

Review

Research Progress on Process-Intensified Water Treatment Applications

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Abstract: Process intensification (PI) is aimed towards essentially smaller, cleaner, safer, energy-efficient sustainable technologies involving the application of a number of strategies, including reducing the number of devices, miniaturization, process integration, improving mass and heat transfer, novel energy and separation techniques and combined optimization and control methodologies. Over the recent years, PI has attracted attention in the domain of aqueous medium adsorptive separations and wastewater treatment as well. Thus far, a limited number of investigations have appeared in the literature; in addition, there is yet a lack of published methods to follow the intensified solutions for processes in wastewater treatment. In this connection, this article aims to present an overview of the recent applications and advances in process-intensified decolorization of dyes; removal of aromatic hydrocarbons from wastewaters; and recovery of proteins, heavy metals and rare earth elements from aqueous media. Selected applications have been identified in terms of the PI techniques, and the corresponding process improvements have been discussed for a variety of examples with the aim of contributing to the future progress of applications. It has been confirmed that considerable process improvements could be possible, such as intensified process efficiency, improved adsorption and separation performance, and minimized sorbent requirement and processing time. Even though there have been considerable developments in the field, there is still a need for further developments for the enhancement of the technologies in adsorption wastewater treatment using a systems approach.



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1. Introduction

PI research in chemical engineering applications has attracted considerable interest recently. The applications have led to several innovations in most chemical industries due to the satisfaction of the requirements both in an environmentally friendly manner and in remaining cost competitive. PI is aimed towards substantially smaller, energy-efficient, safer sustainable technological developments, in which the major tools involve the reduction in the amount of equipment via the integration of process steps and functionalities; miniaturization; heat and mass transfer improvements by novel mixing strategies, supplementary energy input, external force fields or improved surface configurations; novel energy and separation techniques; batch to continuous mode process transformations to reduce process volumes; and integrated optimization and control strategies [1–5].

Process-intensifying strategies are usually studied under two main classifications, namely PI equipment and methods [3,5–7]. Process-intensifying equipment, also called hardware, mainly involves rotating packed beds, catalytic packings, microreactors, and structured reactors. Various other examples of equipment types are structured packed columns; static mixers; microchannel, spinning disc, loop, oscillatory baffled, spinning tube-in-tube and heat-exchange reactors; and compact heat exchangers. Process-intensifying methods, also referred to as software, involve hybrid separations, such as membrane

absorption and absorptive distillation; functional materials, such as ionic liquids; alternative sources of energy, such as ultrasound, microwaves, solar energy and centrifugal fields; and multifunctional reactor systems involving reactive extraction and chromatographic reactors. Combining intensified reactors together with renewable energy sources such as solar energy could provide higher motivation for the achievement of green processing targets. A decrease in material and energy consumption would lead to a direct reduction in capital costs [3,6–8].

Ramshaw's research group initiated PI application by developing a rotating packed bed (RPB) for reactive distillation [3,4,8–11]. Since then, PI has received considerable appreciation and significance due to its potential for more innovative and viable process design options. Significant developments have been achieved in the field over recent years and have resulted in both successful industrial applications and expanding research interests [5,7,12]. PI has emerged as an integral part of the retrofit design and provided intensified environmental and economical benefits. Significant efforts have been devoted to expressing it better for the satisfaction of the requirements of various industrial sectors, including essentially the manufacturing, energy and chemical sectors [8,13].

Various definitions proposed for PI [1–3,6,7,9,10,14–25] during the years starting in the early 1980s have been discussed in detail [5]. Although the emerging definitions were quite diverse in nature, they were commonly focused on innovation. The European Roadmap of Process Intensification ERPI [17] presented PI as a set of intensely innovational principles in process as well as equipment design benefiting process and chain efficiency, operational and capital costs, quality, process safety and wastes. Baldea [25] defined PI as chemical engineering developments leading to substantially smaller, energy-efficient, safe, cleaner technologies or those integrating multiple operations into fewer devices. PI is a growing trend in chemical engineering and should satisfy the requirements of markets and shareholders [6,15,26]. As the concept will be evolving continuously, it will involve challenges and requirements until a universal definition is determined [13].

PI research has also attracted attention recently in aqueous medium adsorptive separations and wastewater treatment as well. However, there is yet a lack of published protocols or methods to follow the intensified solutions for processes in the domain of wastewater treatment. In addition, there is a lack of a comprehensive review of process-intensified solutions for adsorptive separations for wastewater treatment. In this connection, this article attempts to present an overview and analysis of the recent progress in the process-intensified decolorization of wastewaters and the removal of aromatic hydrocarbons and recovery of proteins, heavy metal ions and rare earth elements from aqueous solutions.

2. Process-Intensified Treatment of Wastewaters

PI aims to transform conventional processes into more productive, cost-effective, safer and greener ones. This review presents the evaluations to highlight the challenges involved in many adsorptive separations related to wastewater treatment. PI methodologies are characterized by size reduction via intensified mixing and heat and mass transfer that would result in enhanced selectivity and energy efficiency; improved safety; reduced wastes; and reduced material, capital and operational costs [27,28].

Various adsorbent types could be employed for adsorptive separation, wastewater treatment and recovery or removal of various pollutants from aqueous media; however, most common adsorbents might indicate low adsorption performance for certain pollutants specifically for large-scale processing. There are growing investigations on strategies either to synthesize novel adsorbents or to improve the performance of the existing ones [29–36].

Recently reported studies in the literature for the adsorptive separations of different cases on process-intensified recovery of proteins [37,38]; decolorization of wastewaters [39–45]; and removal of rare earth elements, heavy metals [46,47] and aromatic hydrocarbons [48] from aqueous media are presented in Table 1. Each work was classified according to the applied technology, the kind of adsorbate–adsorbent system and the type of intensification methodology with the inclusion of the intensification parameters.

Table 1. Selected process intensification techniques in the literature applied to the decolorization of dyes; removal of aromatic hydrocarbons from wastewaters; and recovery of proteins, heavy metals and rare earth elements from aqueous media.

Technology	System Adsorbate/Adsorbent	Process Intensification		Reference
		Technique	Parameter	
Adsorption • fluidized bed dye-ligand adsorption of an intracellular protein from unclarified disrupted yeast	• G3PDH/high-density steel–agarose pellicular adsorbent	• novel adsorbent	• adsorbent property • selectivity • protein recovery • adsorption time • mass transfer • dynamic binding capacity • process efficiency	[37]
Adsorption • adsorption and interactions of BSA with DWNT prepared by CCVD synthesis	• BSA/DWNT	• novel adsorbent	• protein adsorption capacity	[38]
Adsorption • decolorization of RR2 in aqueous solutions using RPB-nZVI (a novel treatment of dye-contaminated wastewater)	• RR2/nZVI	• novel adsorbent • RPB	• adsorbent effectiveness • adsorbent reactivity • mass transfer • dye decolorization efficiency • pH, nZVI dosage, temperature effects on decolorization	[39]
Adsorption • PI of dye removal from aqueous media using a hybrid treatment technique involving HC coupled with hydrogel adsorption	• bio-recalcitrant Rh-B dye/PAA/halloysite clay nanocomposite hydrogel	• ultrasound polymerization • novel adsorbent • a hybrid technique involving HC coupled with hydrogel adsorption	• process efficiency • decolorization efficiency • dye removal	[40]
Adsorption • PI for wastewater decoloring, batch adsorption; a data-based multivariate optimization approach, Pareto sensitivity analysis and RSM for PI	• MB/phosphoric acid-treated STR biochar	• novel adsorbent • optimization and PI to achieve maximum MB removal efficiency • a multivariate optimization via combination of CCD algorithm with Pareto sensitivity analysis	• dye removal • dye removal efficiency • adsorption capacity • effect of parameters	[41]

Table 1. Cont.

Technology	System Adsorbate/Adsorbent	Process Intensification		Reference
		Technique	Parameter	
Adsorption <ul style="list-style-type: none"> a hybrid adsorption membrane process coupled with UF for dye removal from synthetic/actual wastewater 	<ul style="list-style-type: none"> MG/MCM-41 	<ul style="list-style-type: none"> novel adsorbent a hybrid adsorption membrane process integration of UF and adsorption process integration 	<ul style="list-style-type: none"> dye removal dye removal efficacy separation performance 	[42]
Adsorption <ul style="list-style-type: none"> application of RSM as an optimization tool for implementing a systematic route for one-step-controlled carbonization of SBE (a waste from an edible oil refinery) and dye adsorption 	<ul style="list-style-type: none"> MB/SBE 	<ul style="list-style-type: none"> novel adsorbent RSM as an optimization tool for carbonization and dye adsorption 	<ul style="list-style-type: none"> dye removal dye removal efficiency optimization of carbonization factors (time, temperature) optimization of adsorption factors (pH, time, adsorbent dose, initial MB concentration, temperature) reusability of adsorbent 	[43]
Adsorption <ul style="list-style-type: none"> adsorption of disperse blue 56 dye on ZnO-magnetic/ZSM-5 as an effective and novel adsorbent with high adsorption capacity and magnetic separation capability 	<ul style="list-style-type: none"> disperse blue 56 dye/ ZnO-magnetic/ZSM-5 	<ul style="list-style-type: none"> novel adsorbent 	<ul style="list-style-type: none"> adsorbent magnetization saturation value dye removal yield of dye removal adsorption yield adsorption capacity adsorbent activity reusability of adsorbent adsorbent regeneration capability 	[44]
Adsorption <ul style="list-style-type: none"> a multistage batch adsorption for MG removal using microwave date stone activated carbons 	<ul style="list-style-type: none"> MG dye/thermally and microwave-treated active carbons from waste date stones 	<ul style="list-style-type: none"> novel adsorbent microwave 	<ul style="list-style-type: none"> adsorbent surface area adsorption capacity adsorbent amount dye removal rate dye removal 	[45]

Table 1. Cont.

Technology	System Adsorbate/Adsorbent	Process Intensification		Reference
		Technique	Parameter	
Adsorption <ul style="list-style-type: none"> PI of Ni(II) adsorption in a fixed bed column through subcritical conditions 	<ul style="list-style-type: none"> Ni(II)/commercial activated carbon 	<ul style="list-style-type: none"> intensification of Ni(II) adsorption in a fixed bed column through subcritical conditions 	<ul style="list-style-type: none"> adsorption capacity mass transfer breakthrough time mass transfer zone length activated carbon characteristics resistivity of activated carbon to high pressure and temperature fixed bed performance under subcritical conditions 	[46]
Adsorption/desorption <ul style="list-style-type: none"> evaluation of possible use of the macroporous ion exchanger (Purolite S957) for the adsorption of rare earth elements and heavy metal ions from spent batteries (acidic) solutions 	<ul style="list-style-type: none"> La(III), Ni(II) ions/Purolite S957 La(III), Ce(III), Nd(III), Fe(III), Ni(II), Co(II), Cu(II), Zn(II) mixture 	<ul style="list-style-type: none"> novel adsorbent 	<ul style="list-style-type: none"> La(III), Ni(II) ion removal from acidic solutions separation sorption capacity sorption process efficiency effect of parameters (HNO₃ concentration, contact time, initial metal concentration, temperature) ion exchanger regeneration intraparticle and film diffusions recovery of rare earth elements from waste solutions 	[47]
Adsorption/desorption <ul style="list-style-type: none"> synthesis and adsorption behavior of a magnetic ZSM zeolite (with TPA⁺ as template) for the selective removal of PX from wastewater 	<ul style="list-style-type: none"> PX/magnetic ZSM-5 zeolite 	<ul style="list-style-type: none"> novel adsorbent a molecular simulation method to select the appropriate template for the synthesis of magnetic molecular sieve adsorbent with better adsorption properties for PX 	<ul style="list-style-type: none"> selectivity selective removal of PX magnetic separation performance selective adsorption capacity film diffusion intraparticle diffusion 	[48]

In the presented studies, the kind of intensification techniques (Figure 1) involved mainly the utilization of novel adsorbents, rotating packed bed, ultrasound, microwave, process integration, adsorption with hydrodynamic cavitation, adsorption with ultrafiltration membrane, fixed bed adsorption with subcritical conditions, optimization via response surface methodology and molecular simulations.

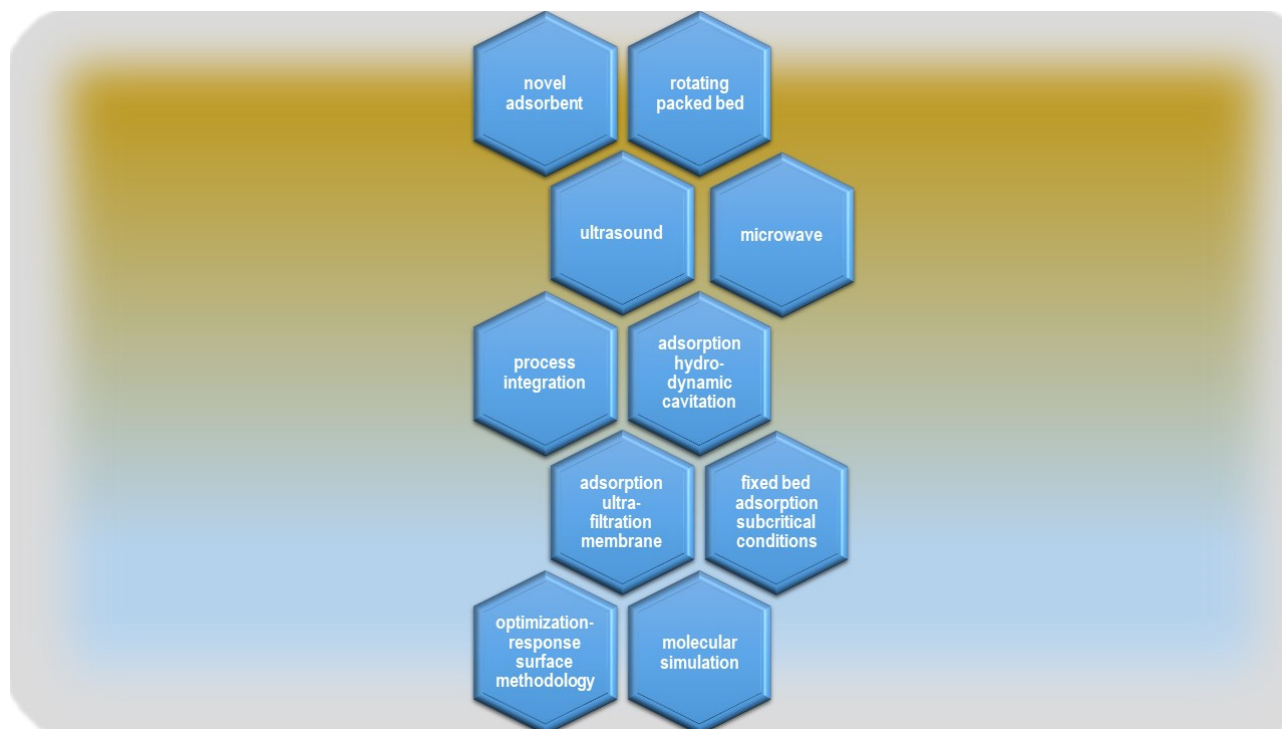


Figure 1. Intensification techniques applied to decolorization of dyes; removal of aromatic hydrocarbons from wastewaters; and recovery of proteins, heavy metals and rare earth elements from aqueous media.

The intensification parameters (Figure 2) involved the adsorbent property, surface area of adsorbent, adsorbent effectiveness, adsorbent amount, adsorbent magnetization saturation value, magnetic separation performance, adsorbent reactivity, adsorption capacity, dynamic binding capacity, mass transfer, film diffusion, intraparticle diffusion, adsorption time, breakthrough time, length of mass transfer zone, fixed bed performance under subcritical conditions, adsorbent resistivity to high pressure and temperature, selectivity, selective adsorption capacity, separation, separation performance, process efficiency, adsorbate recovery, adsorbate removal, adsorbate removal efficiency, adsorbate removal percentage, adsorbate removal yield, adsorption yield, adsorbate removal rate, effect of process parameters (pH, adsorbent dosage, initial adsorbate concentration, acid concentration, contact time, temperature), adsorbent reusability, adsorbent activity and adsorbent regeneration capability.



Figure 2. Major intensification parameters considered for water treatment.

3. Process-Intensified Recovery of Proteins from Aqueous Media

Protein–nanoparticle interactions are important for the investigation of the potential utilization of specific particles in drug delivery systems. The parameters influencing protein–nanoparticle interactions, involving temperature, pH, concentration, particle size, modifier type, cytotoxicity and biocompatibility, need to be explored extensively [5,49–53]. In the following examples, process-intensified recovery or adsorption of proteins from aqueous media was studied via the utilization of novel adsorbents as PI methodology.

3.1. Process Intensification System and Strategy: Novel Adsorbents

Ling and Lyddiatt [37] studied PI for the adsorption system of a dye–ligand and an intracellular protein from bakers’ yeast extract in a fluidized bed for the investigation of the performance of a steel–agarose pellicular adsorbent (UpFront, 51–323 μm). They studied the recovery of glyceraldehyde 3-phosphate dehydrogenase (G3PDH). Kopac et al. [38] investigated the interactions and enhanced adsorption of bovine serum albumin (BSA) protein with double-walled carbon nanotubes (DWNTs). The study involved the investigation of protein adsorption equilibrium and kinetics on DWNTs.

The adsorbent used by Ling and Lyddiatt [37] comprised a stainless steel core (non-porous, 60 μm) coated by a porous agarose layer (20 μm), having an adsorptive coating depth corresponding to 40% of the particle radius and a steel core/agarose volume ratio of 1:3.5. Cibacron Blue 3GA dye was immobilized on the adsorbent particles and tested as an affinity ligand for the selective recovery of the protein from the yeast extract.

DWNTs synthesized via the catalytic chemical vapor deposition (CCVD) method using a MgO-based catalyst were utilized and protein adsorption on carbon nanoparticles was examined by Kopac et al. [38] using a batch technique at optimized process conditions (pH 4, 40 $^{\circ}\text{C}$) for the highest adsorption efficiency. Interactions of positively charged protein molecules with negatively charged nanotubes were examined to understand the electrokinetic properties.

3.2. Process Intensification Achievements

In the study by Ling and Lyddiatt [37], the adsorbent particle density was increased by incorporating a stainless steel core in agarose. A high throughput was obtained by the high-density adsorbent derivatized with Cibacron Blue 3GA, which minimized the adsorption period and maximized the process efficiency. The process of fluidized bed adsorption was enhanced, allowing sufficient time for the protein molecule to diffuse into the pores of sorbent particles. The matrices designed for the optimization of the solid phase required small particle sizes and increased density in order to have a reduced diffusion path and a high superficial velocity for the improvement of film mass transfer. The dynamic binding capacity was enhanced with an increase in bioload as a result of the enhanced driving force for mass transfer. The process was capable of capturing a target protein molecule without predilution of unclarified feedstock with minimized processing time and maximized process efficiency [37].

In the study by Kopac et al. [38], interactions of positively charged protein molecules with negatively charged nanotubes indicated electrostatic attractions. The maximal protein adsorption capacity of carbon nanoparticles was 1221 mg/g. Thermodynamic parameters indicated an endothermic physisorption process of protein adsorption on DWNTs, exhibiting the largest protein adsorption capacity on DWNT samples in comparison to the single-walled CNTs, multiwalled CNTs or metal oxides [54–56]. Using this novel adsorbent significantly intensified the protein adsorption [38].

4. Process-Intensified Decolorization of Wastewaters

Decolorization of wastewaters is important as almost 30–40% of dyes are discharged into the environment during dyeing processes [39]. In the examples, novel adsorbents have been used commonly in all of the applications for PI. Additionally, techniques such as ultrasound polymerization, microwave treatments and optimization have been utilized in the synthesis of novel adsorbents. Rotating packed bed, process integration (hydrodynamic cavitation and hydrogel adsorption, ultrafiltration membrane and adsorption) and optimization for maximum process efficiency are the other methods utilized.

4.1. Decolorization of Reactive Red 2 Dye

4.1.1. Process Intensification System and Strategy: Novel Adsorbent, Rotating Packed Bed

Lin and Chen [39] investigated the feasibility of decolorization of a reactive dye (Reactive Red 2, RR2) utilized extensively in cotton, wood and silk dyeing treatments from aqueous media exploiting a nanoscale zero-valent iron (nZVI). An RPB was used for the preparation of the adsorbent by reductive precipitation ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, NaBH_4). The performance of nZVI and the effects of various characteristics, such as pH, adsorbent dosage and temperature, on the decolorization efficiency were studied.

4.1.2. Process Intensification Achievements

Higher temperature and adsorbent amount and lower pH favored the efficiency of decolorization. The decolorization kinetics was compatible with the pseudo-first-order model, indicating that the diffusion of dye controlled the process in the 30–50 °C range. nZVI had significantly better reactivity than ZVI for the decolorization. The results demonstrated that an efficiency of about 88% was obtained, and nZVI had potential for the decolorization of dyes in textile wastewater treatment [39].

4.2. Decolorization of Rhodamine-B Dye

4.2.1. Process Intensification System and Strategy: Novel Adsorbent, Ultrasound Polymerization, Process Integration, a Novel Hybrid Technique (Hydrogel Adsorption and Hydrodynamic Cavitation)

Bethi et al. [40] investigated the decolorization of bio-recalcitrant Rhodamine-B (Rh-B) dye by exploiting a hybrid method that involved hydrogel adsorption and hydrodynamic cavitation (HC). For the synthesis of hydrogel adsorbent (poly-acrylic acid PAA/halloysite

clay nanocomposite), an ultrasound polymerization was employed, and the adsorption column packed with the synthesized hydrogels was placed after the cavitation device (orifice) for removal of dye from aqueous solutions.

4.2.2. Process Intensification Achievements

While a decolorization of 65% at optimum operational conditions was obtained, H₂O₂ addition into the hybrid system further enhanced the decolorization to 72.85%. The ultrasound polymerization process showed uniform dispersion of halloysite clay within the polymer matrix. A combination of HC and hydrogel adsorption provided intensification of dye removal and showed that the nanocomposite PAA hydrogels had higher adsorption capacity than the PAA hydrogel (bare) for dye removal in the hybrid system. The system performance was significantly influenced at the optimum conditions (cavitation device inlet pressure, halloysite clay content of hydrogel, hydrogel dosing, pH). The dye removal percentage was better at lower hydrogel clay content and medium pH. Integration of HC with hydrogel adsorption enhanced the process efficiency as compared to an individual process. The novel hybrid technique resulted in the intensification of the removal of Rh-B dye [40].

4.3. Decolorization of Methylene Blue Dye (Spent-Tea Residue)

4.3.1. Process Intensification System and Strategy: Novel Adsorbent, Optimization for Maximum Process Efficiency

Salehi et al. [41] investigated biochar production exploiting spent-tea residue (STR) by phosphoric acid (H₃PO₄) treatment and studied the optimal process conditions for the intensification of the methylene blue (MB) dye adsorption from aqueous solutions. For achieving the first criterion of intensification of adsorption, they fabricated high-quality biochar having optimal physicochemical properties by pyrolysis of H₃PO₄-pretreated STR at 300, 400 and 500 °C. The utilization of H₃PO₄ as an activating agent was useful for reducing the precursor decomposition temperature as a result of the catalytic reactions and pyrolysis with a lower corrosion rate; also, various types of oxygen-containing functional groups could be formed on the surface during pyrolysis, leading to improvement in the physicochemical properties. In order to achieve a process-intensified performance, the adsorption was studied by exploiting a data-based multivariate optimization strategy, Pareto sensitivity analysis with response surface methodology (RSM). The design of the experimental method coupled with RSM was used to study the influence of process variables, and optimization of the process was accomplished for maximum adsorption performance. The mechanism of dye adsorption with biochar was studied through isothermal and kinetic analysis.

4.3.2. Process Intensification Achievements

Results indicated that the surface area and the porous structure of biochars would increase with increasing pyrolysis temperature, whereas some of the oxygen-containing functional groups might exist to some extent. A data-based consistent optimization and intensification methodology for maximum dye removal efficiency was obtained. The biochar produced at 400 °C pyrolysis temperature was found to have the maximum dye removal percentage (99.26%) at optimum conditions, where contact time and pH were the parameters with the greatest effect on the adsorption. The pseudo-second-order and the Langmuir isotherm models were found to describe the process of adsorption. The work presented the potential of STR to produce high-quality low-cost biochar in decolorization applications [41].

4.4. Decolorization of Methyl Green Dye

4.4.1. Process Intensification System and Strategy: Novel Adsorbent, Process Integration, a Novel Hybrid Technique (Adsorption–Ultrafiltration Membrane)

Alardhi et al. [42] worked on the adoption of a new configuration applying a hybrid adsorption–membrane technique (HAMT) for the decolorization of methyl green (MG) dye from aqueous media using both synthetic and actual wastewater samples from the textile industry. The integral adsorption–membrane system did not operate sequentially as in conventional systems but operated simultaneously. The hybrid MCM-41 ultrafiltration membrane (UF) process involving the simultaneous activity of MCM-41 adsorbent having a mesoporous structure was examined. In the study, the hollow fiber was used in the form of a shell and tube design and proposed to be highly efficient with easy application in comparison to the submerged system design used commonly. The applicability of the hybrid system was examined by determining the effect of MCM-41 on the process performance (feed flow rate, dye concentration, adsorbent dose) using MG dye as a simulated pollutant and by applying the optimal conditions using actual samples from a biological treatment plant.

4.4.2. Process Intensification Achievements

The results showed the significant effects of the adsorbent dosage, feed concentration and flow rate on permeate flux and dye removal. The optimal configuration performance was reported as follows: batch filtration with the retentate full recycled > semi-batch filtration > single-pass continuous filtration. The technique was shown to be considerably effective in the treatment of wastewaters by the application of the optimized conditions. Dye removal of 97% was obtained, indicating that the application of the new configuration hybrid system and the MCM-41 sorbent was effective for dye removal from wastewater, and the process intensification achieved demonstrated promise in industrial applications. Process integration involving UF-coupled adsorption in a single system allowed the removal of large molecules (colloids) via UF and the removal of low-molecular-weight components (dyes) by adsorption [42].

4.5. Decolorization of Methylene Blue Dye (Spent Bleaching Earth)

4.5.1. Process Intensification System and Strategy: Novel Adsorbent, Optimization (Carbonization and Dye Adsorption)

Merikhy et al. [43] applied RSM for accomplishing one-step-controlled carbonization of spent bleaching earth (SBE), a spent clay from an edible oil refinery, as a powerful tool for examining the changes in operational parameters and optimization designed with a minimized number of experiments. The factors affecting the carbonization process were optimized through RSM for MB dye removal efficiency. The comparison of the characterizations of SBE, carbonized SBE (CSBE) and virgin BE, as well as the optimization of the effects of the adsorption conditions on dye removal efficiency, were studied via RSM together with a face-centered composite design. Samples regenerated at different temperatures (400–600 °C) and periods (30–120 min) were exploited in the experiments.

4.5.2. Process Intensification Achievements

Optimum parameters for the carbonization of SBE for the maximum dye removal efficiency were found (520 °C, 120 min). Both clay and carbonaceous material were involved in the adsorption process. The maximum removal efficiency predicted (31.07%) was in good agreement with experimental findings (28.15%) at the optimal conditions. The removal of dye by CSBE was investigated at various conditions (pH, temperature, contact time, adsorbent dosing, initial dye concentration). The adsorption mechanism was described by the pseudo-second-order rate and Langmuir isotherm models (53.91 mg/g maximum adsorption capacity). The thermodynamic analysis confirmed the endothermic and spontaneous nature of the process. The reusability of the adsorbent was confirmed. RSM provided simultaneous investigation of process parameters and better process opti-

mization. The methodology used offered a practical simple pathway for the intensification of the carbonization process [43].

4.6. Decolorization of Disperse Blue 56 Dye

4.6.1. Process Intensification System and Strategy: Novel Adsorbent

Nanoparticles, due to their advantages such as smaller size, higher surface area and rapid and easier separation capability, can be utilized effectively in the modification of adsorbents, and high-performance sorbents can thus be produced by using nanomaterials. Due to the high porosity and capacity of zeolites in ion exchange processes, they can also interact with other ions such as iron, zinc and aluminum. Their surfaces can be exposed to modification by the use of specific surfactants that could lead to a positive charge network for the elimination of various anions from wastewaters. In adsorption processes, rapid and easier separation exploiting magnetic adsorbents such as magnetic zeolites could be possible [44].

Mohammadi et al. [44] studied the adsorption of disperse blue 56 dye from aqueous media with ZnO-functionalized magnetic/ZSM-5 as a novel adsorbent that had high magnetic separation capability and adsorption capacity.

4.6.2. Process Intensification Achievements

The optimized parameters for the removal of dye were determined for maximum dye adsorption >91%.

The kinetics of dye removal showed a pseudo-first-order rate with a chemically controlled process. For the adsorbent, the maximum adsorption capacity (Langmuir model) was 6.23 mg/g, and the magnetization saturation value was 3.2 emu/g, which was an indication of a high potential for effective utilization in magnetic separation applications. ZnO-magnetic/ZSM-5 had a considerably high magnetization saturation value which made the separation from the solution easier. The adsorbent could be reused three times without any significant loss in magnetic intensity and adsorbent activity, indicating significant potential for dye removal from wastewaters [44].

4.7. Decolorization of Malachite Green Dye

4.7.1. Process Intensification System and Strategy: Novel Adsorbent, Microwave Treatment

Activated carbons can generally be synthesized by applying physical or chemical activation processes. Chemical activation requires chemical treatment, while thermal treatment is applied for physical activation by use of either conventional heating or microwave treatment [45,57]. During the conventional process, heat transfer takes place from the periphery of the samples to the core inside via the heat transfer mechanisms in the form of conduction, convection and radiation from a heating source. In microwave treatment, however, heat transfer takes place via electromagnetic waves from the core inside to the sample surface, enabling a high heating rate and uniform heating. Microwave treatment has advantages such as considerably lowered heating time, exceptional control of the heating process, and ease of handling of samples having high moisture content. Hence, microwave activation is considered to be a good alternative method of heating for activated carbon production. During microwave treatment of carbonaceous materials, particles are heated up rapidly, and the volatile matter (oxygen, sulfur, hydrogen) content of materials is significantly decreased, giving rise to the enrichment of the fixed carbon content. Microwave heating has been successfully applied to obtain effectively activated carbons from a number of carbonaceous precursors for the adsorptive separation of dyes, heavy metals, aromatics, gases, herbicides and antibiotics [45,57].

Hijab et al. [45] applied microwave and thermal treatment approaches in the production of activated carbons utilizing wastes of date stones/pits obtained from a date syrup processing plant and investigated the assessment of their adsorption capacity for malachite green (MG) dye, which is applied generally in plastics and textile industry, in a two-stage

batch adsorption unit. They performed an optimization analysis for the prediction of the minimum adsorbent amount requirements.

4.7.2. Process Intensification Achievements

The adsorption data on the conventionally heated and microwave-heated products were found to be expressed by the Langmuir–Freundlich and the Redlich–Peterson models, respectively. The surface area and the maximum dye adsorption capacity were 669.3 m²/g and 58 mg/g for the conventionally activated samples and 1123 m²/g and 98 mg/g for the microwave-activated samples, respectively. They developed a two-stage batch adsorber model for the optimization of the adsorption process and correspondingly obtaining minimized adsorbent amounts and costs. It was reported that the adsorbent requirements were reduced considerably in the two-stage process in comparison to a single-stage one, providing a basis for the design of an industrial-scale two-stage batch adsorber unit for the removal of dyes from wastewater [45].

5. Process-Intensified Recovery of Heavy Metals and Rare Earth Elements from Aqueous Media

Process-intensified separation of heavy metals and rare earth elements from aqueous media has been achieved through the application of novel adsorbents and carrying out adsorption under subcritical conditions.

5.1. Adsorptive Removal of Ni(II) Ions

5.1.1. Process Intensification System and Strategy: Fixed Bed Adsorption under Subcritical Conditions

Metal ions are among the major contaminants contributing to aquatic environment pollution significantly. They present high hazards to living organisms due to their non-biodegradable nature. Nickel (Ni(II)) is among the toxic heavy metals that are used widely in metal processing, mining, smelting and battery manufacturing industries. The accumulation of high levels of nickel in living organisms may lead to severe consequences. In the adsorptive removal of metallic ions from aquatic systems, subcritical and supercritical fluids were also utilized in adsorption processes to enhance the processes due to their high mass diffusivity and low viscosity characteristics [46].

Reske et al. [46] investigated the adsorptive removal of Ni(II) ions from a stream of subcritical water using an activated carbon fixed column. They evaluated the structural changes of activated carbon after exposing it to column adsorption under subcritical conditions, and they investigated the effects of pressure (5–25 MPa) and temperature (100–200 °C) on adsorption bed performance (breakthrough time t_r , adsorption capacity Q_{eq} , length of mass transfer zone MTZ) in comparison to adsorption under normal conditions (25 °C, 0.1 MPa).

5.1.2. Process Intensification Achievements

According to the results, the pretreatment was found to be effective in improving the adsorbent characteristics for adsorption and resistance to high pressure and temperature conditions without any significant loss of property. The bed performance was significantly enhanced under subcritical conditions, specifically at 200 °C and 25 MPa. Q_{eq} , t_r and MTZ values were 1.54 mg/g, 5 min and 28.31 cm under normal conditions; at subcritical conditions, they were 6.30 mg/g, 166 min and 10 cm, respectively [46].

5.2. Adsorptive Removal of Heavy Metals and Rare Earth Elements from Acidic Solutions

5.2.1. Process Intensification System and Strategy: Novel Adsorbent

Nickel–metal hydride (Ni-MH) storage batteries are commonly used as a source of energy in most portable electronic devices, such as mobile phones, hybrid cars and digital cameras. They contain elements involving Co(II), Cu(II), Mn(II), Ni(II), Zn(II), Al(III) and Fe(III), besides rare earth metals such as La(III), Ce(III), Pr(III) and Nd(III), and a large

amount of waste released from spent batteries and electronic devices leads to environmental pollution. Adsorption can be applied as a cheap and convenient method for the separation of those metals from the spent battery solutions. Ion exchangers contain different kinds of functional groups, such as amine, carboxylic, phosphonic and sulfonic groups. Among those, Purolite S957 can be effectively used for the recovery of metal ions from electrolytic and concentrated acid solutions and selective recovery of trace amounts of some metals from drinking water [47].

Kołodziejńska et al. [47] studied the sorption ability of Purolite S957 towards heavy metals and rare earth elements (Ni(II), La(III)) from acidic solutions and assessed its potential applicability for recovery from spent Ni-MH batteries. They performed preliminary studies for the sorption of mixtures of Co(II), Ce(III), Cu(II), Fe(III), La(III), Nd(III), Ni(II) and Zn(II) and investigated the influence of experimental conditions (HNO₃, metal concentrations, temperature, time) for the optimization of the removal of Ni(II) and La(III) ions from acidic solutions because of large contents of these metals in Ni-MH batteries. Adsorption capacities were compared for the assessment of the possibility of further separation. Sorption studies were also carried out with the mixture of metal ions in real solutions of spent Ni-MH battery leaching, and the effect of experimental conditions on the sorption effectiveness was studied. The metal–ion exchanger interactions for the sorption and the desorption processes were investigated for the possible sorbent regeneration.

5.2.2. Process Intensification Achievements

Maximum sorption capacities were found at about 0.46 mmol/g and 0.38 mmol/g for La(III) and Ni(II) ions, respectively. Sorption effectiveness was influenced by factors such as HNO₃ and initial metal concentrations, temperature and contact time. The sorbent exhibited a higher affinity for La(III) ions as compared to Ni(II) in the one-component system, indicating its preference for larger-charge ions. The resin exhibited 100% effectiveness for La(III) ion sorption and 50% for Ni(II). For the multicomponent mixture, the resin had a higher affinity for metal ions in the third oxidation state than for those in the second state. The sorption effectiveness was about 100% for Ce(III), Fe(III), La(III) and Nd(III) ions and about 50–60% for Co(II), Cu(II), Ni(II) and Zn(II). The kinetics analysis indicated a pseudo-second-order model for the sorption of La(III) and Ni(II) ions, while the intraparticle and film diffusions were the controlling mechanisms. Adsorption was largely of chemical character, while physical forces could also take part. La(III) and Ni(II) sorption was expressed by the Langmuir model, while analysis showed the exothermic and spontaneous nature of the process. Nitric acid was an efficient desorbent for resin regeneration and the recovery of all kinds of metal ions from the acidic solutions. The chelating resin Purolite S957 containing phosphonic and sulfonic groups had a high potential for the effective recovery of La(III) and Ni(II) from acidic nitrate solutions and could be effectively applied for the removal and separation of heavy metals and rare earth elements from spent electronic equipment, including Ni-MH batteries [47].

6. Process-Intensified Removal of Aromatic Hydrocarbon (p-Xylene) for Wastewater Treatment

Process-intensified removal of aromatic hydrocarbon p-xylene (PX) from aqueous media for wastewater treatment has been accomplished via the application of process integration, novel adsorbents and molecular simulations.

6.1. Process Intensification System and Strategy: Process Integration, Novel Adsorbent, Molecular Simulations

Purified terephthalic acid (PTA) is commonly used as a raw material in the synthesis of polyester, while the effluents from the production process contain some organics (p-methyl benzoic acid, TA), and some metal ions (Co²⁺, Mn²⁺). The application of an integrated process involving extraction–UF–reverse osmosis–adsorption was presented as an optimum technology for PTA wastewater treatment. Nevertheless, a low level of an aromatic hydrocarbon PX (as extractant) existing in the effluent leads to the dissolving of

the polyamide reverse osmosis membrane, seriously shortening membrane life. PX is one of the three isomers of dimethylbenzene (xylenes) and is not acutely toxic; however, vapors over the recommended exposure limit can cause serious health problems. Hence, a novel extraction–adsorption–UF–reverse osmosis–adsorption process was developed by placing an adsorber between the extracting and the UF–reverse osmosis units for the treatment of PTA-containing wastewater. The quaternary ammonium salt template having a tetrahedral structure (+charge) is appropriate for the synthesis of ZSM-5 zeolite, having structural template, space-filling and charge-balancing roles [48].

Ye et al. [48] synthesized a magnetic ZSM-5 zeolite sorbent by the coprecipitation method using a tetrapropyl ammonium (TPA⁺) salt template for the selective removal of PX from aqueous media. They investigated the correlation between the sorbent and the template via molecular simulations for the selection of the suitable template in the synthesis of the magnetic sorbent. They modified the magnetic ZSM-5 further with better adsorption properties towards PX from wastewater, and they also studied the desorption process.

6.2. Process Intensification Achievements

The magnetic H-ZSM-5 exhibited highly selective adsorption performance for PX along with a better magnetic separation property than H-ZSM-5. The magnetic samples with a highly microporous structure had a saturation magnetization value (11.72 emu/g) that could be effectively separable from the liquid phase. There was not any competitive adsorption of PX with the metal ions taking place on the magnetic sorbent. It was an exothermic, entropy reduction, physical adsorption process expressed by the Langmuir model and the pseudo-second-order kinetics, with a maximum adsorption capacity of 106.71 mg/g (298.15 K) for PX. The adsorption was controlled by both film and intraparticle diffusions. NH₄Cl modification of magnetic H-ZSM-5 did not change the specific surface area, pore volume or pore size significantly as compared to the magnetic ZSM-5. PX to Co²⁺ and Mn²⁺ selectivity factors changed from 908.9 and 1079.4 to 6517.3 and 7887.6, respectively, following modification. It was proposed that high-temperature roasting was a suitable regeneration technique. PX adsorption capacity of magnetic H-ZSM-5 was about 91.53 mg/g at saturation, corresponding to 146.7% of the adsorption capacity of the nonmagnetic H-ZSM-5 [48].

7. Process Intensification Results

The process improvements accomplished through PI related to the investigated studies are presented in Table 2. In the applications discussed, either one or more techniques were applied as intensification tools for the enhancement of the processes depending on the intensification parameters. In those studies, considerable process enhancements and benefits were obtained. Figure 3 shows the achieved process enhancements in the applications discussed. Those are process-intensified selective protein recovery; increased dynamic binding capacity due to the increased mass transfer driving force; minimized adsorption processing time; maximized process efficiency for fluidized bed adsorption; increased protein adsorption capacity; increased effectiveness and reactivity with novel sorbents in decolorization of dyes; intensified adsorptive dye removal and process efficiency using HC combined with hydrogel adsorption; enhanced decolorization and total organic carbon removal via the hybrid system; intensified dye removal efficiency; reduced cost and improved quality biochar production for decolorization; improved dye pollutants reduction via hybrid membrane–adsorption system; improved separation performance; increased dye removal efficacy via the integration of adsorption by mesoporous sorbents and UF membrane filtration; flux enhancement and increased hybrid process efficacy; improved regeneration process; improved adsorption capacity; magnetic separation capability; magnetization saturation value of adsorbent; improved reusability without significant adsorbent activity and magnetic intensity loss; easier adsorbent separation from solution; improved adsorption capacity via microwave treatment; minimized adsorbent requirement in two-stage batch process in comparison to a single-stage process; improved sorbent

characteristics; improved resistivity to high pressure and temperature; improved fixed bed column adsorption performance under subcritical conditions in comparison to ambient conditions: higher breakthrough time, adsorption capacity, lower mass transfer zone length, enhanced sorption effectiveness by sorption parameter optimization (initial solution and acid concentrations, contact time, temperature); greater sorbent affinity for La(III) ions over Ni(II) in one-component system due to larger charge; greater resin affinity for metal ions in a multicomponent system; higher resin effectiveness towards Ce(III), Fe(III), La(III) and Nd(III) ions in a multicomponent system; enhanced heavy metal and rare earth element recovery from spent Ni-MH batteries via the resin method; enhanced desorption, resin regeneration and metal ion recovery from acidic solutions by use of nitric acid; enhanced separation of heavy metal ions and rare earth elements from spent electronic equipment, including Ni-MH batteries; enhanced adsorption performance with magnetic sorbents; better saturation magnetization value of a magnetic sorbent; more effective separation from liquid and better adsorbent properties with a magnetic sorbent (improved specific surface area, pore size, pore volume, larger micropore number, smaller mesopore and macropore number); enhanced selectivity factors for PX over Co^{2+} , Mn^{2+} via magnetic sorbent modification; enhanced regeneration via high-temperature roasting method; higher selective PX adsorption using magnetic adsorbent; and enhanced magnetic separation performance.

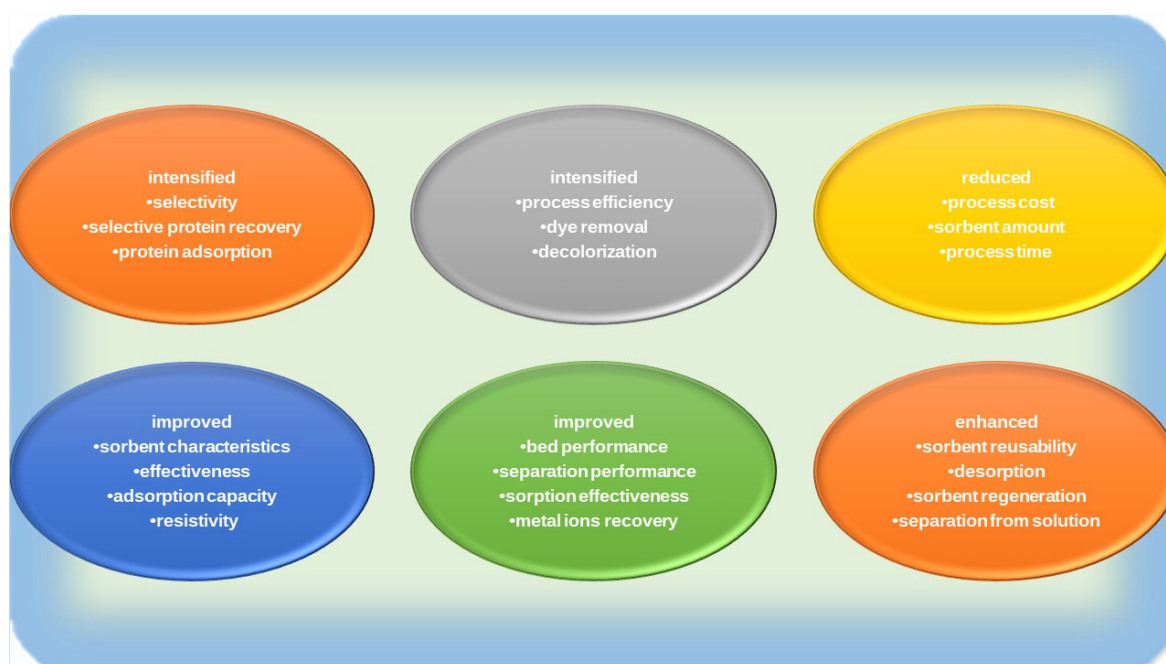


Figure 3. Major process intensification results in adsorption processes: decolorization of dyes; removal of aromatic hydrocarbons from wastewaters; and recovery of proteins, heavy metals and rare earth elements from aqueous media.

Table 2. Process intensification achieved in adsorptive separations: decolorization of dyes; removal of aromatic hydrocarbons from wastewaters; and recovery of proteins, heavy metals and rare earth elements from aqueous media.

Study	Major Findings	Process Intensification Achieved	Reference
<ul style="list-style-type: none"> PI of fluidized bed dye-ligand adsorption of G3PDH from unclarified disrupted yeast 	<ul style="list-style-type: none"> process capable of capturing a target protein molecule without predilution of unclarified feedstock 	<ul style="list-style-type: none"> development of a process-intensified primary capture step for the direct selective recovery of intracellular proteins from very dense particulate-containing yeast extract increased dynamic binding capacity with increasing bioload yeast extract due to the increased driving force for mass transfer minimized adsorption processing time, maximized process efficiency of fluidized bed adsorption 	[37]
<ul style="list-style-type: none"> adsorption and interactions of BSA with DWNTs prepared by CCVD synthesis that involved the use of a MgO-based catalyst 	<ul style="list-style-type: none"> maximum BSA adsorption capacity (Q_0) DWNT 1221 mg/g at optimum conditions 	<ul style="list-style-type: none"> increased protein adsorption capacity 	[38]
<ul style="list-style-type: none"> feasibility of decolorizing RR2 in aqueous solutions using nZVI; examining pH, nZVI dosage, temperature effects on decolorization efficiency 	<ul style="list-style-type: none"> effectiveness of nZVI in decolorizing RR2 in aqueous solutions ~88% decolorization efficiency lower pH, higher nZVI dosage, higher temperature for more efficient RR2 decolorization a diffusion control decolorization 	<ul style="list-style-type: none"> increased effectiveness and reactivity with nZVI in decolorization of RR2 in comparison to ZVI potential of nZVI for effectively decolorizing dyes in textile wastewater treatment 	[39]
<ul style="list-style-type: none"> adsorption PI of dye removal from aqueous media using a hybrid treatment technique involving HC coupled with hydrogel adsorption 	<ul style="list-style-type: none"> 65% decolorization at optimized conditions further enhancing the decolorization of dye to 72.85% with 45% of total organic carbon removal at optimum conditions by addition of H_2O_2 	<ul style="list-style-type: none"> intensification of adsorptive dye removal using combination of HC and hydrogel adsorption more efficient process by integration of HC and hydrogel enhanced decolorization and total organic carbon removal by addition of H_2O_2 into the hybrid system 	[40]

Table 2. *Cont.*

Study	Major Findings	Process Intensification Achieved	Reference
<ul style="list-style-type: none"> • adsorption PI for wastewater decoloring, batch adsorption; data-based multivariate optimization approach, Pareto sensitivity analysis and RSM for PI 	<ul style="list-style-type: none"> • 99.26% MB removal at optimal conditions with STR biochar • adsorption capacity of optimal biochar: 91.13 mg/g • strong influence of pH, contact time on MB/STR-derived biochar adsorption • establishing a multivariate study via combination of CCD algorithm with Pareto analysis to find the effects of operating parameters 	<ul style="list-style-type: none"> • a reliable optimization and PI to achieve maximum MB removal efficiency • enhanced MB removal efficiency (>99%) at the optimized conditions • potential of recycled STR for production of a low-cost and high-quality biochar for decolorization 	[41]
<ul style="list-style-type: none"> • a hybrid adsorption membrane process for dye removal from synthetic/actual wastewater, which involved the simultaneous activity of mesoporous MCM-41 coupled with a UF membrane • examining the applicability of the hybrid MCM41-UF membrane process <ul style="list-style-type: none"> ■ to determine the effects of MCM-41 on the UF process performance in terms of the feed flow rate, MG concentration, MCM-41 dose for synthetic wastewater ■ applying to the best operating conditions for actual wastewater from textile/leather industry • adopting three new configurations in a HAMT for the removal of MG from synthetic wastewater, testing the capability of HAMT for textile/leather industry wastewater 	<ul style="list-style-type: none"> • successful dye removal from synthetic/actual wastewater via the hybrid system • >97% dye removal from actual sample, indicating HAMT is effective in removing dyes from synthetic/actual wastewater • a highly efficient technique in actual wastewater treatment at optimum conditions 	<ul style="list-style-type: none"> • hybrid membrane–adsorption system improved MG dye removal • improved separation performance • coupling of adsorption by MCM-41 and filtration by UF membrane increased the removal efficacy of MG, improved flux and increased the efficacy of the hybrid process • integration of UF and adsorption in one system allows for the removal of large molecules (colloids) by UF and of low-molecular-weight compounds (dyes) via adsorption 	[42]

Table 2. Cont.

Study	Major Findings	Process Intensification Achieved	Reference
<ul style="list-style-type: none"> • application of RSM as an optimization tool for a systematic route for one-step-controlled carbonization of SBE • carbonization of SBE • optimization of carbonization parameters (time, temperature) based on MB adsorption efficiency through RSM along with a face-centered composite design • optimization of MB adsorption parameters of CSBE (pH, time, adsorbent dose, initial MB concentration, temperature); isotherms, kinetics, thermodynamics, reusability study 	<ul style="list-style-type: none"> • preparation of a carbonized sorbent based on spent clay from an edible oil refinery (CSBE) • optimization of SBE carbonization process for MB removal • 31% maximum removal efficiency (predicted) at estimated optimal conditions in agreement with experimental results (28%) • adsorption mechanism: pseudo-second-order kinetics, Langmuir isotherm (maximum adsorption capacity 53.91 mg/g) • confirmation of spontaneity and endothermic nature of adsorption process, adsorbent reusability 	<ul style="list-style-type: none"> • optimization of the carbonization factors via RSM for MB removal • a simple practical methodology to improve the SBE thermal regeneration process 	<p>[43]</p>
<ul style="list-style-type: none"> • adsorption of disperse blue 56 dye on ZnO-magnetic/ZSM-5 surface as a novel, effective adsorbent with high adsorption capacity and magnetic separation capability 	<ul style="list-style-type: none"> • ZnO-magnetic/ZSM-5 as a novel adsorbent for removal of disperse blue 56 from aqueous solutions • maximum dye removal >91.0% at optimum conditions • maximum adsorption capacity for disperse blue 56: 6.23 mg/g • reusability: 3 times (without significant loss in adsorbent activity and magnetic intensity) • high magnetization saturation value of adsorbent making separation from solution easier 	<ul style="list-style-type: none"> • improved adsorption capacity and magnetic separation capability of magnetic adsorbent for adsorption of dye • improved magnetization saturation value of adsorbent • better reusability without significant loss in adsorbent activity and magnetic intensity • easier separation of adsorbent from solution • ZnO-magnetic/ZSM-5 indicating great potential for application in magnetic separation technologies • showing promise for adsorption of dyes from wastewaters 	<p>[44]</p>

Table 2. Cont.

Study	Major Findings	Process Intensification Achieved	Reference
<ul style="list-style-type: none"> developing a 2-stage batch adsorber model to optimize MG adsorption, minimizing adsorbent requirements and costs for both thermally treated and microwave-treated date stones 	<ul style="list-style-type: none"> 669.3 m²/g (thermally treated), 1123.0 m²/g (microwave-treated) surface areas maximum adsorption capacity 58 mg/g (thermally), 98 mg/g (microwave) high-surface-area carbon from microwaved waste date stone optimized adsorber design for minimum adsorbent providing a basis for the design of industrial-scale 2-stage batch adsorption plant for treatment of dye in effluents 	<ul style="list-style-type: none"> improved surface area for the microwave-treated waste date stone higher adsorption capacity for the microwave-treated products optimized 2-stage batch adsorber design for minimum adsorbent requirement significant decrease in adsorbent amount in 2-stage batch process in comparison to an equivalent single-stage process 	[45]
<ul style="list-style-type: none"> intensification of Ni(II) adsorption in a fixed bed column through subcritical conditions 	<ul style="list-style-type: none"> improving activated carbon characteristics by the pretreatment, improving resistivity to high pressure and temperature conditions while maintaining its properties performance of fixed bed containing activated carbon for adsorption under subcritical water and ambient conditions under ambient conditions: maximum adsorption capacity 1.54 mg/g under subcritical conditions: maximum adsorption capacity 6.30 mg/g adsorption performance increased with temperature and pressure under subcritical conditions verification of the possibility to adsorb Ni(II) from a subcritical water stream in a fixed bed column packed with activated carbon 	<ul style="list-style-type: none"> improved activated carbon characteristics, improved resistivity to high pressure and temperature better fixed bed column performance with water under subcritical conditions instead of ambient conditions: higher adsorption capacity and breakthrough time, lower length of mass transfer zone greatly improved fixed bed performance under subcritical conditions subcritical conditions favorable for enhancing the adsorption process 	[46]

Table 2. Cont.

Study	Major Findings	Process Intensification Achieved	Reference
<ul style="list-style-type: none"> • evaluation of possible use of macroporous ion exchanger Purolite S957 for adsorption of rare earth elements and heavy metal ions from spent battery solutions • determination of the most effective conditions for the separation of La(III) and Ni(II) ions from acidic solutions, optimal parameters, optimization for metal ion mixture • investigation of desorption for ion exchanger regeneration 	<ul style="list-style-type: none"> • sorption effectiveness affected by HNO₃ concentration, contact time, initial metal ion concentration, temperature • the most favorable sorption conditions (0.2 M HNO₃, contact time 60 min, temperature 293 K) • ion exchanger exhibiting greater affinity for La(III) ions than for Ni(II) ions in the one-component system due to its preference for larger-charge ions (La(III) ions ~100%, Ni(II) ions 50% effectiveness) • La(III), Ce(III), Nd(III), Fe(III) ion sorption on the resin ~100%; Ni(II), Co(II), Cu(II), Zn(II) ion sorption, ~50–60% effectiveness • intraparticle and film diffusions being the rate-controlling mechanisms of sorption • adsorption largely of chemical character, while physical forces also take part; exothermic and spontaneous process • nitric acid as an efficient metal ion desorbent, allowing resin regeneration and recovery of all metal ions removal from acidic solutions 	<ul style="list-style-type: none"> • enhanced sorption effectiveness by optimization of sorption parameters (HNO₃ and initial solution concentration, contact time, temperature) • greater affinity of ion exchanger for La(III) ions than for Ni(II) ions in the one-component system due to larger charge • greater affinity of the resin for metal ions in the 3rd oxidation state in the multicomponent system compared to those in the 2nd state in the multicomponent system • greater affinity of the resin effectiveness for La(III), Ce(III), Nd(III) and Fe(III) ion sorption in the multicomponent system • enhanced recovery of rare earth elements and heavy metals from spent Ni-MH batteries via the resin • enhanced desorption, regeneration of resin and recovery of all metal ions from the acidic solutions by use of nitrate acid • enhanced removal and separation of rare earth elements and heavy metal ions from spent electronic equipment, including Ni-MH batteries 	<p>[47]</p>

Table 2. Cont.

Study	Major Findings	Process Intensification Achieved	Reference
<ul style="list-style-type: none"> • synthesis and adsorption behavior of magnetic ZSM zeolite for selective removal of PX from complex aqueous media • a molecular simulation method to select the appropriate template for the synthesis of the magnetic ZSM-5 zeolite, synthesizing magnetic ZSM-5 with TPA+ as a template for the selective adsorption of PX from industrial wastewater, further modification of the magnetic ZSM-5 to selectively adsorb PX from wastewater, desorption 	<ul style="list-style-type: none"> • physical, exothermic, entropy reduction adsorption of PX on magnetic ZSM-5 (maximum adsorption capacity: 106.71 m²/g, 298 K) • better adsorption performance of PX on magnetic H-ZSM-5 • saturation magnetization value of magnetic H-ZSM-5 prepared by coprecipitation with TPA+ template: 11.72 emu/g • better adsorbent properties for magnetic H-ZSM-5 (surface area 322.7027 m²/g, pore volume 0.1859 cm³/g) • film and intraparticle diffusion control for PX adsorption on magnetic ZSM-5 • high-temperature roasting, a preferable regeneration method, saturated adsorption capacity of magnetic H-ZSM-5 for PX 91.53 mg/g (~146.7% of nonmagnetic H-ZSM-5) 	<ul style="list-style-type: none"> • enhanced adsorption performance of PX with magnetic H-ZSM-5 compared to H-ZSM-5 • better saturation magnetization value of magnetic H-ZSM-5, with more effective separation from liquid • better adsorbent properties for magnetic H-ZSM-5 (improved specific surface area, pore volume and pore size; larger micropore number; smaller mesopore/macropore number) • enhanced selectivity factors of PX for Co²⁺ and Mn²⁺ for magnetic H-ZSM-5 modified with NH₄Cl • enhanced and preferable regeneration method via high-temperature roasting • highly selective adsorption of PX by using magnetic ZSM-5 • enhanced magnetic separation performance and selective adsorption capacity of magnetic ZSM-5 for PX 	<p>[48]</p>

8. Conclusions and Future Perspectives

The effective implementation of environmentally friendly, energy-efficient, safer, sustainable chemical processes at the industrial scale necessitates the development and application of innovative processing and novel separating technologies that yield high productivity and high-purity products. PI presents an expanding research field and industrial development which requires satisfying current needs and challenges in chemical process industries and has already created many innovations.

PI may be achieved through several ways, including process integration, combination of various functionalities into a single device, improvement of mixing and heat and mass transfer, novel energy and separation techniques, miniaturization, integrated optimization and control methodologies, process transformation modes from batch to continuous for handling reduced process volumes and integrating process steps in hybrid technologies. The development of novel materials is among the approaches investigated for the intensification of adsorptive separations. A number of emerging lines of research have been focused on utilizing cost-effective thermal energy sources such as microwaves, solar energy and ultrasound. The development of novel adsorbent structures coupled with hybrid systems offers a promising way of intensifying the removal of pollutants from wastewaters.

Among the selected PI studies in the literature for the adsorptive separation of different cases, intensification techniques mainly involved the utilization of novel sorbents and the use of rotating packed bed, ultrasound, microwave, process integration, adsorption with hydrodynamic cavitation, adsorption with ultrafiltration membrane, fixed bed adsorption under subcritical conditions, optimization via response surface methodology, optimization via combination of sensitivity analysis and response surface methodology and molecular simulation techniques. Most studies included the utilization of more than one intensification technique with a number of intensification parameters.

The intensification parameters involved adsorbent properties (surface area, amount, magnetization saturation value, magnetic separation performance, reactivity, effectiveness, capacity, dynamic binding capacity, resistivity to high pressure and temperature, reusability, activity, regeneration capability) and process properties (mass transfer, film diffusion, intraparticle diffusion, adsorption time, breakthrough time, length of mass transfer zone, adsorber performance under subcritical conditions, selectivity, selective adsorption capacity, separation, process efficiency, adsorbate recovery, adsorbate removal (efficiency, percentage, yield, rate), process parameters (pH, adsorbent dosage, initial adsorbate concentration, acid concentration, contact time, temperature)).

In the studies, PI led to several beneficial advantages, such as process-intensified capture for selective protein recovery, increased dynamic binding capacity, increased protein adsorption capacity, minimized adsorbent requirement, minimized processing time, intensified process efficiency, increased sorbent effectiveness in dye decolorization, intensified adsorptive dye removal, enhanced decolorization, enhanced total organic carbon removal, reduced process cost, improved quality biochar, improved separation performance, increased process efficacy, improved adsorption capacity (microwave treatment), improved resistivity (high pressure and temperature), improved column adsorption performance under subcritical conditions (higher breakthrough time and adsorption capacity and lower length of mass transfer zone), enhanced sorption effectiveness, greater sorbent affinity for specific metal ions, greater sorbent effectiveness for specific metal ions, enhanced heavy metal/rare earth element recovery from spent Ni-MH batteries, enhanced metal ions recovery from acidic solutions, enhanced separation of heavy metals/rare earth elements from spent electronic equipment, improved sorbent reusability, enhanced desorption, enhanced sorbent regeneration, enhanced separation from solution, enhanced selectivity factors, higher selectivity (magnetic adsorbent), enhanced magnetic separation performance, improved sorbent characteristics (adsorption capacity, magnetic separation capability, magnetization saturation value), enhanced adsorption performance (magnetic sorbents) and enhanced saturation magnetization value (magnetic sorbents).

Despite the significant progress accomplished so far, there is still a considerable need for further study to increase the economical and technical feasibility of the related technologies. In wastewater treatment, the intensification of adsorber volume and the development and application of novel sorbents and novel energy technologies for the reduction in energy requirements deserve further research work and progress. In many processes, there is still a lack of sufficient understanding of the mechanism of surface interactions between the solid and the pollutant. There is a need for more fundamental research for optimal sorbent design, specifically through materials that can couple efficiently with the thermodynamic and kinetic requirements of pollutant reduction. Enhancement of mass transfer and separation in reactors is also of vital importance. Despite recent advancements in the field, particularly how catalysts and reaction conditions can be used to control selectivity and product synthesis routes is yet to be understood. Further development of this promising technology is much needed to realize its full potential in wastewater treatment applications.

PI concerning the effective design of novel equipment and production methodologies has been one of the most promising and important progress fields for wastewater treatment. The present review presented an overview of the recent progress in process-intensified decolorization of wastewaters and the removal of aromatic hydrocarbons and recovery of proteins, heavy metals and rare earth elements from polluted aqueous media. In terms of adsorptive separations, PI has been shown to give significant process improvements and efficiency along with the development of more effective adsorbents and represents a promising technology for adsorptive separations in the area of water treatment.

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