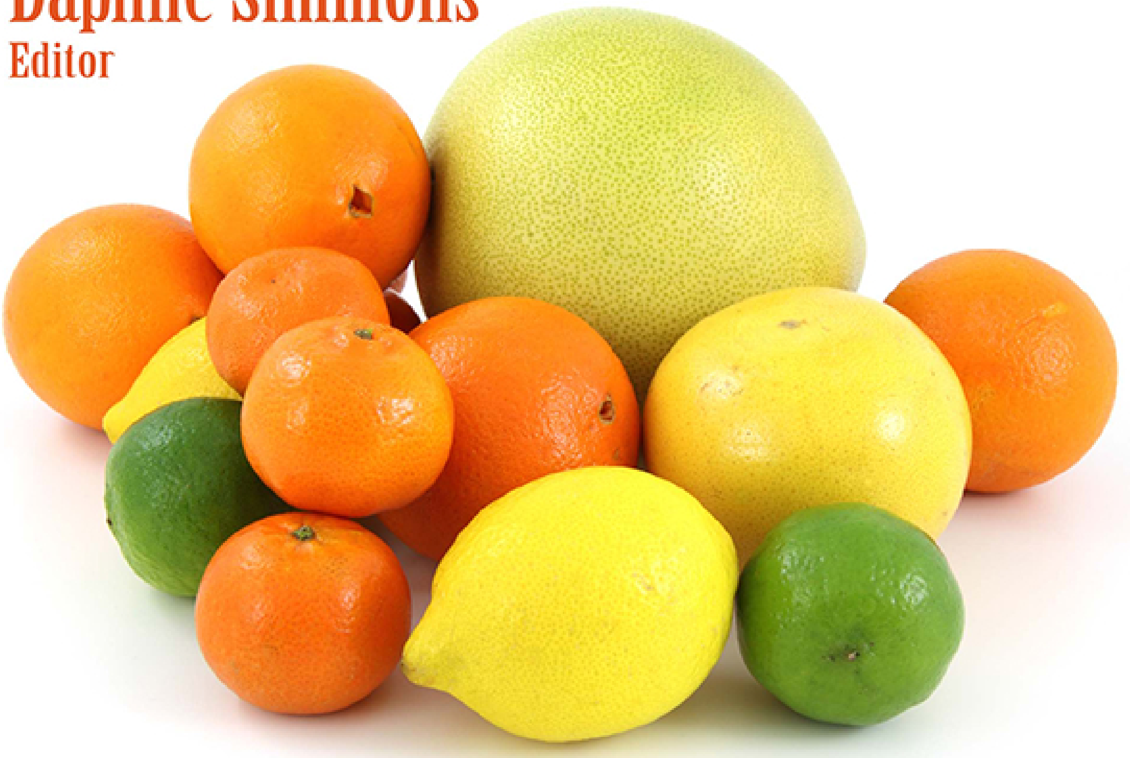
Citrus Fruits

Production, Consumption and Health Benefits

Daphne Simmons
Editor



FOOD AND BEVERAGE CONSUMPTION AND HEALTH

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nova publishers
New York

Library of Congress Cataloging-in-Publication Data

Library of Congress Control Number: 2015955200

ISBN: 978-1-63484-079-8 (eBook)

Published by Nova Science Publishers, Inc. † New York

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PREFACE

Citrus is the most widely produced fruit in the world and it is grown in more than 80 countries. Due to its varied and wide chemical composition as a consequence of its nature, citrus is an exceptional feedstock to the designing and assessing of biorefineries. A wide spectrum of products are obtained from citrus, which nowadays are extracted and purified into essential oils, antioxidants and other compounds. This book provides research on the production, consumption and health benefits of citrus fruits. The first chapter begins with an overview of citrus based refineries. Chapters two and three discuss hesperidin and narirutin, which are citrus flavonoids. Chapter four studies the use of citrus residues as raw materials for biomolecules and energy. Chapter five collects information from published works about the alternative use of citrus residues as efficient and promising adsorbents in clean water technology. The final chapter examines citrus genetic improvement.

Chapter 1 - Citrus is the most widely produced fruit in the world and it is cultivated in more than 80 countries. Brazil leads in citrus production, with more than 18.90 million metric tons of fruit produced during 2004–05, followed by the United States and China. Brazilian citrus production is oriented toward processing, while USA citrus production is focused toward processing and the fresh fruit market. Nowadays Colombia is a smallholder producer compared to Brazil and USA, nevertheless many expansion possibilities appear in the west zones of the country. Citrus production in Colombia was around 187 million tons for 2010. Nowadays citrus agroindustry in Colombia is not a well-established chain and many opportunities appear. On the other hand, citrus is one of the most exceptional feedstock to design and assess biorefineries due to its varied and wide chemical composition as a consequence of its nature.

From citrus are obtained a wide spectrum of products, which nowadays are extracted and purified such as essential oils, antioxidants and other value-added compounds as pectin. It is also important to obtain products for human consumption to guarantee food security, such as concentrated juices factories which has the major producers in Brazil and USA. Therefore, the aim of this chapter is to evaluate a citrus-based biorefinery for the integrated production of essential oil, concentrated juice, antioxidant, citrus seed oil, pectin, xylitol, PHB, ethanol, citric acid, lactic acid and electricity. The evaluation consists in the influence of energy and mass integration on the economical feasibility, environmental impact and possible social aspects that contribute in some way in rural development and food security preservation.

Chapter 2 - Hesperidin is the principal bioflavonoid found in citrus fruits, with very interesting bioactivity properties that still are the object of intensive research. Hesperidin and its aglycon form, hesperetin, are present in large quantities in oranges (*Citrus sinensis*) in particular. In young, immature oranges, these flavones can account for up to 14% of the fruit weight. Hesperetin is the 3',5,7-trihydroxy-4'-methoxy flavanone, and hesperidin contains not only the flavanone moiety, but also a rutinose disaccharide that has one D-rhamnose united with glycoside bond to the D-glucose unit. This paper presents and discusses chemical and physical properties of the orange bioflavones, as well as the most common methods of isolating and purifying these compounds. As a secondary plant metabolite, hesperidin is produced as a protective agent in citrus, and its defense role and biosynthesis will also be briefly discussed here. Many interesting bioactive properties of these phytochemicals have been reported, including antioxidant, anti-inflammatory, hypolipidemic, vasoprotective and anticarcinogenic properties, and an extensive review of these properties will be presented. Last but not least, the authors will present the most up-to-date developments in the research field that account for the mechanisms of action of these compounds.

Chapter 3 - *Citrus unshiu* is one of the most important varieties of citrus grown in Northeast Asia. Its peel is known as 'Chinpi,' a non-toxic edible ethnopharmaceutical herb in China and Korea, and has been clinically used as a traditional medicine to treat common cold, dyspepsia, cough and phlegm. Modern therapeutic studies have proven that citrus flavonoids have anti-oxidative, anti-inflammatory and anti-allergic activities. In this chapter, an efficient way to isolate citrus flavonoids, narirutin and hesperidin, from *Citrus unshiu* was introduced. Physiological properties such as anti-inflammatory activities and anti-alcoholic liver disease were also reviewed with suggestions on improving their bioavailability in a body through enzymatic modifications.

Chapter 4 - The replacement of the fossil-based raw materials either fully or partially is an objective in many countries, being of special interest the use of local biomass such as agricultural, forest, agro-industrial and industrial wastes, due to its low cost and large availability. According to FAOSTAT, by 2011 approximately 120 million tons of citrus were produced worldwide, with oranges accounting approximately 63.1 million tons. Approximately 60% of the total citrus production is market for fresh consumption, while the other 40% is used in the agroindustry to extract no more than the 50% of the fruit weight as juice. Residues from agroindustrial processing are composed by peel, seeds and remaining pulp and, in most of the cases, are used to spread soils, to produce animal feed, or to be burned. However, these conventional disposal methods can cause negative effects on the soil and superficial waters. Moreover, several value-added products, such as phytochemicals, pharmaceuticals, food products, essential oils, seed oil, pectin and dietary fibers, can be obtained from orange residues. In this chapter, simulation results of the production of biofertilizers, gibberellic acid and electricity from orange peel as stand-alone products are presented. Moreover, the experimental characterization was assessed. Results from the characterization procedures have been used to feed the simulations to obtain the mass and energy balances that were subsequently used to perform the economic and environmental analysis of the above mentioned processes. Moreover, comparisons from the techno-economic and environmental points of view of the stand-alone processes were performed. Besides, and based on the experimental results of the physicochemical characterization, two biorefinery schemes were techno-economic and environmentally evaluated.

Chapter 5 - Water pollution is still a serious problem for the entire world. Adsorption technology is a promising process which based on fabrication of novel, cheap, non dangerous and highly sorptive materials for application in wastewater purification processes. *Citrus* species generally produced for the fresh consumption or the production of fruit juice but also have lot of application in medicine, food processing and agriculture sectors. This review collects information from published works about the alternative use of *Citrus* residues as efficient and promising adsorbents in clean water technology.

For this purpose, isotherm (Langmuir, Freundlich, etc.), kinetic (pseudo-first, -second order, etc.), thermodynamic (free energy Gibbs, enthalpy, entropy) and desorption-regeneration studies were discussed in detailed. Moreover, significant factors such as pH, agitation time, temperature, adsorbent dosage and initial dye concentration are also reported extensively.

Chapter 6 - The Citrus genetic improvement is obtained throughout the application of several breeding procedures of extant species. Main aims of such breeding approaches are to obtain seedless fruits with easily removable peel, optimal size, excellent and original organoleptic characters, and possibly fruits endowed with precocious or late ripening. Citrus fruits and some of their transformation products, such as juices, fall in the large category of the functional foods owing to their content of important secondary metabolites defined nutraceutical components, whose beneficial effects on the human health are continuously evidenced. In this context the aim of the breeding processes is to obtain new varieties with an increased amount of nutraceutical components. Besides these characters mainly associated to the new fruits, other important agronomic and economic aspects concern the production of plants with high productivity and improved resistance against biotic and abiotic stresses.

On these bases, the authors' groups have focused the research activity in the genetic improvements of high quality cultivars and the production of new citrus fruits, namely hybrids. In particular, the authors' interest, has been addressed to the study of the chemical composition (mainly polyphenols from juices and peel essential oils) of new Citrus hybrids, with the aim of an exhaustive phytochemical characterization and, possibly, the evaluation of these new fruits for their introduction into the fresh market and into the industrial chain of transformation.

The new hybrids have been obtained through somatic hybridization by protoplast fusion. This technique, enabling to combine fully or partially, nuclear and cytoplasmic genomes at the interspecific and intergeneric levels, allows to widen the gene pool and to increase the genetic diversity of a species, circumventing the naturally occurring sexual incompatibility barriers (nucellar polyembryony, long juvenility and pollen/ovule sterility). Following this approach, the authors' breeding program has given rise to dozens of somatic hybrid and cybrids that are now being evaluated for their agronomic and productive characters.

A wide description of the different adopted breeding strategies and a summary of the phytochemical analyses of the new varieties obtained in these last years will be given.

In: Citrus Fruits
Editor: Daphne Simmons
ISBN: 978-1-63484-078-1

Chapter 5

CITRUS RESIDUES AS SUPER-ADSORBENTS

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ABSTRACT

Water pollution is still a serious problem for the entire world. Adsorption technology is a promising process which based on fabrication of novel, cheap, non dangerous and highly sorptive materials for application in wastewater purification processes. *Citrus* species generally produced for the fresh consumption or the production of fruit juice but also have lot of application in medicine, food processing and agriculture sectors. This review collects information from published works about the alternative use of *Citrus* residues as efficient and promising adsorbents in clean water technology.

For this purpose, isotherm (Langmuir, Freundlich, etc.), kinetic (pseudo-first, -second order, etc.), thermodynamic (free energy Gibbs, enthalpy, entropy) and desorption-regeneration studies were discussed in detailed. Moreover, significant factors such as pH, agitation time, temperature, adsorbent dosage and initial dye concentration are also reported extensively.

Keywords: citrus peels, isotherms, kinetics, heavy metals, thermodynamics, modeling

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1. INTRODUCTION

Water pollution is still a momentous global issue that distresses the human population around the world. Every day, large amount of wastewater are generated by industrial, agricultural and domestic activities and are deposited to the land or water receptors. The latter is the common opinion causing the water pollution on a global scale. This is the reason why polluted wastewater must be depurated and returned to water receptors or to land.

There are many pollutants which contributing to environmental pollution such as dyes, radionuclides, phenolics, pesticides, etc. However, heavy metals are recognized as one of the most toxic groups which reach in food chain through the disposal of wastes to water receptors or land. Heavy metals are taxed in causing toxic effects, cancer and diseases because they cannot be degraded [1-3].

Various methods such as adsorption, coagulation, advanced oxidation, and membrane separation have been used for the removal of heavy metals from wastewaters. However, adsorption is one of the most effective processes of advanced wastewater treatment [4, 5]. Some of the widely used adsorbents materials especially for heavy metals removals from aqueous solutions are chitosans [6], nanoadsorbents [7], wastes from olive oil industry [8], algae [9], composts [10], zeolites [11], clay soils [12] and betonites and vermiculites [3]. In this study, the use of *Citrus* residues for heavy metal biosorption is discussed.

Citrus is a genus in the family Rutaceae and it is an important fruit crop with a total world production of 11.65 million metric tons. Colombia, China and Nigeria are on top (56.1% combined production of the world) among the citrus produces [13]. Citrus can be generally classified into the following categories: sweet oranges (most are *C. sinensis*), mandarins (*C. reticulata*), sour/bitter oranges (such as Seville, *C. aurantium*), lemons (*C. limon*), limes (*C. aurantifolia* and *latifolia*), grapefruit (*C. paradisi*) and pummelos (*C. grandis*), hybrids (e.g., tangelos, tangors, and limequats), and citrons (*C. medica*) [14]. World production of citrus by fruit type in 2010 was 56% oranges, 17% tangerines, clementines and mandarins, 11% lemons and limes, 6% grapefruit and pomelo and 10% other [15]. Generally, they are produced for the fresh consumption or the production of fruit juice. Moreover, the by-products generated following their industrial process are source of important bioactive compounds with potential for animal feed, manufactured foods and health care. They also consists of variety of phytonutrients such as alkaloids, flavonoids, tannins, phenols and saponins, which are closely related with health promotion and disease prevention [16]. Citrus species, also, pay attention for the production of essential oils which have plethora application in food, agriculture, pharmaceutical, cosmetology and sanitary areas [17].

Citrus biomass, has received a great deal of attention for decontamination of water by biosorption process. Their interest lies in the existence of functional groups such as sulfonic acids, carboxyl, that interact with the molecules of the contaminants found in the water resulting in their adsorption (physical or chemical) onto adsorbents surface. Another parameter which affects the adsorption is the surface area that taking place the adsorption process. High specific area increases the adsorption. A general sorbents production is as follows: citrus residues chopped, rinsed with distilled water, dried at constant temperature and then ground and sieve to a special particles size. Many scientists use different methods physical (heating/boiling) or chemical (alkali or acid solutions) to improve their adsorption capacity.

For first time, this review article summarizes and discusses *Citrus* residues (raw or treated) acting as biosorbents. Isotherm, kinetic, and equilibrium modeling were discussed in details. Moreover parameters which affect the biosorption process, such as the effect of solution pH, contact time, temperature and biosorbent's dose are also commented.

2. MODELING

In order to organize, establish and understand an adequate design model for the removal of pollutants from aqueous media, isotherm, kinetics and thermodynamic studies are essential basic prerequisites.

Adsorption isotherms models are extensively used to provide information about the amount of adsorbed ion by a certain biomass and about the interaction between the adsorbents and adsorbate [18, 19].

In a recent review, Rangabhashiyam et al. [20] studied the use of two, three, four and five parameters isotherms models and concluded that in case of two parameters isotherm model, Langmuir and Freundlich models have the best fit. Langmuir isotherm assumes that all binding sites have equal affinity for the adsorbate, resulting to the formation of monolayer of adsorbed molecules [21] and Freundlich isotherm describes adsorption onto heterogeneous surfaces that provide adsorption sites of varying affinities [22]. The linear and non-linear expressions of Langmuir and Freundlich isotherms are listed in Table 1.

Kinetics studies are useful tool to found the optimum condition for full-scale batch adsorption process [23]. Kinetic modeling reveal the mechanism of adsorption and potential rate-controlling steps such as mass transport or chemical reaction processes [23, 24]. The most common are the pseudo-first and the pseudo-second order kinetic equations. The linear and non linear forms of pseudo-first and pseudo-second-order kinetic models are presented in Table 1.

For better understanding the sorption mechanism, thermodynamic studies are basic requirements. They predict the spontaneity of adsorption and found the temperature range in which the adsorption was favorable or unfavourable [25]. The thermodynamic parameters for the adsorption process, Gibbs energy (ΔG^0), enthalpy of adsorption (ΔH^0) and entropy of adsorption (ΔS^0), are calculated by fitting data obtained by the adsorption experiments at different temperatures to the equations included in Table 1.

3. CITRUS RESIDUES

3.1. Citrus Sinensis (Orange)

Bhalerao et al. reports the removal of Cd^{2+} by using treated with 0.1 M HNO_3 orange rind [26]. Optimum adsorption condition was observed at pH 7 and 5 mg/ml biomass dose. Based on kinetic studies, the adsorption process was rapid and equilibration time was carried out after 90 min. FTIR analysis established that carboxyl, hydroxyl and carbonyl group was get involved in adsorption process. Mean free energy was equal to 1.118 kJ/mol, suggesting that the adsorption was a physical process.

Table 1. Isotherms, kinetics and thermodynamic equations

Expression	Equation form	Plot
Non linear Langmuir	$q_e = q_m \frac{b_L C_e}{1+b_L C_e}$	–
Linear Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b_L q_m}$	$\frac{C_e}{q_e}$ vs C_e
Linear Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{b_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
Linear Langmuir-3	$q_e = q_m - \left(\frac{1}{b_L}\right)\frac{q_e}{C_e}$	q_e vs $\frac{q_e}{C_e}$
Linear Langmuir-4	$\frac{q_e}{C_e} = b_L q_m - b_L q_e$	$\frac{q_e}{C_e}$ vs q_e
Non-linear Freundlich	$q_e = K_F \mathrm{C_e}^{1/\mathrm{n}}$	–
Linear Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs $\ln C_e$
Non-linear pseudo-first order kinetic	$q_t = q_e(1\text{-}\exp^{-k_1 t})$	–
Linear pseudo-first order kinetic	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs t
Non-linear pseudo-second order kinetic	$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t}$	–
Linear pseudo-second order kinetic	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$	t/q_t vs t
Gibbs	[a] $\Delta G^0 = -RT \ln b_L$ or [b] $\Delta G^0 = -RT \ln\left(\frac{q_e}{C_e}\right)$ [c] $\Delta G^0 = -RT \ln K$	–

Expression	Equation form	Plot
	[d] $\Delta G^0 = -RT\ln K_o$	
Van't Hoff	$\ln(b_L) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ or $\ln\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ $\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ $\ln(K_0) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln(b_L)$ vs $\frac{1}{T}$ or $\ln\left(\frac{q_e}{C_e}\right)$ vs $\frac{1}{T}$ or $\ln(K)$ vs $\frac{1}{T}$ $\ln(K_0)$ vs $\frac{1}{T}$
Clausius Clapeyron	$\Delta H^0 = \frac{RT_1T_2}{T_2 - T_1}\left(\frac{\ln C_{e1}}{\ln C_{e2}}\right)$	–

C_e (mg/L) and q_e (mg/g) are the equilibrium liquid phase concentrations and amount of solute adsorbed at equilibrium, respectively; a: b_L in (L/mole) from Langmuir model; b: q_e/C_e is the ratio where q_e is adsorbed dye at concentration (mg/L) and C_e is the residual dye concentration in the solution (mg/L); c: $K = q_m X b_L$ calculated from Langmuir constants (q_m) is the maximum adsorption capacity in mg/g and b_L units in L/mg; d: K_0 can be evaluated by plotting ln (q_e/C_e) versus q_e by extrapolating to $q_e = 0$.

Table 2. List of models for adsorption isotherms, kinetics and thermodynamic for adsorption of metals on citrus peels

Adsorbent	Metal	Initial exp. conditions	Isotherm models	Kinetic models	q_m (mg/g)	Thermodynamics	Ref.
Citrus aurantifolia residues treated with $FeCl_3$	As^{5+}	t = 300-2280 min	-	ps1	0.475[a]	-	[28]
Grapefruit peel	As^{5+}	pH = 1-9; t = 0-1440 min T = 20-45°C	L, F	ps2, R, WM	37.77	-	[29]
Orange peel treated with 0.1 M HNO_3	Cd^{2+}	C_0 = 5-300 mg/L; pH = 2-10 t = 5-180 min	L	ps2	83.33	-ΔG, +ΔS, +ΔH	[26]
EDTA modified *Citrus sinensis* mesocarp	Cd^{2+}	C_0 = 10-50 mg/L; pH = 1-8 t = 20-120 min; T = 20-100°C	L	ps2	25.77	+ΔG, -ΔS, +ΔH	[30]

Table 2. (Continued)

Adsorbent	Metal	Initial exp. conditions	Isotherm models	Kinetic models	q_m (mg/g)	Thermodynamics	Ref.
Pomelo peels	Cd^{2+}	C_0 = 25-100 mg/L; pH = 1-6 t = 0-240 min; T = 25°C	L	ps2	21.83	-	[31]
Pretreated pomelo peels (isopropyl alcohol, sodium hydroxide)	Cd^{2+}	C_0 = 25-200 mg/L; pH = 2-6; t = 0-240 min; T = 25°C	L	-	26.88	-	[32]
Pretreated pomelo peels (isopropyl alcohol, sodium hydroxide, citric acid)	Cd^{2+}	C_0 = 25-200 mg/L; pH = 2-6; t = 0-240 min; T = 25°C	L	ps2	27.10	-	[32]
Orange peels	Ce^{3+}	C_0 = 50-350 mg/L; pH = 3-9; t = 120-420 min; dose = 0.05-0.35 g/L	L	–	71.40	-	[27]
Natural and chemically modified orange peels	Cu^{2+}	C_0 = 5-100 mg/L; pH = 2-10 t = 0-120 min	F	Ps2	(1.25-1.73)[a]	-	[33]
Orange peels	Cu^{2+}	C_0 = 1-100 mg/L; pH = 2-6.5 t = 30-90 min	L, F	ps2	14.75	-	[34]
Pomelo peels	Cu^{2+}	C_0 = 25-125 mg/L; pH = 3-6 t = 0-180 min; T = 25-45°C	L	ps2	19.7	-ΔG, +ΔS, -ΔH	[35]
Depectinated pomelo peels	Cu^{2+}	C_0 = 25-125 mg/L; pH = 3-6 t = 0-180 min; T = 25-45°C	L	ps2	21.1	-ΔG, +ΔS, -ΔH	[35]
Sour orange peels (*Citrus aurantium*)	Co^{2+}	C_0 = 5-50 mg/L; pH = 1-6 t = 30-150 min; T = 20-60°C dose = 0.5-3.0 g	F	-	-	-	[36]
Citrus reticulata waste biomass	Co^{2+}	C_0 = 25-800 mg/L; pH = 1-7 t = 15-1440 min; dose = 0.05-0.4 g T = 30-70°C	F	ps2	181.18	-	[37]
Orange peel treated with formaldehyde	Cr^{3+}	C_0 = 1-100 mg/L; pH = 2-3.5 t = 1-360 min	MCL	ps2	9.43	-	[38]
Citrus sinensis peels	Cr^{3+}	C_0 = 0.1- 0.3 mol/L; pH = 2-12 dose = 1-2 g; T = 30-60°C	F	-	-	±ΔG, -ΔS, -ΔH	[39]
Skin of orange peels	Cr^{6+}	C_0 = 40-100 mg/L; pH = 1-7 t = 20-90 min; T = 10-70°C	L	-	8.07	-	[40]
Orange peel treated with	Cr^{6+}	C_0 = 5-250 mg/L; pH = 1-8	L	ps2	10.74	-ΔG, +ΔS, +ΔH	[41]

Adsorbent	Metal	Initial exp. conditions	Isotherm models	Kinetic models	q_m (mg/g)	Thermodynamics	Ref.
0.1 M H_2SO_4		t = 10-180 min; dose = 1-15 g/L					
Mandarin peels	Cr^{6+}	C_0 = 50-500 mg/L; pH = 1-4 t = 0-480 min; T = 28-60°C dose = 1-5 g	-	-		-	[42]
Lemon skin	Cr^{6+}	C_0 = 10-30 mg/L; pH = 3-10 t = 10-80 min; T = 10-50°C dose = 0.025-0.2 g	L, F	ps1	13.69	-	[43]
Sweet lime skin	Cr^{6+}	C_0 = 10-30 mg/L; pH = 3-10 t = 10-80 min; T = 10-50°C dose = 0.025-0.2 g	L, F	ps1	6.53	-	[43]
Raw sweet lime	Ga^{3+}	C_0 = 40-200 mg/L; pH = 1-3 t = 0-300 min; T = 30°C	L	ps2	46.54	-	[44]
Alkali-treated sweet lime	Ga^{3+}	C_0 = 40-200 mg/L; pH = 1-3 t = 0-300 min; T = 30°C	L	ps2	76.26	-	[44]
Orange peel treated with formaldehyde	Fe^{3+}	C_0 = 3-300 mg/L; pH = 2-3.5 t = 1-360 min	MCL	ps2, Elv	18.20	-	[38]
Citrus reticulata waste biomass	Pb^{2+}	C_0 = 25-800 mg/L; pH = 1-5 t = 15-1440 min; dose = 0.05-0.4 T = 30-70°C	F	ps2	238.09	-	[37]
Pomelo peels	Pb^{2+}	C_0 = 25-100 mg/L; pH = 1-6 t = 0-180 min; T = 28°C	F	ps2	24.52[a]	-	[45]
EDTA modified *Citrus sinensis* mesocarp	Pb^{2+}	C_0 = 10-50 mg/L; pH = 1-8 t = 20-120 min; T = 20-100°C	L	ps2	13.94	+ΔG, -ΔS, +ΔH	[30]
EDTA modified *Citrus sinensis* mesocarp	Ni^{2+}	C_0 = 10-50 mg/L; pH = 1-8 t = 20-120 min; T = 20-100°C	L	ps2	33.44	+ΔG, -ΔS, +ΔH	[30]
Citrus Limettioides peel carbon	Ni^{2+}	pH = 2-12; t = 30-420 min dose = 0.05-3.5 g; T = 27-47°C	L	ps2	38.46	-ΔG, -ΔS, -ΔH	[46]
Citrus Limettioides seed carbon	Ni^{2+}	pH = 2-12; t = 30-420 min dose = 0.05-3.5 g; T = 27-47°C	L	ps2	35.54	-ΔG, -ΔS, -ΔH	[46]
Skin of orange peels	Zn^{2+}	C_0 = 40-100 mg/L; pH = 1-7 t = 20-90 min; T = 10-70°C	L	-	1.08	-	[40]

L: Langmuir; F: Freundlich; MCL: Multi component Langmuir; ps1: pseudo-first order; ps2: pseudo-second order; Elv: Elovich; R: Richenberg; WM: Weber-Morris; [a] Q_m values obtained from experimental results.

Orange peel was used for the adsorption of Ce^{3+} from aquatic system [27]. Maximum adsorption was noticed at pH 6 and 0.20 g/L of adsorbent dose. The kinetic study showed that an increase of the adsorbed amount was noticed till 4 h. A synopsis of best fitted isotherm and kinetic models, maximum adsorption capacities (obtained from Langmuir isotherm) and thermodynamic results are tabulated in Table 2.

Citrus sinensis peels were used for sequestration of Cr^{3+} by Ugbe et al. [39]. Increase of pH and temperature negatively affected the removal uptake and maximum adsorption was at pH 2 and 30°C. At low pH values, Cr^{3+} oxidised to form CrO_4^{2-} which is adsorbed by positively protonated adsorbent surface. It was observed that the removal of Cr^{3+} increase with increasing adsorbent dose. Gibbs free energy values were between -20 and 0 kJ/mol suggesting physisorption process.

The ability of orange rind treated with 0.1 M H_2SO_4 to adsorb Cr^{+6} from aqueous media was investigated by Poojari et al. [41]. Optimum adsorption conditions was observed at pH 2, 5 mg/ml adsorbent dose. Higher adsorbent dose leads to the reduction of metal uptake due to partial aggregation of adsorbent contributing to the decrease in effective surface area. Equilibrium was reached in 150 min. Based on estimated mean free energy the adsorption was found to be physical in nature.

Natural (OP-Natural) and chemically modified orange peels (OP-NaOH, OP-Methanol, OP-H_2SO_4, OP-Formaldehyde, OP-Acetic anhydride) were tested for their ability to adsorb Cu(II) ions from water media by Khalfaoui and Meniai [33]. pH was found to affect significant the adsorption process and optimum adsorption was observed at pH 5-6. Chemical treatments via NaOH, H_2SO_4 and methanol (esterification), were found to increase the adsorption percentage from 75% (natural OP) to 91-99%, suggested the success of modification process to improve the adsorption capacity. Adsorption was rapid and equilibrium was achieved in 5 min for OP-NaOH, OP-Methanol, OP-H_2SO_4 and 10 min for OP-Natural.

Orange peel was also examined for the removal of Cu^{2+} from aqueous solution by khan et al. [34]. Adsorption increased with the increase of pH and 6.5 pH value was chosen as optimum pH value for adsorption experiments. At pH > 6.5, Cu precipitates as $Cu(OH)_2$, hindering the biosorption process. Kinetic studies were conducted and showed that the adsorption was fast and equilibrium was attained at 60 min.

EDTA modified *Citrus sinensis* mesocarp was used as adsorbent for its ability to sequestrate Pb^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution [30]. The results showed that at low pH values, the hydrogen ions act competed thus maximum adsorption was observed at pH values 5, 6 and 7 for Ni^{2+}, Cd^{2+} and Pb^{2+}, respectively.

Adsorption was found to increase as contact time increased and equilibrium was attained in 100 min. The increase of temperature was positively affected the adsorption capacity due to the fact that at high temperatures the thickness of the outer surface reduces and the number of pores increases resulting in more efficiently attachment of the metal ion onto the surface of adsorbent.

The utilization of pretreated via formaldehyde orange peel as adsorbent for the uptake of Fe(III) and Cr(III) in single and binary systems was examined by Lugo-Lugo et al. [38]. The increase of pH lead to the increase of uptake amount and maximum adsorption was achieved at pH 4 due to the decrease of H^+ ions and the formation of metal hydroxide complexes. To avoid iron precipitation, pH 3 was selected for the rest of the experiments. In single metal system, for Cr(III) and Fe(III) equilibrium was found at 260 and 120 min, respectively. On the contrary, in binary system, 120 min was observed to be sufficient for both metals to equilibrate.

In binary systems removal uptake was found to decrease from 7.6 to 4.79 mg/g and 17.4 to 8.96 mg/g for Cr(III) and Fe(III), respectively. This is the reason why both metals have antagonism character, for the same binding sites. Hydroxyls groups on the carboxylic acids, based on FTIR spectra, recognized as the active binding sites.

Another research team was examined the removal of Cr^{6+} and Zn^{2+} by skin of orange peel [40]. Optimum removal of Cr and Zn ions was observed at pH 3. The increase of adsorption capacity was achieved by raising the temperature up to 30°C while the opposite results were observed with further increase. It is explained that at high temperatures the entropy increases as a result the reduction of the stability of metals ions; finally lower amount of heavy metals is available to adsorb. Adsorbent dose of 1 g leads to highest uptake percentage due to greater availability of exchange binding sites or larger surface area. Kinetic studies showed that 30 min was sufficient for equilibration.

3.2. Citrus Paradisi (Grapefruit), Citrus Grandis (Pomelo), Citrus Reticulata (Mandarin), Citrus Aurantium (Sour Organge)

Batch experiments were applied to examine the uptake of As^{5+} from wastewater [29]. Maximum adsorption was found at pH 4 and 45°C. Kinetic studies revealed that equilibrium was attained in 120 min.

The mechanism of the adsorption indicated that both surface adsorption and intra-particle diffusion get involved in adsorption process. FTIR characterization affirms the involvement of carbonyl and hydroxyl in adsorption process. Application of grapefruit peel in real wastewater proved to be good adsorbent for the removal of As^{5+} lead to water up to safe limits for As contamination, as proposed from WHO.

Tasaso [35] utilized pomelo and depectinated pomelo peels as adsorbents for the removal of Cu^{2+} from aqueous solutions. Maximum adsorption was at pH 4 and equilibrium was achieved at 60 min. Increase of temperature from 25 to 45°C, negatively affected the adsorption of Cu^{2+}. FTIR spectra (before and after adsorption) indicated significant shift of COO^- groups, indicating the involvement in adsorption process.

Pomelo peels were also used for adsorption of Pb^{2+} [45]. Biosorption was found to be rapid and equilibrium was reached in 90 min. Optimum pH value was 4 with maximum adsorption percentage 96.79%.

Raw pomelo peels (RPP) and its modified forms (PPI: washed with isopropyl alcohol, PPIS: washed with isopropyl alcohol and sodium hydroxide, PPIC: washed with isopropyl alcohol and citric acid, PPISC: washed with isopropyl alcohol, sodium hydroxide and citric acid) were used as efficient adsorbents to remove Cd^{2+} [31, 32].

Maximum adsorption was achieved at pH 5. For all adsorbents, kinetic studies revealed a rapid biosorption process in the first 20-30 min and after 60 min a plateau was noticed. Maximum adsorption capacity was observed by PPISC adsorbent at pH 5.

The use of mandarin peel was examined for Cr^{6+} removal from aqueous media using batch trial approached [42]. At 28°C, optimum pH and time conditions was 1 and 6.5 h, respectively. Increase of temperature up to 60°C positively affected the adsorption uptake capacity. At 5 g of adsorbent and 35 min, 100% removal of Cr^{6+} was observed. The authors explained that higher amount of adsorbent dose contributing to more active binding sites thus facilitating the adsorption process. Desorption studies were conducted by using 0.1 and 0.5 N NaOH and the results showed that desorption percentage was 83 and 62.86% with 0.1 N and 0.5 N NaOH, respectively.

Citrus reticulata was also used for the adsorption of Co^{2+} and Pb^{2+} from water media [37]. Experiments were carried out as function of pH, adsorbent dose, adsorbent size, contact time and temperature. Pb^{2+} and Co^{2+} maximum adsorption was found at pH 5, 0.1 g dose, 0.31 mm size, and pH 7, 0.05 g dose, 0.5 mm size, respectively. Pb^{2+} removal was temperature independent while Co^{2+} uptake positively affected by increasing of temperature, giving maximum adsorption at 60°C. Among tested modifications of raw biomass, sodium hydroxide and simply heated pre-treatments gave maximum capacity for Pb^{2+} (83.77 mg/g) and Co^{2+} (95.55 mg/g), respectively.

Sour orange was investigated as potential adsorbent for the removal of Co from aqueous solution [36]. Optimum adsorption condition were found at pH 2, 30°C, adsorbent dose 2 g and contact time 90 min. Desorption studies were carried out using sodium chloride, EDTA, hydrochloric acid, ammonium chloride and calcium chloride. NH_4Cl gave the highest desorption efficiency 95.12%. FTIR analysis before and after adsorption demonstrated significant changes to hydroxyl and carboxyl groups suggested the potential participation in adsorption process.

3.3. Citrus Aurantifolia (Key Lime), Citrus Limettioides (Sweet Lime), Citrus Lemon (Limon)

Marín-Rangel et al. [28] utilized *Citrus aurantifolia* residues treated with $FeCl_3$ for the adsorption of As^{5+}. Chemical composition analysis showed that the adsorbent consisted of lignin, hemicellulose, pectin, cellulose, carbohydrates and proteins. SEM studies indicated the heterogeneous surface of adsorbent with smooth and rough areas. Kinetic studied concluded that equilibrium was reached at 24 h, giving uptake rate of 58.28%.

Activated carbon from *Citrus Limettioides* peel (CLPC) and seed (CLSC), respectively, were fabricated and tested for its ability to adsorb Ni^{2+} [46]. Optimum pH value and equilibrium time was determined at pH 4-7 and 4 h, respectively. Adsorbent dose of 1.5 g/L gave the maximum adsorption capacity (99%) for both activated carbons. Regeneration studies were achieved by using 0.7 N HCl and after 5 adsorption-desorption cycles the uptake removal was decreased from 96.20 to 80.70% and from 94.50 to 78.90%, for CLPC and CLSC, respectively. CLPC and CLSC were also applied in real wastewaters containing Ni^{2+} ions, giving satisfactorily adsorptive results (maximum removal of 98% (± 0.5) at adsorbent dose of 3 g/L).

Sweet lime and lemon skin were used for the adsorption of Cr^{6+} from water media by Phadtare and Patil [43]. pH was found to control strongly the adsorption process and maximum adsorption was obtained at pH values 4-6. Increase of temperature negatively affected the adsorption removal demonstrated the exothermic nature of adsorption process. A decrease of adsorbent size and increase of adsorbent dose was found to enhance the adsorption procedure. Initial concentration had not have significant impact on the removal of Cr^{6+} by both adsorbents.

Gondhalekar and Shukla [44] utilized raw (RCP) and alkali treated (ACP) *Citrus limetta* peels for their adsorption capacity for Ga^{3+}. FTIR spectra showed that the alkali pretreatment converted ester functional groups to carboxylic acid groups. Batch studies were carried out and the results showed that optimum adsorption was obtained at pH 3 and equilibrium was attained in 180 min. Maximum adsorption capacity was found to be enhanced by alkali pretreatment (RCP: 46.54 mg/g, ACP: 76.26 mg/g), indicated the success of pretreatment. After 3 adsorption-desorption cycles the adsorption capacity decreased from 58.98 to 37.08% and 68.51 to 55.46%, for RCP and ACP, respectively.

Table 3. Thermodynamic parameters for studied adsorbents

Adsorbent	Metal	T (K)	ΔG^0 (kJ/mole)	ΔH^0 (kJ/mole)	ΔS^0 (kJ/mole K)	Ref.
Orange peel treated with 0.1 M HNO_3	Cd^{2+}	303	-0.77	13.32	0.046	[26]
		313	-0.96			
		323	-1.68			
Orange peel treated with 0.1 M H_2SO_4	Cr^{6+}	293	-0.21	8.84	0.030	[41]
		303	-0.81			
		313	-0.84			
		323	-1.19			
Pomelo peels	Cu^{2+}	298	-5.38	-32.18	0.09	[35]
		308	-4.19			
		318	-3.49			
Depectinated pomelo peels	Cu^{2+}	298	-5.40	-24.89	0.08	[35]
		308	-4.72			
		318	-4.02			
Orange peel treated with 0.1 M H_2SO_4	Cr^{+6}	293	-0.21	8.84	0.030	[41]
		303	-0.81			
		313	-0.84			
		323	-1.19			
Citrus Limettioides peel carbon	Ni^{2+}	300	-6.09	-21.88	-0.053	[46]
		310	-5.67			
		320	-5.06			
Citrus Limettioides seed carbon	Ni^{2+}	300	-5.49	-19.09	-0.045	[46]
		310	-4.90			
		320	-4.60			

4. Isotherm, Kinetic and Thermodynamic Analysis

In most cases, experimental data well described from Langmuir model, pseudo-second-order kinetic and the sorption process is spontaneous (Table 2). Thermodynamic studies were calculated by many ways, as described in Table 1. In the majority of adsorption studies, authors, without explanation use one of these equation and plots and the final decision of the most suitable plot was proved by R^2 values.

Thermodynamic parameters by using citrus residues for metals adsorption are tabulated in Table 3. As we can see, sorption data from three to four temperatures were used in a range 293-323. Thermodynamic studies showed that the adsorption process was spontaneous ($\Delta G^0 < 0$) and endothermic ($\Delta H^0 > 0$) or exothermic ($\Delta H^0 < 0$).

Conclusion

Adsorption process is still a promising technology in clean water science. Among tested adsorbents, citrus based biomass is noticeable attractive adsorbents due to its higher adsorption capacity for target heavy metal. Adsorption was found to be controlled by initial concentration, adsorbent dose, contact time, solution pH and temperature. Among tested isotherm and kinetic models, Langmuir and pseudo-second order were found to express well the adsorption process.

Despite the number of published adsorption studies, there is a lack of information regarding the behavior of citrus adsorbents in multi-metal systems and the application in real wastewaters. Mechanism of adsorption is a very complicate issue and must be accompanied by multi-faceted studies and not only numerically by modeling equations.

Based on the fact that most of studies focus only on laboratory experiments, future work must give emphasis to estimate the cost of fabrication and the application of citrus based adsorbents in industry effluents.

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