., Tang, J. and Crittenden, J. (2017). Experimental and modelling investigation of ball-milled biochar for the removal of aqueous methylene blue. *Chemical Engineerimng*. doi:

Mukkanti, V. and Tembhurkar, A. (2022). Taguchi optimization for water defluoridation by thermally treated biosorbent developed from the waste snail shells. *Journal of Dispersion Science and Technology*,.

Murtaza, G., Ditta, A., Ahmed, Z., Usman, M. F. amd Akash, A, T. (2021). Co-biosorption potential of Acacia nilotica bark in removing Ni and and aminoazobenzene from contaminated watewater. *Desalination and Water Treatment, 233*, pp. 261-270.

Pap, S., Knudsen, S. T., Radonic, J., Maletic, S., Igic, S. M. and Sekuli, M. T. (2917). Utilization of fruit processing industry waste as green activated carbon for the treatment of heavy metals and chlorophenols contaminated water. *Journal of Cleaner Production*, pp. 958-972.

.Park, S., Lee, J., Kim, J., Kang, G., Kim, H. and Choi, Y. (2022). Adsorptive behavior of Cu2+ and benzene in single and binary solutios onto alginate composite hydrogel beads containing pitch pine-based biochar. *Ploymer, 14*(3468),

Poorebrahim, F., Ghaedi, F., Dashtian, K., Hidari, M. and Kheirandish, S. (2016). Simultaneous removing of Pb2+ and alizarin red S dye after their complexation by ultrasonic waves coupled adsor[ptio process. *Ultrasonics Sonochemistry*. doi:doi:

Popoola, L. (2019). Characterization and adsorptive behaviour of snail shell-rice husk calcined particles towards cationic dye. *Heliyon, 5*. doi:.

Premarathna, K., Rajapaksha, A., Eilhan, B., Kwon, E., Bhatnagard, A., Ok, S. and Vithanag, m. (2019). Biochar-based engineered composites for sorptive decontamination of water: A review. *Chemical Engineering Journal*, pp. 536-550.

Ramalingam, B., Parandhaman, T., Choudhary, P. and Das, S. (2018). Biomaterial Functionalized Graphene-Magnetite Nanocomposite: A Novel approavh for simultaneous removal of anionic dyes and heavy metal ions. *ACS Susutainable Chem Eng,* pp. 6328-6341

Ramola, S., Belwal, T., Li, C., Wang, Y. L., Yang, S. and Zhou, C. (2019). Improved lead removal from aqueous solution using novel porous bentomite and calcite biochar composites. *Science of the Total Environment.*

Ranasinghe, S., Navaratne, A. and Priyantha, N. (2018). Enhancement of Adsorption Characteristics of Cr(III) and Ni(II) by Surface Modification of Jackfruit Peel Biosorbent. *Journal of Environmental Chemical Engineering.*

Rashed, M., & Palanisamy, P. (2018). Adsorption and Ion Exchange Properties of Zeolites for Treatment of Polluted Water. In *Xeolites and thier Application.* Intech Open.

Renu, M., Singh, K., Upadhaya, S. and Dohare, R. (2017). Removal of heavy metals from wastewater using modified agricultural adsorbents. *Materials Today: Proceedings, 4*(9), pp.10534-10538.

Rosales, E., Meijide, J., Pazos, M. and Sanromá, M. (2017). Challenges and recent advances in biochar as low-cost biosorbent: from batch assays to continuous systems batch. *Bioresource Technology*.

Salih, S., Mohammed, H., Abdullah, G., Kadhom, M., & Tushar, K. G. (2019). Simultaneous Removal of Cu(II), Cd(II), and Industrial Dye onto a composite chitosan biosorbent. *Journal of Polymers and the Environment*.

Saravanan, A., Karishma, S., Senthil Kumar, P., Varjani, S. and Yaashika, P. (2021). Simultaneous removal of Cu(II) and reactive green 6 dye from wastewater using immobilized mixed fungal biomass and its recovery. *Chemosphere, 271*.

Shakya, A. and Vithanage, M. (2022). Influence of pyrolysis temperature on biochar properties and Cr(VI) adsorption from water with groundnut shell biochars: Mechanistic approach. *Environmental Research, 215*

Shim, J., Lima, J., Sheab, P. and Oha, B. (2014). Simultaneous removal of phenol, Cu and Cd from water with corn cobsilica-alginate beads. *Journal of Hazardous Materials, 372*, pp.129–136.

Sigdel, A., Jung, W., Ming, B., Minsun, L., Choi, U., Timmes, T., . . . Jeon, B. (2016). Concurrent removal of cadmium and benzene from aqueous solution by powdered activated carbon impregnated alginate beads. *Catena*,

Simantiraki, F. and Gidarakos, E. (2015). Comparative assessment of compost and zeolite utilisation for the simultaneous removal of BTEX, Cd and Zn from the aqueous phase: Batch and continuous flow study. *Journal of Environmental Management, 159*, pp.218-226.

Singh, N. and Balomajumder, C. (2016). Simultaneous removal of phenol and cyanide from aqueous solutionby adsorption onto surface modified activated carbon prepared fromcoconut shellNeetu. *Journal of Water Process Engineering, 9*(2016),pp. 233-245.

Singh, R., Bishnoi, N., Kirrolia, A. and Kumar, R. (2013). Synergism of Pseudomonas aeruginosa and Fe0 for treatment of heavy metal contaminated effluents using small scale laboratory reactor. *Bioresource Technology, 127*, pp.49-58.

Slimani, R., El Ouahabi, I., Abidi, F., El Haddad, M., Regti, A., Laamari, M., . . . Lazar, S. (2014). Calcined eggshells as a new biosorbent to remove basic dye from aqueous solutions: Thermodynamics, kinetics, isotherms and error analysis. *Journal of the Taiwan Institute of Chemical Engineers, 45*(4), pp.1578-1587.

Sulaymon, A., Abbood, D. and Ali, A. (2012). Competitive biosorption of phenol and lead from synthetic wastewater omto live and dead microorganisms. *Desalination and Water Treatment, 45*(1-3),pp. 331-342.

Thines, K., Abdullah, E., Mubarak, M. and Ruthiraan, M. (2017). Synthesis of magnetic biochar from agricultural waste biomass to enhancing route for waste water and polymer application: A review. *Renewable and Sustainable Energy Reviews*, pp.257-276.

Velinov, N., Mitrovic, J., Kostic, M., Radović, M., Petrović, M., Bojić, B., & Bojić, A. (2019). Wood residue reuse for a synthesis of lignocellulosic biosorbent: characterization and application for simultaneous removal of copper (II), Reactive Blue 19 and cyprodinil from water. *Wood Sci Technol, 53*, pp.619-647.

Vigneshwaran, S., Sirajudheen, P., Karthikeyan, P. and Meenakshi, S. (2021). Fabrication of sulfur-doped biochar derived from tapioca peel waste with superior adsorption performance for the removal of Malachite green and Rhodamine B dyes. *Surfaces and Interface*.

Vithanage, M., Ashiq, A., Ramanayaka, S., & Bhatnagar, A. (2020). Implications of layered double hydroxides assembled biochar composite in adsorptive removal of contaminants: Current status and future perspectives. *Science of the Totqal Environment, 737*(1).

Wang, B., Gao, B., and Wan, Y. (2018). Entrapment of ball-milled biochar in Ca-alginate beads for the removal of aqueous Cd(II). *Journal of Engineering and Industrial Chemistry, 61*(25), pp.161-168.

Wang, J., and Can, C. (2009). Biosorbents for heavy metals removal and their future. *Biotechnology Advances, 27*, pp. 195-226.

Wang, J. and Chen, C. (2006). Biosorption of heavy metals by Saccharomyces cerevisiae: a review. *Biotechnol. Adv*, pp. 427-451.

Wang, L., Wang, J. and Wei, Y. (2021). Facile synthesis of eggshell biochar beads for superior aqueous phosphate adsorption with potential urine P-recovery. *Colloids and Surfaces A: Physicochemical andEngineering Aspects, 622*,

Wang, R., Huang, D., Liu, Y., Zhang, C., Lai, C., Wang, X., . . . Xu, P. (2019). Synergistic removal of copper and tetracycline from aqueous solution by steam-activated bamboo-derived biochar. *Journal of Hazardous Materials*.

Wang, S. O., Tsang, D., Alessi, R. J., Mašek, O., Bolan, N., & Hou, D. (2021). Biochar composites: Emerging trends, field successes and susutaimanility implications. *Wiley*, pp. 14-38

Wang, S., Biana, S., Liua, J., Lia, J., Xua, S. and Liang, S. (2021). Highly adsorptive pristine and magnetic biochars prepared from crayfish shell for removal of Cu(II) and Pb(II). *Journal of the Taiwan Institute of Chemical Engineers*, pp. 1-11.

Wang, S., Zhong, S., Zheng, X., Xiao, D., Zheng, L., Yang, Y., . . . Sheng, Z. (2021). Calcite modification of agricultural waste biochar highly improves the adsorption of Cu(II) from aqueous solution. *Journal of Environmental Engineering, 9*,

Wi´sniewska, M., Nowicki, P. S.-K., Gęca, C., Jędruchniewicz, K.and Oleszczuk, P. (2021). Simultaneous removal of toxic Pb(II) ions, poly(acrylic acid) and Triton X-100 from their mixed solution using engineered biochars obtained from horsetail herb precursor – Impact of post-activation treatment. *Separation and Purification Technology, 276*,

Wisniewska, M. and Nowicki, P. (2019). Simultaneous removal of lead(II) ions and poly(acrylic acid) macromolecules from liquid phase using of biocarbons obtained from corncob and peanut shell precursors. *Journal of Molecular Liquis, 296*(2019),

Wu, J., Huang, D., Liu, X. and Meng, J. (2018). Remediation of As(III) and Cd(II) co-contamination and its mechanism in aqueous solution by a novel calcium-based magnetic biochar . *Journal of Hazardous Material, pp. 10-19.*

Wu, W., Chen, D., Li, J., Su, M., Chen, N., & Chen, N. (2018). Enhanced adsorption of uranium by modified red mud: adsorption behaviour study. *Environ Sci Pollut Res*, 25(18), pp. 18096-18108.

Xiang, J., Lin, Q., Cheng, S., Guo, J., Yao, X., Liu, Q., . . . D, L. (2018). Enhanced adsorption of Cd(II) from aqueous solution by a magnesium oxide–rice husk biochar composite. *Environ Sci Pollut Res, 25*, pp14032–14042.

Xiang, W., Wan, Y., Zhang, X., Tan, Z., Xia, T., Zheng, Y. and Gao, B. (2020). Adsorption of tetracycline hydrochloride onto ball-milled biochar: Governing factors and mechanisms. *Chemosphere, 255*(127057).

Yan, N., and Chen, X. (2015). Don't waste seafood waste. *Nature, 524*, pp. 155-157.

Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Creamer, A. and Yang, L. (2014). Characterization and environmental applications of clay–biochar. *Chemical Engineering Journal, 369*, pp. 136-143.

.Yasmin, C., Mariam, K., Lobna, E., Abdelwahe, C., & Ismail, T. (2019). Simultaneous removal of organic compounds and heavy metals from Tunisian landfilllLeachate using dairy processing wastes. *Water Practice & Technology, 14*(2).

Yu, D., Wang, L., and Wu, M. (2018). Simultaneous removal of dye and heavy metal by banana peels derived hierarchically porous carbons. *Journal of the Taiwan Instutute of Chemical Engineers*,

Zafar, N., Nadeem, R. and Hanif, M. (2007). Biosorption of nickel from protonated rice bran. *J.Hazard. Mater., 143*, pp. 478-495.

Zhan, L., Xhaoyan, W., Wu, X., Li, M. and Liu, X. (2020). Competitive adsorption of tylosin, sulfamethoxazole and Cu(II) on hydrxyhapatite modified biochar. *Chemosphere, 240.*

Zhang, C., Chen, Z., Tao, Y., Ke, T., Li, S., Wang, P., and Chen, L. (2020). Enhanced removal of trichlorfon and Cd(II) from aqueous solution by magnetically separable chitosan beads immobilized Aspergillus sydowi. *International Journal of Biological Macromolecules*, pp. 457-465.

Zhang, C., Chen, Z., Tao, Y., Ke, T., Li, S., Wang, P. and Chen, L. (2020). Enhanced removal of trichlorfon and Cd(II) from aqueous solution by magnetricall seoarable chitosan beads immobilized Aspergillus sydowii. *International Journal of Biological Macromolecules, 148*, pp. 457-465

Zhang, J., Hu, X., Yan, J., Long, L. and Xue, Y. (2020). Crayfish shell biochar modified with magnesium chloride and its effect on lead removal in aqueous solution. *Environmental Science and Pollution Research.*, pp. 9582-9588

Zhang, N., Cheng, N. and Li, Q. (2021). Functionalized Biomass Carbon-Based Adsorbent for si,ultaneous adsor[tion of Pb^{2+} and MB in waste water. *Materials, 14*(3537).

Zhang, Y., Cao, B., Zhao, L., Sun, L., Gao, Y., LI, J. andYang, F. (2017). Biochar-supported reduced graphene oxide for adsorption and co-adsorption of atrazine and lead. *Appled asurface ascience, 427*(Part A), 427

Zheng, Y., Wan, Y., Chen, J., Chen, H. and Gao, B. (2019). MgO modified biochar produced through ball milling: A dual-funtional adsorbent for the removal of different contaminanatss. *Chemosphere*.

Zhou, Y., Liu, X., Xiang, Y., Wang, P., Zhang, J., Zhang, F., . . . Tang, L. (2017). Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: adsorption mechanism and modelling. *Bioresource Technology*,

Zou, H., Zhao, J., Xhong, Z., Huang, J., Yang, Y., Yu, F. and Bashir, A. B. (2021). Ball milling biochar iron oxide composites for the removal of chromium (C (Cr)VI)) from water: perfornance and mechanisms. *Journal of Hazardous Material, 41,*